



Spatial distribution, environmental risk assessment, and source identification of potentially toxic metals in Atikhisar dam, Turkey

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Abstract The objective of this study was to determine the ecological risk created by metal contents of the surface sediments of Atikhisar dam, Çanakale, NW Turkey. Enrichment factor (EF) and geoaccumulation index (*I_{geo}*) were calculated to determine anthropogenic effects. Ecological risk was assessed using the modified potential ecological risk index (mPER), with its levels being evaluated using the modified ecological risk index (mER). Toxic effects were determined using the toxic risk index (TRI). The ecological risk indices were mapped to provide their spatial distributions. Our findings indicate that enrichment was very high for Hg and significant for Pb, Tl, Cd, and As. The following mER pattern was detected: Hg > Cd > Tl > As > Pb > Ni > Cr > Co > Zn > Mn > V. Hg and Cd exhibited extremely high and

very high ecological risks, respectively, while Tl and As had a significant ecological risk, with Pb exerting a medium ecological risk. Hg, Pb, Tl, Cd, As, Cr, Ni, Zn, and Cu were enriched via anthropogenic effects exceeding their natural concentration levels. Due to their high toxic effects, Hg, Cd, Tl, As, and Pb were identified as the very high risk elements. Mining, household wastes, agriculture, and natural mineral deposits were identified as the possible sources of the potential ecological risk.

Keywords Metal pollution · Ecological risk assessment · Environmental degradation · Potential ecological risk · Geographic information systems

Introduction

Though naturally found in certain concentrations in (a)biotic environments, metals are enriched anthropogenically and discharged into surface water, groundwater, or sewerage networks. This process continues with the accumulation and storage of metals in sediment. Ecological risk assessments of the metals serve to determine the extent to which their risks adversely affect the natural health, also known as ecosystem health, as well as to distinguish their natural and anthropogenic sources. For this purpose, various indices proven to give reliable results have been developed such as enrichment factor (EF) (Brady et al., 2015; Sutherland, 2000; Vrhovnik et al., 2013),

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modified ecological risk index (mER) (Brady et al., 2015; Hakanson, 1980), geoaccumulation index (Igeo) (Müller, 1969), modified potential ecological risk index (mPER) (Brady et al., 2015; Hakanson, 1980), and the toxic risk index (TRI) (Zhang et al., 2016). Anthropogenic effect is detected with EF and Igeo, toxic effects with TRI, and ecological risk assessment with mER and mPER. Dams are more sensitive than wetlands to the ecological risks created by metals due to their direct contamination effects on ecosystem health (Audry et al., 2004; Deng et al., 2020; Goher et al., 2014; Karthikeyan et al., 2020; Kükrer, 2016; Kükrer et al., 2020; Naz et al., 2016; Ustaoglu et al., 2020; Yang et al., 2016). Even though generally equipped with treatment systems, metals in dams are not degraded through microbiological processes, thus rendering most treatment systems ineffective (Eid et al., 2012). Rising metal concentrations in surface sediment have been attributed to mining, agricultural, and industrial activities (Chen et al., 2018). For example, mining activities and land-use and land-cover (LULC) changes were reported as the source of ecological risks in Asia and Europe (Ma et al., 2020; Zhou et al., 2020). In this context, the objective of

this study was to quantify the ecological risks of the surface sediment metals of Atikhisar dam under the human-induced pressures from settlements, agriculture, and mining and their spatial distributions.

Method

Description of study area

Atikhisar dam, located 11 km southeast of Çanakkale city in NW Turkey, was established on Sarıçay river in 1975 for the purposes of drinking and irrigation water supplies and flood control (Fig. 1). The basin area of the dam is 471 km², with the crest height and length of 68 and 420 m, respectively; a maximum water elevation of 61 m; and a maximum volume of 52.5 million m³. The normal water surface is 4 km². Agriculture, mining, rural settlements, and transportation networks are the most dominant anthropogenic activities in the catchment of Atikhisar dam. Au, Fe, and kaolinite deposits are mined, while Cu, Pb, Zn, Mn, and Quartz are the primary ore deposits. Most of the basin is covered with Tertiary andesite and tuffs.



Fig. 1 Location map of the study area

Paleozoic metamorphic rocks, Tertiary sedimentary rocks, and limestone of Upper Miocene-Pliocene constitute the other lithological units (Öztürk & Erginal, 2001).

Sampling and analytical procedures

The sediment metal concentration may change seasonally or remain constant for a long time depending on the sedimentation rate and is considered one of the best indicators of ecological risk (Luczynska & Kang, 2018). Sediment metals can be released back into water due to changes in dissolved oxygen, organic-inorganic carbon, pH, and oxidation reduction (Çevik et al., 2009; Wang et al., 2012). In the study, surface sediments were sampled from 19 points on the dam base, while rocks were sampled from the nine locations in order to determine their metal background values (ppm): Al (30.689), As (2.89), Au (0.006), Cd (0.05), Cr (6.20), Cu (32.88), Co (17.50), Fe (44.611), Hg (0.006) Mn (815), Ni (8.99), Tl (0.053), Pb (3.18), V (137), and Zn (50.10). For the analysis of the organic carbon (OC) and metal contents, wet sediment samples were dried in the oven for 24 h, pounded in a mortar, and pulverized. Metal analyses were carried out using ICP-MS by the Bureau Veritas Analytical Labs in Canada. Reference materials, duplicate measurements, and blind sampling measurements were used to test the validity of the analyses. The recovery values of the metal measurements varied between 95.45 and 146.80%. OC analysis was carried out using the Walkley-Black titration method (Gaudette et al., 1974), while chlorophyll degradation products (CDPs) were determined using the acetone extraction and spectrophotometric methods (Lorenzen, 1971). CaCO₃ analysis was conducted using a Scheibler calcimeter (Schlichting & Blume, 1966). The metal concentrations of the rock samples were averaged to determine the metal background to be used in EF analysis (Brady et al., 2015; Sutherland, 2000; Vrhovnik et al., 2013). Al was used as a conservative metal as follows:

$$EF = \left[\frac{Cn \text{ sample}}{CAI \text{ sample}} \right] / \left[\frac{Bn \text{ Background}}{BAI \text{ Background}} \right] \tag{1}$$

where *Cn* is the metal whose *EF* is calculated, *CAI* sample is Al concentration, *Bn* background is metal background value, and *BAI* background is Al

background. *EF* refers to a deficiency-to-minimal enrichment when *EF* < 2, a moderate enrichment when *EF* = 2–5, a significant enrichment when *EF* = 5–20, a very high enrichment when *EF* = 20–40, and an extremely high enrichment when *EF* > 40 (Sutherland, 2000).

