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Assessment of heavy metal pollution with different indices in Süreyyabey dam lake in Turkey

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ABSTRACT

The current study, for the first time, focused on the determination of pollution levels and spatial distribution of heavy metals in Süreyyabey Dam Lake which is an important water source for the surrounding area. Water and sediment samples were taken seasonally from six sites exposed to different anthropogenic impacts. The most enriched elements in the Dam Lake were As, Cd, Mo, and Pb. In all sampling sites, the average heavy metal concentrations indicated low risk except for Cd and Pb which were classified in the moderate ecological risk class. Overall, the ecological risk was low for one site (S3) because of the far distance from the residential areas, while the ecological risk of the other stations was moderate. According to water analysis results, the aquatic life criteria could not be met for Zn, Cu, Cr, and Hg in Süreyyabey Dam Lake. Although the dam lake is used only for irrigation purposes, the Süreyyabey Dam Lake water is not suitable for drinking according to the metal limit values of the World Health Organisation. The results of the current study will contribute to the awareness of local authorities by using several indices on taking the necessary precautions.

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reservoir; surface water;
sediment

Introduction

The term “heavy metal” is used to refer to metal/metalloids that have five times greater density than water and are toxic at low concentrations in the aquatic ecosystems [1]. Because of their toxicity, non-degradable structure, and bioaccumulation in the food chain; understanding how heavy metal pollution impacts aquatic ecosystems is of global concern [2,3]. Heavy metals (HMs) can be transported to aquatic ecosystems through natural processes such as rock weathering, volcanic eruption, atmospheric deposition, or anthropogenic activities such as urban and industrial wastewater, mining activities, smelting operations, and fertilisation [4–7]. While some heavy metals like (copper, iron, zinc, nickel, etc.) are essential as trace elements in biological systems, many (arsenic, cadmium, mercury, lead, etc.) are nonessential and toxic at low concentrations

[8]. Long-term exposure to heavy metals may lead to potential risks not only for aquatic organisms, terrestrial organisms, and also for human beings [2].

Dams play a critical role in human life such as drinking and agricultural water supply, fish farming, and flood control [9]; however, these ecosystems are very sensitive to chemical pollutants, such as nutrient loading (total phosphorus, nitrogen) and heavy metal accumulation [10] via surface flow, groundwater inputs, and precipitation. Heavy metals are more concentrated in sediment than in water [11], thus sediments in dam lakes and reservoirs serve as both sinks and sources for heavy metal pollution [12]. In the international scientific and public community, HMs have been one of the important topics due to their severe impacts [13]. Nowadays, the dam lakes in Turkey are suffering several environmental problems such as eutrophication [14], microbial pollution [15], and microplastic pollution [16]. Recently, the concern of heavy metal pollution has also raised in dam lakes due to providing domestic and agricultural water for surrounding areas [17].

Detecting the total heavy metal concentration in the sediment of these systems is a crucial proxy for identifying the source and magnitude of heavy metal contamination as well as determining their ecological status [18]. In evaluating the potential sources, background enrichments of heavy metals, and ecological risks to biodiversity [19]. Different indices such as enrichment factor (EF), geoaccumulation index (Igeo) contamination factor (CF), pollution load index (PLI), potential ecological risk index (PERI) have used [20]. These indices can provide useful information for the management of dam lakes particularly in those impounded to supply several activities like Süreyyabey dam lake, Turkey [17]. Thereby, in the current study, the heavy metal pollution was assessed for the first time in Süreyyabey Dam Lake, a reservoir in Turkey that is used for irrigation, agriculture, flood control, and fishing activities. The aim of the study was; (i) to determine the heavy metal concentration levels in water and sediment samples seasonally, (ii) to specify enrichment levels of the evaluated heavy metals with Contamination Factor (CF), Enrichment Factor (EF), Geoaccumulation Index (Igeo,) and Pollution Load Index (PLI). indices, and (iii) to evaluate the potential risk of heavy metals to aquatic organisms in sediment samples with Threshold Impact Concentration (TEC) and Probable Impact Concentration (PEC sediment quality guidelines and Ecological Risk (ER)) and Potential Ecological Risk (PERI) indices.