The following formula for *Igeo* was used:

$$Igeo = \log_2 \frac{Cm}{(Bm \times 1.5)} \tag{2}$$

where *Cm* is measured metal concentration, and *Bm* is continental crust value of metal. *Igeo* refers to uncontaminated when *Igeo* ≤ 0, uncontaminated to moderate when 0 < *Igeo* < 1, moderate when 1 < *Igeo* < 2, moderate to strong when 2 < *Igeo* < 3, strong when 3 < *Igeo* < 4, strong to very strong when 4 < *Igeo* < 5, and extremely strong when *Igeo* ≥ 5 (Müller, 1969).

TRI was used to detect ecotoxicological risks posed by the metals (Zhang et al., 2016) as follows:

$$TRI_i = \sqrt{\frac{((C_i/TEL)^2 + (C_i/PEL)^2)}{2}} \tag{3}$$

where *C_i* refers to metal concentration, TEL to a threshold effect level, and PEL to a probable effect level (MacDonald et al., 2000).

Integrated TRI was calculated as follows:

$$TRI = \sum_{i=1}^n TRI_i \tag{4}$$

TRI refers to 5 no toxic risk when TRI ≤ 5, low toxic risk when 5 < TRI ≤ 10, moderate toxic risk when 10 < TRI ≤ 15, considerable toxic risk when 15 < TRI ≤ 20, TRI > 20 very high toxic risk.

The following formula was used to estimate mER:

$$mER = EF \times Tr^i \tag{5}$$

where *Trⁱ* indicates the following toxic risk coefficients (Brady et al., 2015; Hakanson, 1980): Hg = 40, Cd = 30, As = 10, Cu = Pb = Ni = 5, Cr = 2, Zn = 1, Mn = 1, Co = 5, Tl = 10, and V = 2. Its results for ecological risk indicate a low potential when mEr < 40, a moderate potential when 40 ≤ mEr < 80, a significant potential when 80 ≤ mEr < 160, a high potential when 160 ≤ mEr < 320, and a very high potential when mEr ≥ 320 (Hakanson, 1980). mPER was used to

determine the integrated ecological risk (Brady et al., 2015; Hakanson, 1980) as follows:

$$mPER = \sum mER \quad (6)$$

Its evaluation regarding ecological risk points to low when $mPER < 150$, moderate when $150 \leq mPER < 300$, significant when $300 \leq mPER < 600$, and very high when $mPER \geq 600$ (Hakanson, 1980). The ecological risk indices were transformed into spatial distribution maps using the kriging interpolation method in Arc-Map 10.7 software. It was used to estimate the optimum values of the response surfaces not measured given the point data as follows:

$$Np = \sum_{i=1}^n Pi \times Ni \quad (7)$$

where N indicates the number of the sampling points, Ni corresponds to the geoid corrugation values of the points used in the calculation of Np , Np indicates the corrugation value to be calculated, and Pi indicates each Ni value used in the calculation of N (Esri, 2021). Factor analysis, cluster analysis, Spearman's correlation analysis, and field studies were carried out to determine the possible sources and transportation processes of the metals, OC, CDP, and $CaCO_3$.

Results and discussion

Spatial distributions of metals, OC, CDP, and $CaCO_3$

The mean metal concentrations (ppm) were as follows: Fe (28.021) > Al (22.742) > Mn (732) > Zn (74.4) > V (49.10) > Cu (40.26) > Pb (35.51) > Ni (29.10) > Cr (24.50) > As (16.90) > Co (12.80) > Hg (0.121) > Tl (0.47) > Cd (0.37) > Au (0.0066) for the surface sediments and Fe (44.611) > Al (30.689) > Mn (815) > V (137) > Zn (50.10) > Cu (32.88) > Co (17.50) > Ni (8.99) > Cr (6.20) > Pb (3.18) > As (2.89) > Cd (0.5) > Tl (0.053) > Au (0.006) = Hg (0.006) for the rocks. The metal concentrations of the surface sediments ranged from 36.300 ppm at the sampling point (SP) 12 to 8.500 ppm at SP 3 for Al, from 25.9 ppm at SP 9 to 5.8 ppm at SP 10 for As, from 64.78 ppm at SP 16 to 9.41 ppm at SP 3 for Cu, from 19.5 ppm at the mouth of Sarıçay to 3.4 ppm at SP 3 for Co, from 57.30 ppm at SP 18 to 3.70 ppm at SP 6 for Cr, from 39.200 ppm at the mouth of Değirmendere to 10.000 ppm at SP 10

for Fe, from 0.74 ppm at SP 6 to 0.024 ppm at SP 10 for Tl, from 79 ppm at the mouth of the Değirmendere to 16 ppm at SP 3 for V, and from 110 ppm at the mouth of the Değirmendere to 22.30 ppm at SP 3 for Zn (Fig. 2). The maximum values were determined as 0.0125 ppm at the mouths of Sarıçay and Değirmendere rivers for Au; 0.59 ppm at the mouths of Sarıçay and Değirmendere rivers and at SPs 4, 5, and 7 for Cd; 0.526 ppm at SP 6 for Hg; 1.763 ppm at SP 12 for Mn; 69.3 ppm at SP 18 for Ni; and 91.49 ppm at SP 11 for Pb. The minimum values were found at SP 10 for Hg (0.023 ppm), at SP 3 for Mn (223 ppm), at SP 10 for Ni (6.4 ppm), and at SP 3 for Pb (13.81 ppm). According to their spatial distributions, the seasonal streams discharging into SP 10 decreased all the metal concentrations. Hg, Pb, Tl, Mn, CDP, and $CaCO_3$ were not distributed homogeneously in the surface sediments, reaching their maximum concentrations with the local peaks (Fig. 2). Its minimum $CaCO_3$ concentration was lower than that of İkizcetepeler Dam (2%) and Aktaş Lake (9.20%) (Kükürer, 2017), while its maximum concentration was higher than that of Çardak Lagoon (5.30%) (Kükürer et al., 2020) and Emerald Lake (9.80%) (Karthikeyan et al., 2020).