Material and methods

Study area

Süreyyabey Dam Lake is a rockfill dam located in the Northern part of Yozgat, Turkey (Figure 1). Çekerek stream, which is one of the most important tributaries of the Yeşilırmak River, and groundwater, are the main water sources of the dam. The surface area, total volume, and max depth of the dam lake are 41.34 km², 1.18 km³, and $\cong$ 50 m, respectively. The water renewal time is ca. 0.47 year and average total phosphorus concentration was 0.074 mg/lit [21]. Moreover, it is serving irrigation water for nearly 42,000 ha. The height of the river bed is 77.5 m [22]. The basin of the dam is not densely populated, only Çekerek province (with a population of approximately 19.000) was located northern part of the dam. The basin is mainly dominated by agricultural and pasture areas. Fish-

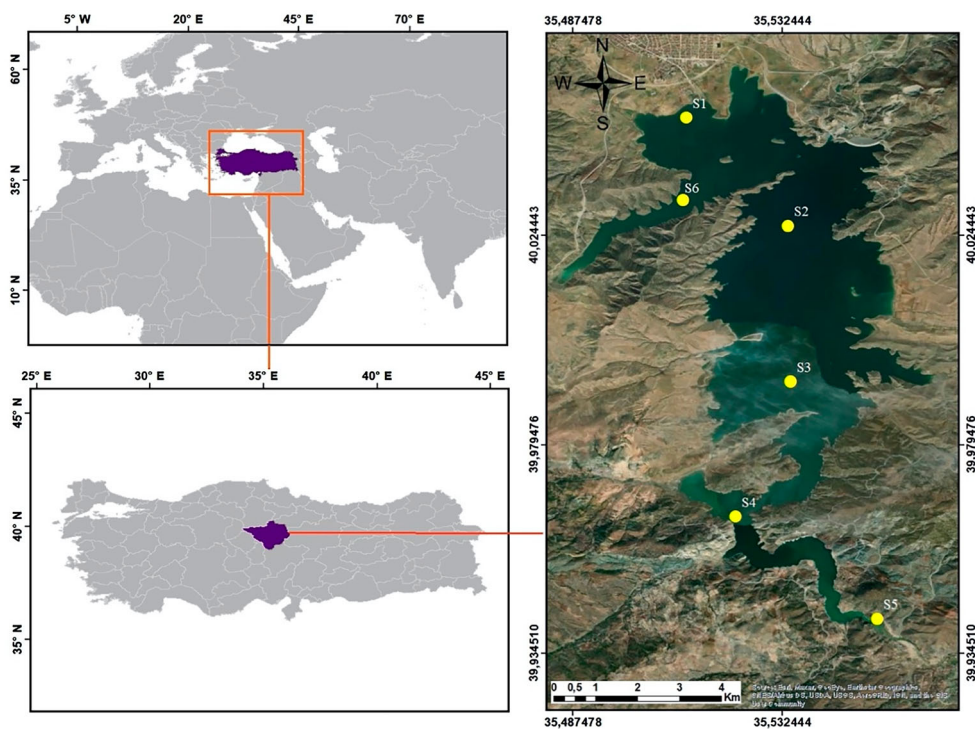


Figure 1. Study site and sampling stations.

cage farming and fishing (trout, carp, mullet, and silverfish) are also common (Turkish Ministry of Agriculture and Forestry).

Sampling and analysis of heavy metals

Sediment and water samples were collected at six stations (S1-S6) seasonally in 2019 (Figure 1).

The sampling sites were selected considering potential anthropogenic sources, proximity to the urban area, fishing activities, and tributaries entering the dam. For the total heavy metal analysis, unfiltered water samples were collected from approximately 10 cm below the surface water and later, ultrapure HNO_3 was added to lower the pH below 2 [23]. Water samples were filtered through the fibreglass filter (pore size; $0.22 \mu\text{m}$) to avoid suspended particles before the analysis.