The Al concentration of Atikhisar Dam was higher than all the wetlands except for Manwan Dam in Table 1. Its concentration was higher than that of Castilseras, Klingenberg, and Çatören dams for As; that of all the dams except for Klingenberg dam for Cd; that of Çardak lagoon for Co; that of İkizcetepeler, Klingenberg, and Jutrosin dams for Cr; that of all the dams except for lake Emerald for Cu; that of all the dams except for lake Emerald and Castilseras dam for Fe; that of all the dams for Hg and Mn; that of Çatören, İkizcetepeler, Castilseras, and Jutrosin dams for Ni; than that of all the dams except for Manwan dam for Pb; and that of Çardak lagoon and Çatören, İkizcetepeler, and Jutrosin dams for Zn. When compared to the various wetlands, the high Al, Cd, Cu, Fe, Hg, Mn, Ni, and Pb concentrations occurred in Atikhisar dam (Table 1).

Indicative of the transportation and storage processes, the spatial distribution of OC plays an important role in the surface sediment metals (Jiang et al., 2018; Tomlinson et al., 1980). When increased with anthropogenic influence, OC concentration poses a risk of water pollution (Xu et al., 2019). Its concentration in Atikhisar dam varied between 3.48% at SP 8 and 0.99% at SP 14, with a mean of 2.26%, and was

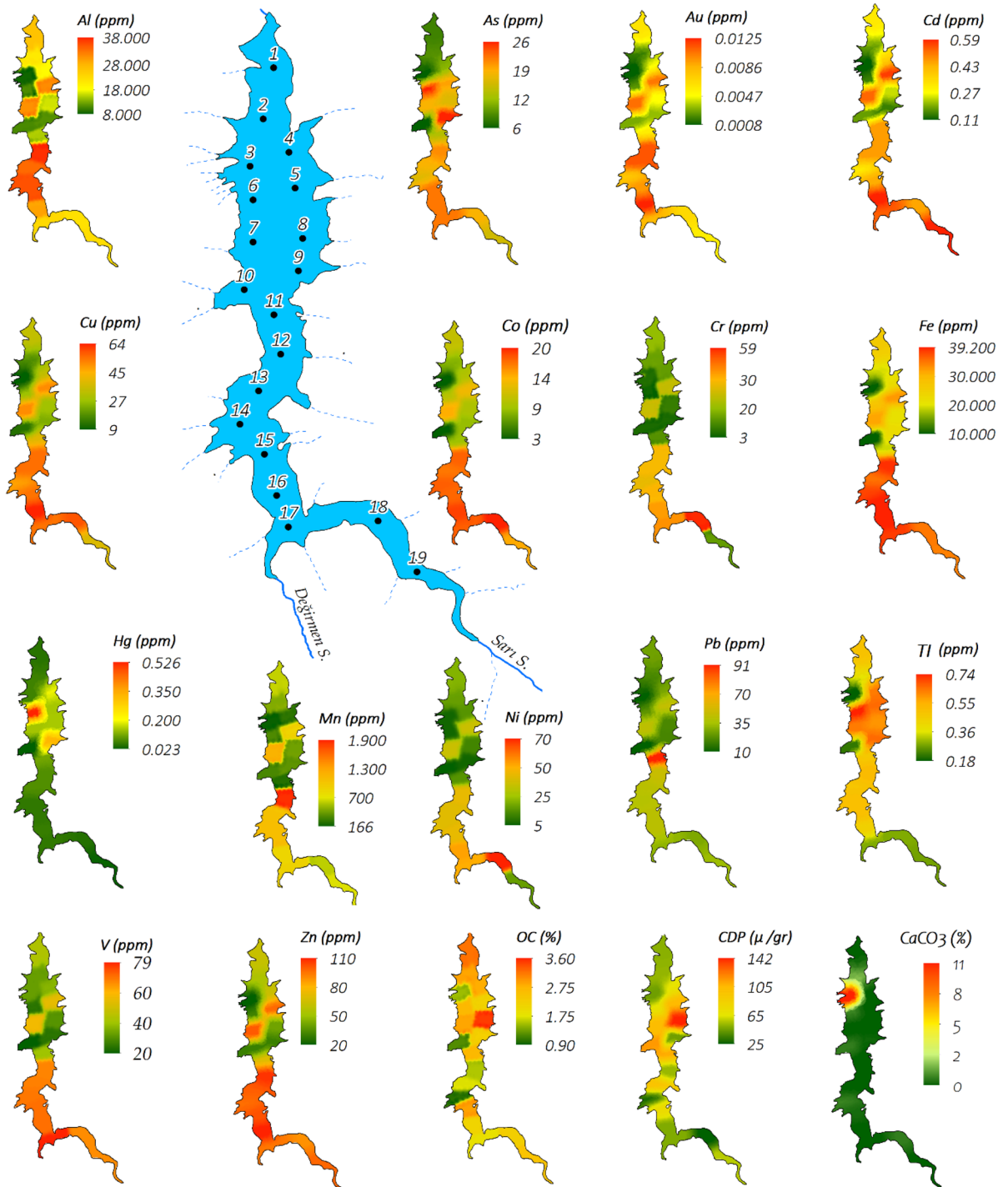


Fig. 2 Spatial distributions of metal, OC, CDP, and $CaCO_3$ concentrations for the surface sediments of Atkhisar dam

Table 1 Comparative metal concentrations (ppm) in related literature (bold values show those higher than that of Atikhisar dam)

Location	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Atikhisar Dam (Turkey) (This study)												
Min	8.500	5.80	0.31	3.50	3.70	9.41	10.000	0.023	223	6.40	10.83	22.30
Max	36.300	25.90	0.59	19.50	57.30	64.78	39.200	0.526	1.763	69.30	91.49	110.30
Çardak Lagoon (Turkey) (Kükreker et al., 2020)												
Min	800	13.6	0.05	7.40	34	12.10	15.000	0.029	212	34.50	7.40	33.30
Max	21.000	29.20	0.32	15.40	70	54.80	33.000	0.070	401	74.30	27.20	92.20
Çatören Dam (Turkey) (Çiftçi, 2015)												
Min	3.500	0.001			30.10	18.50	1.950		112	7.50	12.50	19.23
Max	13.000	0.01			140.70	42.20	1.950		425	38.25	26.83	42.41
İkizecetepeler Dam (Turkey) (Fural et al., 2020)												
Min	10.170	16.60	0.09		12.80	10.60	20.000	0.025	402	16.50	14.68	33.45
Max	20.520	32.90	0.19		30	22.20	30.020	0.108	1.159	54.70	36.56	65.65
Klingenberg Dam (Germany) (Hahn et al., 2018)												
Min		10.60	2.48		1.73	5.62			3.54	6.32	2.63	88.6
Max		13.60	167		3.07	15.10			5.09	112.20	22.60	3.281
Emerald Lake (India) (Karthikeyan et al., 2020)												
Min				91	336	520	7.81		314	151	20.10	128
Max				129.91	523	701	132.90		462	158	53.21	215
Castilseras Dam (Spain) (Ordiales et al., 2015)												
Min	10.400	8.32		15.62	52.69	7.45	30.050		433	27.74	20.95	65.61
Max	15.800	14.30		26.33	85.69	21.51	51.700		666	60.31	50.84	116.82
Manwan Dam (China) (Wang et al., 2012)												
Min	24.500	10.30			38.29	15.85	19.100		246.58		17.03	45.32
Max	61.000	72.56			89.85	56.32	37.900		769.06		92.20	259.84
Jutrosin Dam (Poland) (Sojka et al., 2019)												

Table 1 (continued)

Location	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Min			0.08		0.60	0.45				0.38	3.12	6.08
Max			0.29		5.01	7.48				6.61	13.6	60.10

estimated at 2.75% at the mouths of both Sarıçay and Değirmendere rivers primarily feeding the dam and to be of allochthonous origin. Its minimum concentration was higher than that of Wadi Al-Arab dam (0.80%) (Ghrefat & Yusuf, 2006), while its maximum concentration was higher than that of İkizcetepeler dam (3.48%) (Fural et al., 2019), lake Çıldır (2.55%) (Kükreer et al., 2015), and lake Tortum (1.68%) (Kaya et al., 2017).

As an indicator of net primary production and metal transportation, CDP analysis is frequently used in ecological risk assessment (Laval-Martin, 1985). Its concentration ranged from 142.05 µg/g at SP 8 to 25.32 µg/g at SP 18, with a mean of 69.33 µg/g, and was estimated at 25–30 µg/g in the mouth of Sarıçay and Değirmendere rivers and to be of autochthonous origin. CaCO₃ concentration changed from 0.00 to 11.02% with a mean of 0.85%. Its maximum concentration occurred at SPs 2 and 3. Minimum CDP concentration was higher than that of İkizcetepeler dam (25 µg/g), while its maximum was higher than that of lake Çıldır (47.67 µg/g).

Spatial distribution of EF

The mean values of EF were of the following order: Hg (20.35) > Pb (16.61) > Tl (14.62) > Cd (9.95) > As (9.08) > Cr (4.92) > Ni (4.13) > Zn (2.02) > Cu (1.70) > Au (1.22) > Mn (1.18) > Co (1.01) > Fe (0.90) > V (0.49) (Fig. 3). The areas with the maximum EF were detected as follows: SP 4 for Hg (49), SP 11 for Pb (50), SP 6 for Tl (41), and SPs 11 and 19 for Cd (17). The mouth of Sarıçay river exhibited the maximum EF for Cr (13), Ni (11.50), Zn (3), and Cu (2.55). Au (1.91) peaked at the mouths of both Sarıçay and Değirmendere rivers. The peak values occurred at SP 12 for Mn (1.80), at SP 18 for Co (1.56), at SP 6 for Fe (1.50), and at SP 17 for V (0.78). Figure 3 presents the detailed spatial distributions of EF in the surface sediments. Au, Cd, Co, Cr, Cu, Ni, V, and Zn peaked at the mouths of Sarıçay and Değirmendere rivers and were distributed almost homogeneously in the surface sediments. As, Fe, Hg, Mn, Pb, and Tl were not homogeneously distributed in the surface sediments and exhibited local peaks. The seasonal streams at SP 10 reduced the enrichment of all the metals except for Au, Cd, and Mn (Fig. 3).

The As enrichment in Atikhisar dam (9.08) was lower than that of Gökçekaya (46.13) (Akin &