Sediment samples were collected with an Ekman – Birge grab as three replicates from the approximately 10 cm above the sediment and pooled for each station. Sediment samples were put into a zip-lock plastic bag and kept frozen prior to analysis. Before the analysis, sediment samples were oven-dried ($40\text{--}45^\circ\text{C}$) afterward, powdered within an agate mortar, and sieved through stainless steel sieve griddle ($500 \mu\text{m}$) [24]. To determine background values, rock samples were collected from the research area.

For the sediment analysis, a 0.1 g dried sample was weighed and digested in a combination of a concentrated acid mixture of $\text{HCl}:\text{HNO}_3$ (3:1) in a microwave oven (Start D,

Milestone, Italy) [25]. Digested sediment samples were diluted to 50 ml with ultra-pure water. All used chemicals and reagents were purchased from Merck (Germany).

Inductively-coupled plasma mass spectrometry (ICP-MS, Thermo Scientific ICAPQC, USA) was used to measure the concentrations of 13 metals (Al, Fe, Mn, Cr, Ni, Zn, Co, As, Pb, Cu, Mo, Hg, and Cd) in both sediment and water samples. Regression plots were produced with different standards before the analyses and at least a 99.5% regression coefficient was achieved. Samples were read as three replicates and mean values were considered for the final assessment.

Pollution indices

Environmental pollution indices are extensively used to assess the information about surface sediment contamination levels and toxicity caused by heavy metals in aquatic ecosystems [26]. There are several different indices for this purpose, such as enrichment factor, geoaccumulation index, and contamination factor [25,27].

In the current study, four indices were used to determine the heavy metal contamination levels in sediment samples: (i) Contamination Factor (CF), (ii) Enrichment Factor (EF), (iii) Geoaccumulation Index (I_{geo}) and (iv) Pollution Load Index (PLI). To understand the ecological effect of heavy metals on the dam lake, widely used Ecological Risk (ER) and Potential Ecological Risk (PERI) indices were also evaluated.

1) Contamination factor (CF)

The contamination factor (CF) is used to evaluate the degree of anthropogenic contamination to heavy metal pollution [28]. The formula is:

$$CF = \frac{C_{metal}}{C_{background}}$$

The values of the CF indicate: < 1 low degree, $1 \leq CF < 3$ moderate degree, $3 \leq CF < 6$ considerable degree, $CF \geq 6$ very high degree [28] contamination levels.

ii) Enrichment factor (EF)

Enrichment factor (EF) has been used to assess anthropogenic heavy metal deposition in sediment samples [29]. EF is a robust index to reveal whether the heavy metals detected in the sediment samples are anthropogenic or bedrock originated [30]. The calculation of the EF method is based on the normalisation of measured heavy metals against a reference element, such as Al, Fe, or Mn [12,29]. In this study, EF values were calculated according to the following equation developed by Buat-Menard and Chesselet (1979):

$$EF = \frac{\left(\frac{C_n}{C_{Al}}\right)_{sample}}{\left(\frac{C_n}{C_{Al}}\right)_{background\ value}}$$

Where, C_n : Measured concentration of metal; C_{Al} : Measured concentration of aluminium

The values of the EF indicate: < 1 no enrichment, 1–3 minor, 3–5 moderate, 5–10 moderately severe, 10–25 severe, 25–50 very severe >50 extremely severe enrichments [31].

iii) Geo-accumulation index (I_{geo})

The geo-accumulation index (I_{geo}) proposed by Muller (1979) was applied to quantify the pollution intensity of individual sampling sites. I_{geo} is calculated by the following equation:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \cdot B_n} \right)$$

Where C_n : Measured concentration of metal; B_n : geochemical background concentration of a given element; 1.5: Possible variation of background values due to lithogenic effects.