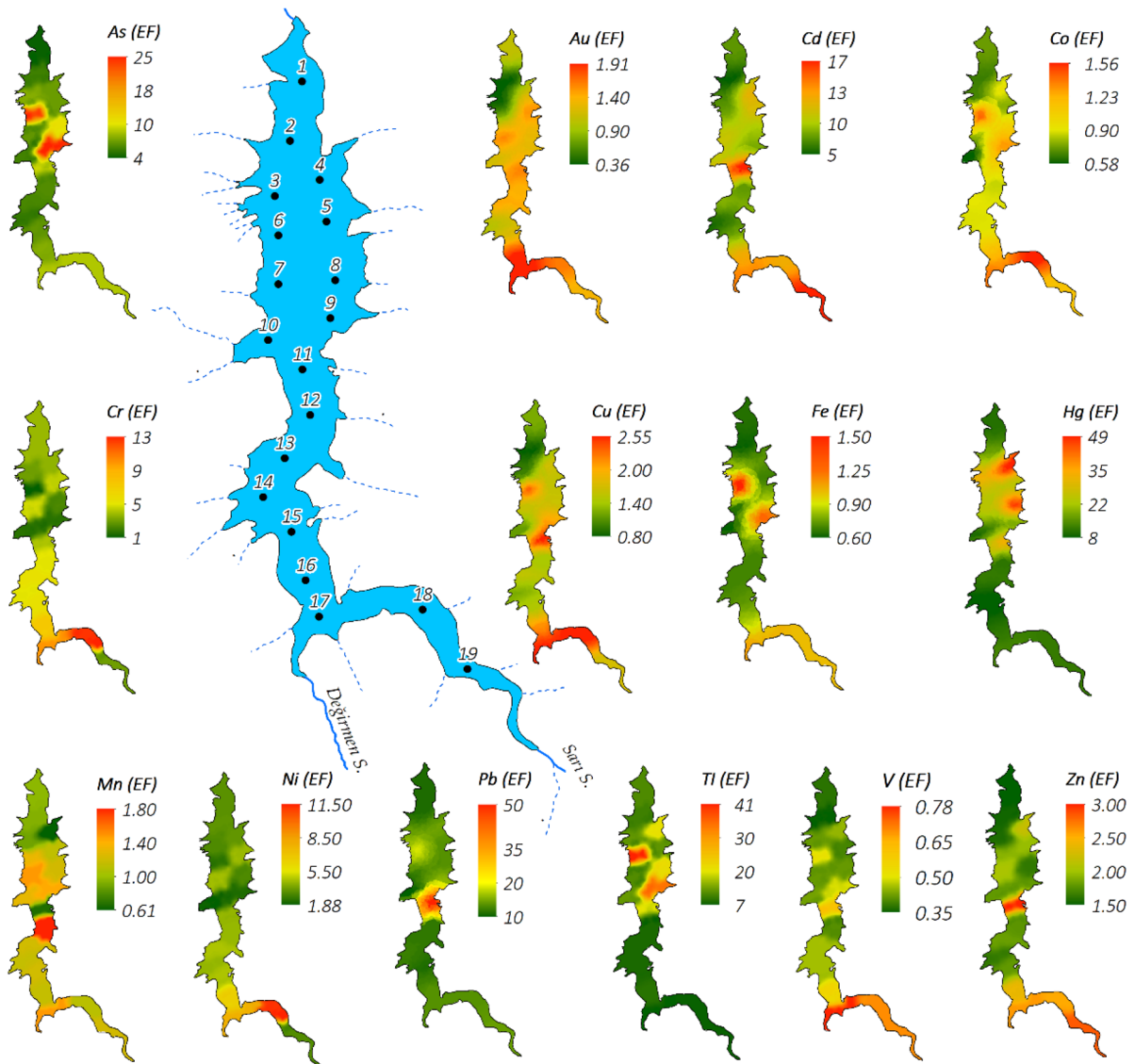


Fig. 3 Spatial distributions of EF for the surface sediments of Atikhisar dam

Kırmızıgül, 2017) and Kapulukaya (47.35) (Başaran, 2010) dams but higher than that of İzkizcetepeler (3.88) (Fural et al., 2020) and Manwan (1.48) (Wang et al., 2012) dams and lake Tortum (1.35) (Kükrer, 2016). Its Cd enrichment (9.95) was higher than that of Gökçekaya (2.04), Kapulukaya (1.89), and İzkizcetepeler (2.04) dams and lake Tortum (1.79). Its Hg enrichment (20.35) was higher than that of İzkizcetepeler (2.34), Aguamilpa (0.46) (Pereza et al., 2015), and Kapulukaya (0.64) dams. Its Cr enrichment (4.92) was lower than that of Gökçekaya (7.58) dam but higher than

that of İzkizcetepeler (2.86), Kapulukaya (3.42), and Manwan (0.72) dams. Its Pb enrichment (16.61) was higher than that of İzkizcetepeler (0.48), Kapulukaya (1.13), and Wadi Al-Aqiq (0.16) dams (Alghamdi et al., 2019) but lower than that of Gökçekaya (23.59) dam. Its Cu enrichment (1.70) was lower than that of Gökçekaya (6.54) and Kapulukaya (18.51) dams but higher than that of İzkizcetepeler (1.15), Manwan (0.95), and Aguamilpa (0.61) dams. Its Ni enrichment (4.13) was lower than that of Kapulukaya (24.44), İzkizcetepeler (6.93), Gökçekaya (5.77)

dams but higher than that of Aguamilpa (1.55) and Wadi Al-Aqiq (0.69) dams and lake Tortum (1.07). Its Zn enrichment (2.02) was lower than that of lake Aygır (2.70) (Kükrer, 2018) and Gökçekaya (13.09) and Kapulukaya (7.03) dams but higher than that of İkizcetepeler (1.08) and Manwan (1.24) dams. Overall, As, Cd, Hg, Cr, and Pb enrichments were higher in Atikhisar dam than in most wetlands in the related literature.

Anthropogenic impact assessment with Igeo

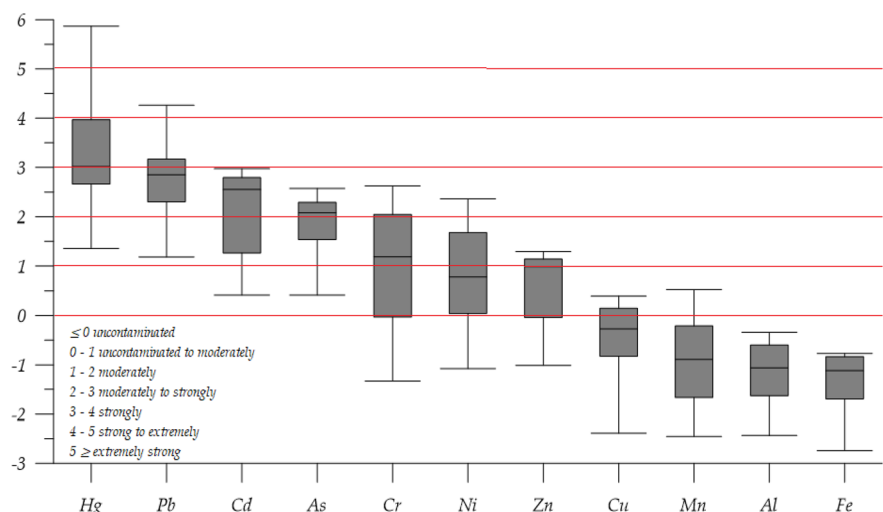
The mean *Igeo* values of the surface sediment metals were as follows: Hg (3.32) > Pb (2.75) > Cd (2.13) > As (1.86) > Cr (0.97) > Ni (0.77) > Zn (0.58) > Cu (-0.45) > Mn (-0.95) > Al (-1.15) > Fe (-1.35) (Fig. 4). EF and *Igeo* were used to identify the natural versus anthropogenic origins of the metals. The source of the Hg enrichment was attributed to the mining activities and municipal waste streams from the extensive settlements in the basin. Our finding was consistent with Hg enrichments reported (Tecra Tech Inc., 2005; Gray & Hines, 2009; Yang et al., 2016). Hg is also used in the recovery of gold in mines (Pinedo-Hernández et al., 2015; Song et al., 2019).