The values of the I_{geo} indicate: < 0 unpolluted, 0 < I_{geo} < 1 unpolluted to moderately polluted, 1 < I_{geo} < 2 moderately polluted, 2 < I_{geo} < 3 moderately to strongly polluted, 3 < I_{geo} < 4 strongly polluted, 5 < extremely polluted [32,33].

iv) Pollution load index (PLI)

The Pollution load index (PLI) for each metal was calculated by the procedure of Tomlinson et al. (1980):

$$PLI = [CF_1 \times CF_2 \times CF_3 \times CF_4 \dots \times CF_n]^{1/n}$$

Where, C_F = contamination factor; n = number of metals [34]:

Since the PLI index was calculated based on the CF values of 13 elements, it can be used to compare overall toxicity at different stations. According to the index result, values of PLI > 1 indicate that there is heavy metal pollution and PLI < 1 implies there is no heavy metal pollution [34].

Ecological risk (ER) and potential ecological risk index (PERI)

To assess the degree of pollution risk, the Ecological Risk and Potential Ecological Risk Index (PERI) were calculated and proposed by Hakanson (1980). The potential ecological risk index of a single heavy metal (ER) was calculated according to formula 1. To calculate the combined potential ecological risk for heavy metals, formula 2 was applied for each station.

$$\text{Formula (1)} \quad E_r^i = T_r^i \times C_r^i$$

$$\text{Formula (2)} \quad PERI = \sum_{i=1}^n E_r^i$$

The values of the Er indicate: < 40 unpolluted, 40 ≤ Er < 80 moderate, 80 ≤ Er < 160 considerable, 160 ≤ Er < 320 high, ≥ 320 very high [25,28].

The values of the PERI indicate: < 150 low, 150 ≤ Er < 300 moderate, 300 ≤ Er < 600 considerable, ≥ 600 very high ecological risks [28,35].

a) Sediment quality guideline

The accumulation of heavy metals in the sediment may cause changes in environmental conditions and cause an inevitable risk to biotic organisms through food web interactions [36]. Therefore, the use of sediment quality guidelines (SQG) is an important tool that can provide information in evaluating the adverse biological effects of heavy metals under current pollution conditions and in taking protective measures on aquatic organisms [37]. The determined values for metals of Threshold Impact Concentration (TEC) and Probable Impact Concentration (PEC) in freshwater ecosystems were used in the current study. If the amounts of metal in the sediment are below the TEC value then considered “no harmful effects can be identified”, while if the metal concentrations are above the PEC value, considered “possible harmful effects may occur” [38].

Statistical analysis

Prior to the analysis, normality and homogeneity of variance assumptions were checked by a Shapiro-Wilk and Levene’s test, respectively. To determine the differences between heavy metal concentration among stations and seasons, a one-way analysis of variance (ANOVA) was run followed by a Tukey post-hoc test. When the data have not met the assumptions of normality, the Kruskal-Wallis test was applied and for the pairwise comparisons, Dunn’s test was applied. To analyse the significant differences between water and sediment Mann – Whitney U test was employed. The principal component analysis (PCA) is very common for detecting the heavy metal pollution sources in the field; thus, PCA was run to identify the possible contributing source of heavy metals [5,39]. All analyses were performed at a 0.05 statistical significance level. All statistical analysis was performed using R statistical software (R Statistical Software (version 4.0.2; R Foundation for Statistical Computing, Vienna, Austria)). The geographic information system (GIS) is a very common approach to delineate the source of heavy metal pollution in the field. To obtain the GIS-based spatial distribution maps, a free and open-source QGIS was used.

Results and discussion

Heavy metal concentrations: surface water

The mean concentration of heavy metals from different dam lakes in surface water and its comparison with other freshwater ecosystems and different standard values were given in Table S1. In the current study, the mean concentrations ($\mu\text{g/L}$) of heavy metals in surface water was determined as follow: Fe (15052 .1) > Al (2814.6), > Zn (916.1) > Mn (425.3) > Ni (155.5) > As (128.3) > Cu (91.9) > Cr (25.0) > Pb (17.7) > Mo (10.5) > Co (9.1) > Hg (4.8) > Cd (1.3) (Figure 2). The heavy metal concentrations showed spatial and seasonal variations (Table S2). The heavy metal concentrations in water were lower than in sediment (Figure 2, Table S2). In all sampling sites and seasons, Fe and Cd were the most and least accumulated heavy metals. The highest heavy metals were detected in rainy seasons which were autumn and winter. However, the high values showed variations among the heavy metals in different seasons. In winter, Fe, Cr, Cu, Zn, Pb, and Hg

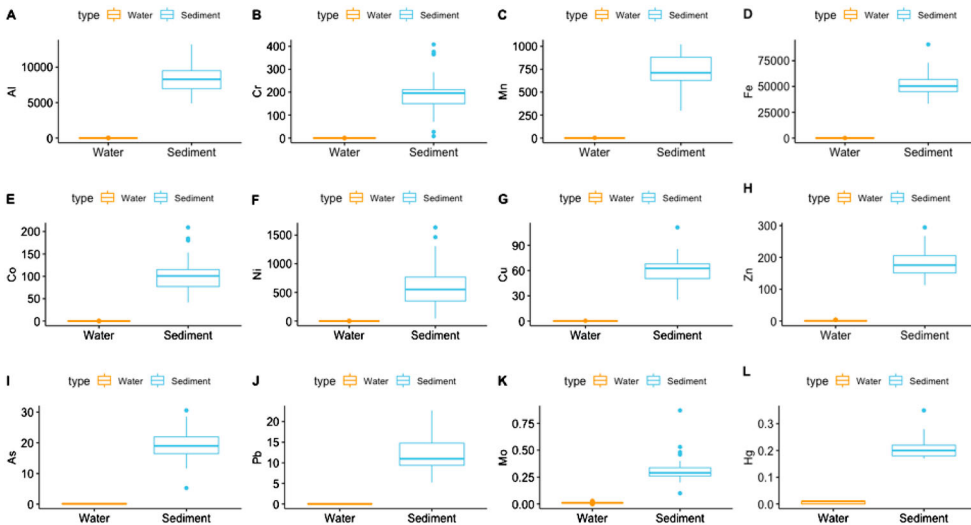


Figure 2. Heavy metal concentration in sediment and water samples from Süreyyabey Dam Lake.

concentrations were high. While in autumn, Al, Ni, As, and Mo was high (Table S2). The elevated levels of heavy metals during the rainy seasons could be related to surface runoffs, agricultural loadings, soil erosion, and the release of municipal waste [36,40,41]. Despite there were no statistically significant difference (Kruskal-Wallis, $p > 0.05$) observed among the sampling sites for Zn, a significant difference was determined between winter (1998.4 $\mu\text{g/L}$) and spring (634.3 $\mu\text{g/L}$). The highest Zn levels may be attributed to cage fish farming activities in this region [42]. These findings were in line with the previous studies that the contribution of fish farming increases the concentration of zinc in the sediments [43] as a result of feed and fecal input [44]. However, the water and sediment chemistry at different locations according to the distance from the trout farms has been determined that the wastes of fish farms cause minor changes in water chemistry [45]. The detected Zn values (2.36–9.25 $\mu\text{g/L}$) were quite low [45] compared to the findings of Zn concentration (916.1 $\mu\text{g/L}$) from the current study.

In water, except for the concentration of Mn between S2 and S5 was statistically significant (Kruskal-Wallis $p < 0.05$), the rest of the metals did not show any significant differences among stations. The heavy metal concentrations in different seasons showed significant variations between autumn and winter for Al, Cr, Cu, Hg, and Mo ($p < 0.05$; Table S3). Among the heavy metals, Cu concentration was the lowest (37.54 $\mu\text{g/L}$) in autumn and the highest in winter (138.81 $\mu\text{g/L}$). The difference was found significant between autumn-winter (Post hoc (Dunn), $p < 0.05$). Similarly, the highest Cu levels in winter (with 119 $\mu\text{g/L}$) were observed in an urban river and the high concentration could be because of domestic waste and intensive agricultural activity [23]. The seasonal difference for Pb was determined only between the autumn-summer and autumn-winter seasons. ($p < 0.05$). The lowest Pb concentration was determined in winter at 7.6 $\mu\text{g/L}$ (Table S2). To identify the possible contributing source of heavy metals in the field, the highest contribution of metals in the water column was made by Hg (22%), Cu (21%), As (17%), Pb (13%), respectively according to PCA results. The first two dimensions for water samples explained 59% of the total variance (Figure 3).