The primary sources of Cr include unexplored natural deposits and industry (Mishra & Bharagava, 2016). It peaked at SP 18 due to kaolinite mines in its immediate vicinity, thus pointing to its anthropogenic source as the mining area. The possible anthropogenic sources of Tl include mines, industrial activities, and

fossil fuels (Karbowska, 2016). It peaked at SP 9 near a mine land (Fig. 3). Its another source was emission from the fossil fuel combustion by the settlements throughout the dam.

Found in low concentrations among the rock samples, Pb was described as a moderate pollutant according to *Igeo*. Since the mining activities did not affect Pb deposits in the basin reaching 26%, the source of the Pb enrichment was evaluated as natural factors. Ilgar (2000) reported that the Pb deposits in the basin increased the Pb concentration in the sediments of Sariçay river. Cd is the raw material of phosphate fertilizers (Karaca & Turgay, 2012). The phosphate measurements of the Atikhisar dam water exceeded the recommended limit values by 10 times (Akbulut et al., 2006). Pesticide residues were also detected in the Atikhisar dam and Sariçay river (Kaya, 2007). The possible source of Cd was related to agricultural activities based on the spatial analysis, field campaigns, and related literature. The probable anthropogenic sources of As included the mines and industrial facilities located in the study area. The possible source of Cr included mineral deposits and municipal and industrial wastes. Agricultural fertilizers as the probable source of Ni (Bolat & Kara, 2017) were also evidenced by the significant relationships between Ni and Cd. Overall, the primary cause of the anthropogenic effects in the basin was improper LULC changes. For example, the environmental protection zones have been compromised in the dam basin by the existing land uses not compatible with vulnerable water resources (Topteye, 2011).

Fig. 4 Box-Whisker diagram of geoaccumulation index (*Igeo*)



TRI

The toxic ecological risk index (TRI) values of the metals were thus As (1.28) > Ni (1.00) > Cu (0.92) > Pb (0.73), Hg (0.48) > Zn (0.45) > Cr (0.43) > Cd (0.27). Given the mean TRI of 5.56, a low level of toxic risk was identified in the surface sediments. The TRI value peaked at 7.89 at the mouths of Değirmendere and Sarıçay rivers and plunged at 1.69 at SP 10 (Fig. 5). The maximum level at the outlets of Sarıçay and Değirmendere rivers pointed to a small quantity of the human-enriched metals discharged from the basin.

Spatial distribution of mER and mPER

The mER values were as follows: Hg (813) > Cd (298) > TI (146) > As (90) > Pb (83) > Ni (20) > Cr (9) > Co (5) > Zn (2) > Mn (1) > V (0.98). The Hg ecological risk (1.900) peaked at SPs 4 and 8. Cd was at its maximum (550) at the mouths of Değirmendere and Sarıçay rivers and at SP 11. The maximum ecological risk was caused by TI (430) at SP 6, As (26) at SPs 6 and 9, and Pb (260) at SP 11. Ni (11), Cr (25), and Co (8) resulted in a low level of ecological risk and peaked at SP 18. The maximum levels occurred with Zn (3) at