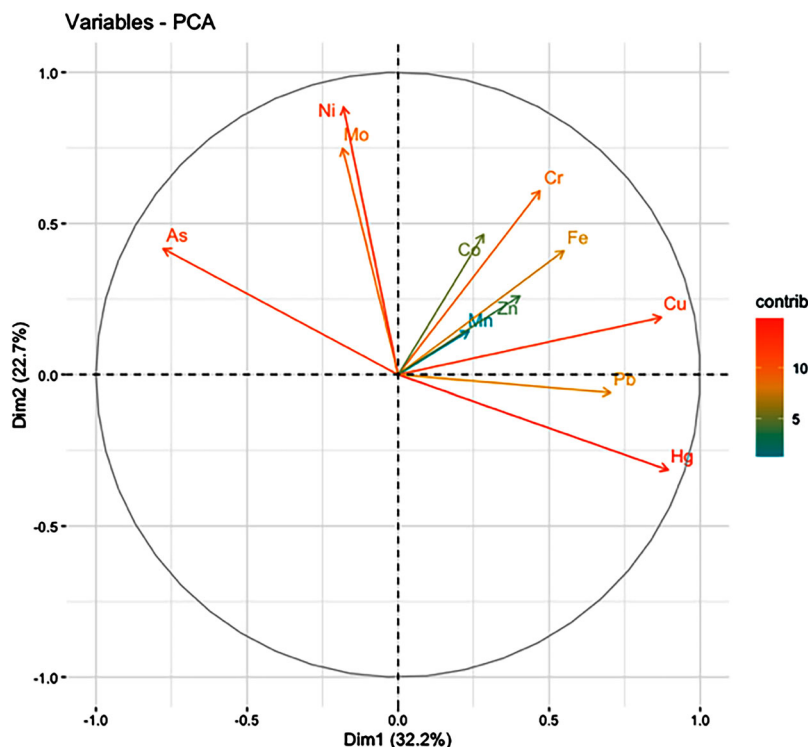


Figure 3. PCA plot for water heavy metals concentrations.

To assess the ecological risk, Toxicity reference values (TRV) by EPA (the United States Environmental Protection Agency) which were obtained from different sources; Ni, Cd, and Pb values were found to be between acute and chronic effects on aquatic life, indicating a long-term toxic effect (chronic) in the current study (Table S1). Accordingly, Zn, Cr, and Hg values were significantly higher than acute and chronic values (USEPA 2021). Thereby, the aquatic life criteria could not be met for Zn, Cr and Hg in Süreyyabey Dam Lake. Although the dam is used only for irrigation purposes, the Süreyyabey Dam Lake water is not suitable for using drinking water according to metal limit values of the World Health Organisation (WHO) (Table S1). Furthermore, the national water pollution control regulations for Inland Water Quality Classes, the water quality classes were IV (the worst water class) and III for Fe, As, Hg and Cr, Ni, Cu, Zn, Pb respectively (Table S1). The regular monitoring of heavy metal concentrations is urgently needed in Süreyyabey Dam Lake for the management of anthropogenic activities.

Heavy metal concentration: sediment

In Süreyyabey Dam Lake, heavy metals were generally higher than in various dam lakes (Table S1). The average heavy metal concentration trend in the sediment samples (mg/kg) were ordered as: Fe (52651.1) > Al (8455.3) > Mn (721.4) > Ni (628.6) > Cr (201.5) > Zn (182.7) > Co (105.5) > Cu (61.7) > As (19.2) > Pb (12.4) > Mo (0.3) > Hg (0.2) > Cd (0.1) (Figure 2). The background values obtained from bedrocks for index calculations were