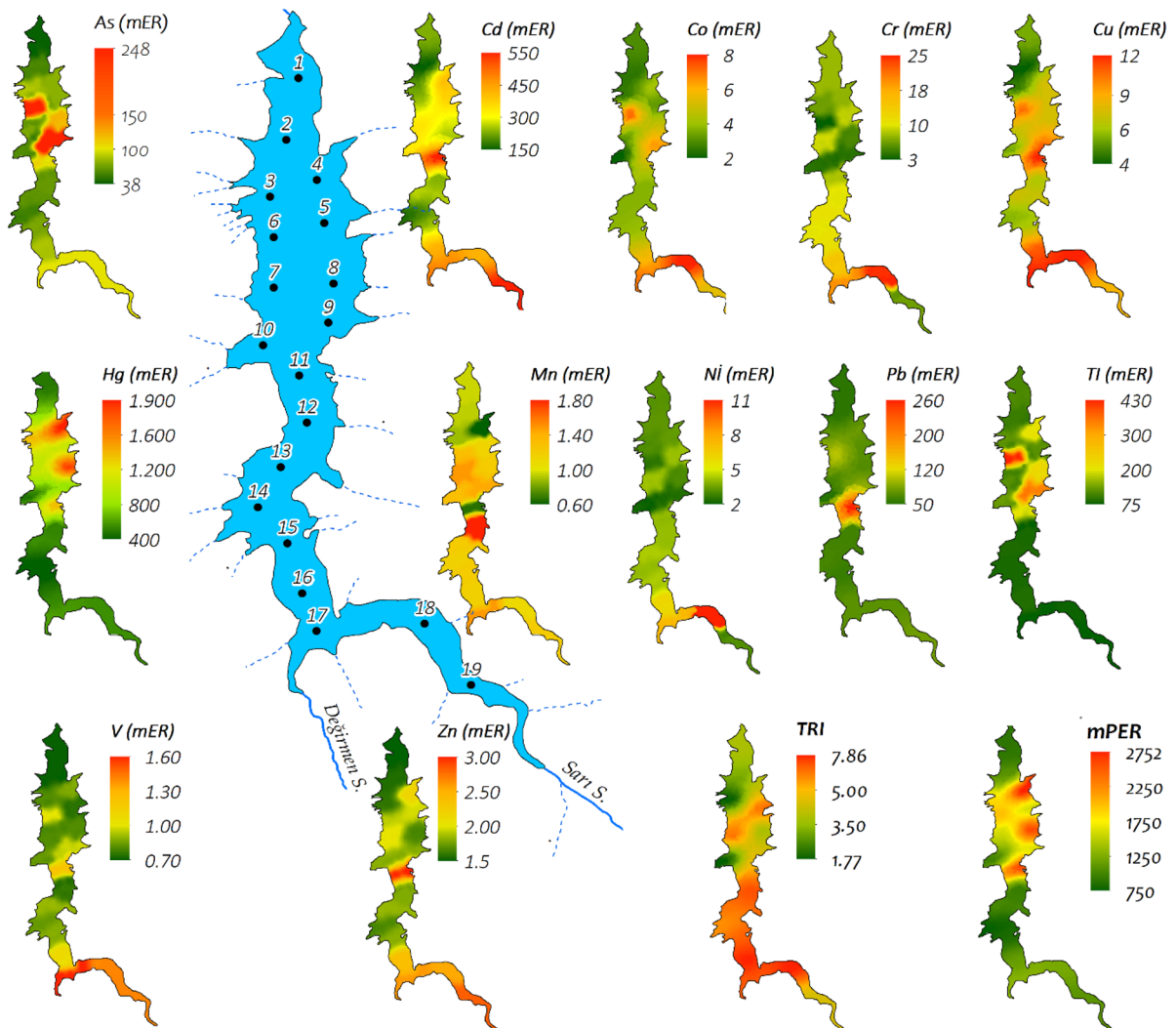


Fig. 5 Spatial distributions of mER, TRI, and mPER

SP 11, Mn (1.80) at SP 12, and V (1.60) at the mouth of Değirmendere river (Fig. 5). Cd, Co, Cr, Cu, Ni, V, and Zn reached their maximum ecological risk levels at the mouths of Sarıçay and Değirmendere rivers. As, Hg, Mn, Pb, and Tl showed local peaks.

The mPER value data pointed to a very high potential ecological risk for the entire surface sediments and peaked at SP 4. The TRI and mPER values were higher in the outlets of the two main streams. The spatial distribution maps showed that TRI and PER decreased as a result of the discontinuous rivers located on the left bank of the dam and increased due to the rivers on the right bank (Fig. 5). This was probably related to the mining facilities on the right bank. Kaolen and Au mines, in operation for many years, are responsible for the high TRI and mPER values in the specified areas.

The mER value of Hg (813) was higher than that of Çardak lagoon (98) (Kükrer et al., 2020), İkiçetepeler dam (94) (Fural et al., 2020), and lake Çıldır (110) (Kükrer et al., 2015). Gold mines in the basin appeared as the cause of its extremely high ecological risk (Pinedo-Hernández et al., 2015; Song et al., 2019). Cd (298) was higher than that of Çardak lagoon (67), İkiçetepeler dam (61) but lower than that of Tailings (711) and D. Duze (2.532) dams. As (90) was higher than that of Çardak Lagoon (17) (Kükrer et al., 2020), İkiçetepeler (38) (Fural, 2020) and Tailings dams (10) (Sey & Belford, 2019) but lower than that of D. Duze dam (96) (Tytla & Kosteci, 2019). Pb (83) was higher than that of D. Duze (45), İkiçetepeler (6), and Wadi Al-Aqiq dams (1.31). Hg, As, Pb, Tl, and Cd were higher than the mER values of some wetlands in related literature. mPER (1481) was higher than that of Çardak lagoon (226) and İkiçetepeler (201) and Wadi Al-Aqiq (20) dams but lower than that of D. Duze (2727) and Tailings (722) dams. The metals that created ecological risks in Çardak Lagoon, 35 km northeast of Atikhisar dam, were as follows: Hg>Cd>As>Tl>Pb (Kükrer et al., 2020). This ranking was similar to our study except for As and Tl although Çardak lagoon and Atikhisar dam had different risk levels. This shows that the anthropogenic effects in the adjacent areas were similar.

Possible sources of metals, OC, CDP, and CaCO₃

Factor analysis identified three factors with an eigenvalue of > 1, explaining 81.80% of the total variance.

The first factor consisted of Cu, Zn, Ni, Mn, Fe, Cd, Cr, Al, Au, Co, and V and explained 56.94% of the variance (Table 2). All the metals had a low enrichment except for Ni, Cr, and Cd in the first factor and had low ecological risk levels except for Cd. Given Al, Fe, Mn, and Au as the main components of the earth's crust, and their enrichment and ecological risk level, the first factor was estimated to be of lithological origin. The enrichments of Ni, Cr, and Cd related to some anthropogenic effects. Agriculture may be responsible for Ni and Cd, while municipal and industrial wastes or undetected ore deposits may be responsible for Cr. According to the spatial distribution maps, all the metals in the first factor were transported from the basin by Sarıçay and Değirmendere rivers. The concentrations in the surface sediments were almost homogeneous except for Ni, Cr, and Cd. Local peaks observed for Ni, Cr, and Cd verified that these metals were of anthropogenic origin. The inclusion of some anthropogenic and lithogenic metals in the first factor was because the source definition and transportation processes were taken together in the statistical data analysis. All the metals in the first factor were transported from terrestrial sources by rivers. The second factor consisted of As, Hg, and Tl, whose anthropogenic

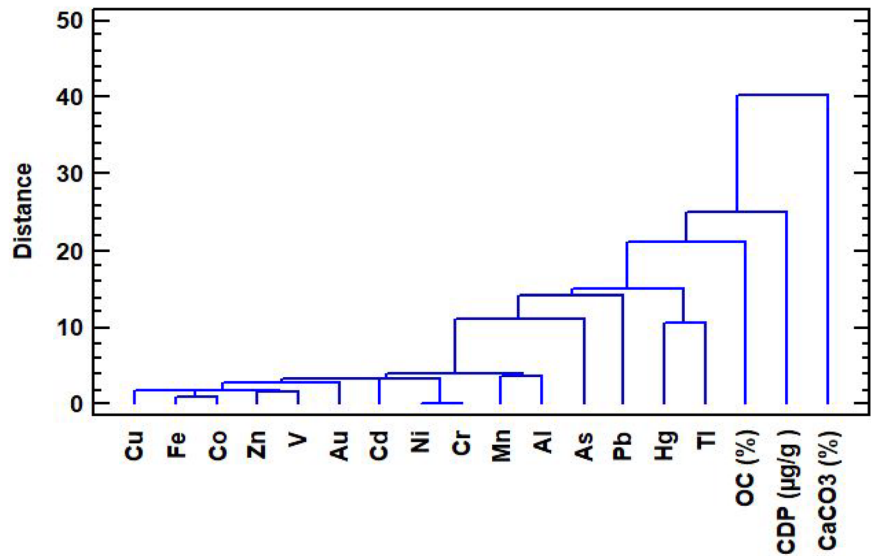
Table 2 Results of factor analysis (bold values show metals within the same factor)

	Factor 1	Factor 2	Factor 3
Cu	0.9682	0.119572	0.0901258
Pb	0.482246	0.0074078	0.548132
Zn	0.973256	-0.0647696	0.125258
Ni	0.906572	-0.0784261	-0.203494
Mn	0.827294	0.0698359	-0.0659511
Fe	0.930637	0.266546	-0.139117
As	0.499	0.781646	-0.0525002
Cd	0.842684	-0.117968	0.336715
Cr	0.912822	-0.109114	-0.221156
Al	0.885423	-0.00803183	0.0505892
Hg	-0.376648	0.886271	-0.0208685
Au	0.917694	0.0483786	0.205257
Co	0.957095	0.179961	-0.129404
Tl	0.0498728	0.844589	0.375798
V	0.972018	-0.0665766	-0.050646
OC	-0.144738	0.332326	0.540522
CDP	-0.229264	-0.0246606	0.822807
CaCO ₃	-0.475076	-0.401639	-0.485244

Table 3 Spearman correlation matrix (bold values show a strong correlation)

	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Al	Hg	Au	Co	Tl	V	OC	CDP
Cu																	
Pb	0.7702																
Zn	0.8754	0.8439															
Ni	0.9206	0.5994	0.8082														
Mn	0.7158	0.6298	0.8333	0.7468													
Fe	0.8474	0.5912	0.8386	0.8609	0.8316												
As	0.4965	0.3439	0.4368	0.4107	0.4596	0.6526											
Cd	0.7705	0.7784	0.8135	0.6476	0.5444	0.5743	0.2357										
Cr	0.8982	0.5719	0.7825	0.9855	0.7316	0.8193	0.3228	0.6464									
Al	0.7579	0.7228	0.8702	0.7898	0.9386	0.8281	0.3386	0.5796	0.7754								
Hg	-0.084	0.1632	-0.057	-0.216	-0.068	-0.097	0.4669	-0.117	-0.299	-0.064							
Au	0.9193	0.8158	0.9263	0.8153	0.8368	0.8193	0.4579	0.7810	0.8035	0.8684	-0.018						
Co	0.9179	0.5985	0.7995	0.9236	0.7459	0.9127	0.4976	0.6366	0.8802	0.7670	-0.174	0.8205					
Tl	0.0149	0.2206	0.0800	-0.079	0.2021	0.1142	0.5343	-0.100	-0.179	0.2012	0.1467	0.1467	0.0295				
V	0.8745	0.6743	0.8736	0.9047	0.7867	0.9043	0.4021	0.7443	0.8946	0.8332	0.8437	0.8437	0.8898	-0.097			
OC	-0.162	-0.061	-0.069	-0.096	-0.110	-0.199	0.0132	-0.051	-0.143	-0.104	-0.184	-0.184	-0.215	0.3327	-0.158		
CDP	-0.147	0.2140	0.0175	-0.337	-0.051	-0.304	-0.154	0.1398	-0.337	-0.074	0.0070	0.0070	-0.352	0.2170	-0.213	0.3221	
CaCO ₃	-0.491	-0.592	-0.524	-0.278	-0.323	-0.274	-0.153	-0.719	-0.283	-0.379	-0.606	-0.606	-0.290	-0.227	-0.407	-0.230	-0.401

Fig. 6 Cluster analysis



effects were detected in all ecological risk indices, and explained 15.87% of the variance. The third factor consisted of Pb, OC, and CDP, explaining 8.98% of the variance. Though highly enriched in the local area, Pb originated from its natural deposits in the basin and was transported from within the basin by Sariçay and Değirmendere rivers. CDP was discharged by the seasonal streams around the dam.

A positive correlation was found between Cu and Pb, Zn, Ni, Mn, Fe, As, Cd, Cr, Al, Au, Co, and V; between Pb and Zn, Ni, Mn, Fe, Cd, Cr, Al, Co, and V; between Mn and Fe, Cd, Cr, Al, Au, Co, and V; between As and Hg; between Co and Tl; between Cd and Cr, Al, Au, Co, and V; and between Cr and Al, Au, Co, V. A negative correlation was detected between Cu and CaCO₃; between Pb and CaCO₃; between Cd and CaCO₃; between Al and Au, Co, V; between Hg and V; between Au and Co, V; and between Co and V (Table 3). Though effective in the transport processes of the metals, OC and CDP did not correlate with any metal. CaCO₃ showed a negative correlation with Cu, Pb, Zn, and Cd. Some metals that created ecological risks were in positive correlation with the metals of lithological origin. This is due to the similar transportation processes of the metals of anthropogenic and lithogenic origins.

According to the cluster analysis, Cu, Fe, Co, Zn, V, Au, Cd, Ni, Cr, Mn, and Al were transported from the same source. When the factor analysis data and spatial distribution maps were examined, the

forementioned metals were transported from terrestrial sources by the rivers and were of lithologic origin. These metals were exposed to anthropogenic effects in addition to lithologic sources (Fig. 6). Ni, Cr, and Cd are of mixed origin. As, Pb, Hg and Tl were included in the same class and of anthropogenic origin except for Pb. OC, CDP, and CaCO₃ were also in the same class, but no common source identifications could be made for them. Findings from cluster analysis were consistent with those from the factor analysis and spatial distribution maps.

Conclusion

This study quantified the ecological risk levels in the surface sediments of Atikhisar dam under the pressures by mining, agriculture, settlements, and transportation networks and detected an extremely high level of ecological risk. Among the possible reasons for this were Hg and Tl pollutions from mines and municipal waste, Cd from phosphate fertilizers, Pb from its natural deposits, and anthropogenic As. OC, CDP, and CaCO₃ were not positively correlated with the metals, thus showing their slight effect on the transportation and deposition processes of the metals. An extremely high potential ecological risk in the sediments of Atikhisar dam exists as a result of mining and agricultural activities. This requires that rehabilitation projects be put in practice for Çanakkale

not to have pollution of its drinking water resources, LULC changes be regulated to ensure their sustainable use, the leach pools of the mines be relocated, municipal waste be controlled, and organic agriculture be encouraged.

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Data availability statement The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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