Fe (104292.0) > Al (14669.3) > Mn (1629.97) > Cr (598.3) > Ni (563.4) > Zn (431.1) > Co (261.3) > Cu (215.6) > As (6.7) > Pb (1.4) > Hg (0.3) > Mo (0.1) > Cd (0.04). There is a statistically significant difference in the heavy metal concentrations between water and sediment ($p < 0.05$) (Table S5, Figure 2). The metals in the aquatic ecosystems are attached to fine-grained particles and are rapidly deposited in bottom sediments. So heavy metal concentrations are higher in the sediment than in the water. Al and Fe are the most abundant metal in the earth's crust [46]. In the current study, the concentrations of Al and Fe were also determined highest in all stations and seasons in both water and sediment (Table S2, Figure 2) which concurs with the previous study (Table S1). Al and Fe values did not higher than background values at any station and any season. The third most abundant metal was Mn in the sediment that consistent with the literature (Table S1). Therewithal, the mean value of Mn (0.12 mg/kg) in sediment samples in Karakaya Dam Lake (Euphrates, Turkey) was quite lower than the current study [47]. Cd was the least accumulated (0.03–0.15 mg/kg) heavy metal in the sediment as seen in the other studies except for the study carried out in Kapulukaya Dam Lake [12] (Table S1). However, Cd values were slightly higher than background value (0.04 mg/kg) in all stations and seasons (except S3 station; 0.03 mg/kg).

The metal concentrations in sediment samples showed variations among stations (Figure 4, Table S4); however, there was not any seasonal difference observed except for Hg. The differences between seasons for Hg were found significant between summer and winter and autumn and winter (Post hoc (Dunn), $p < 0.05$). The highest heavy metal accumulations were mainly detected in the S4 and S5 stations, where the Çekerek River, the main inlet of the dam, has proximity to the urban site (Figure 5). The concentrations of Cr (317.5 mg/kg), Mn (910.9 mg/kg), Ni (1255 mg/kg), Co (165.4 mg/kg), Cd (0.15 mg/kg) values were highest at S4 and Zn (213.8 mg/kg), Pb (19.7 mg/kg) values were highest at S5 station. The background values of these elements were higher than determined concentrations, except Ni and Pb. In developing and under-

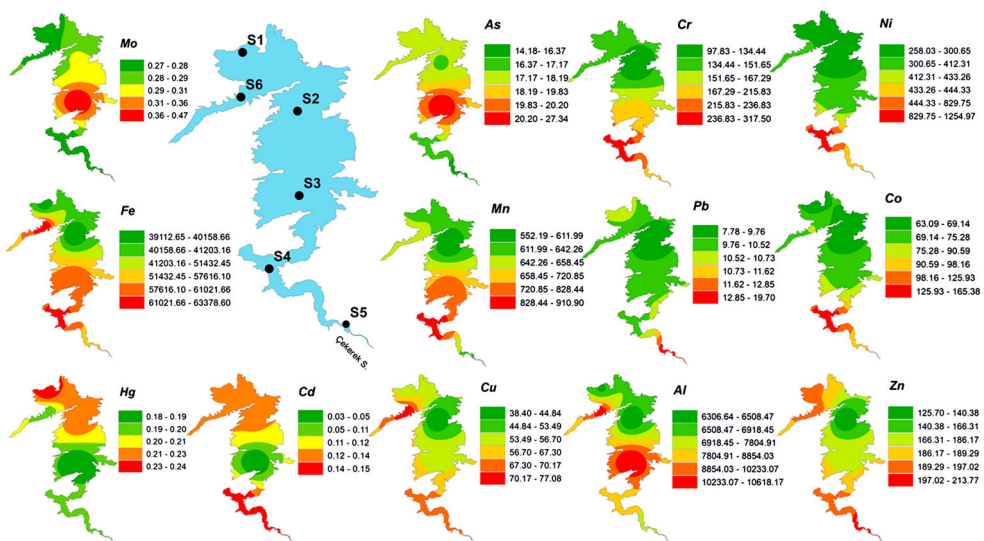


Figure 4. Sediman heavy metal concentrations (ppm) in sampling stations.

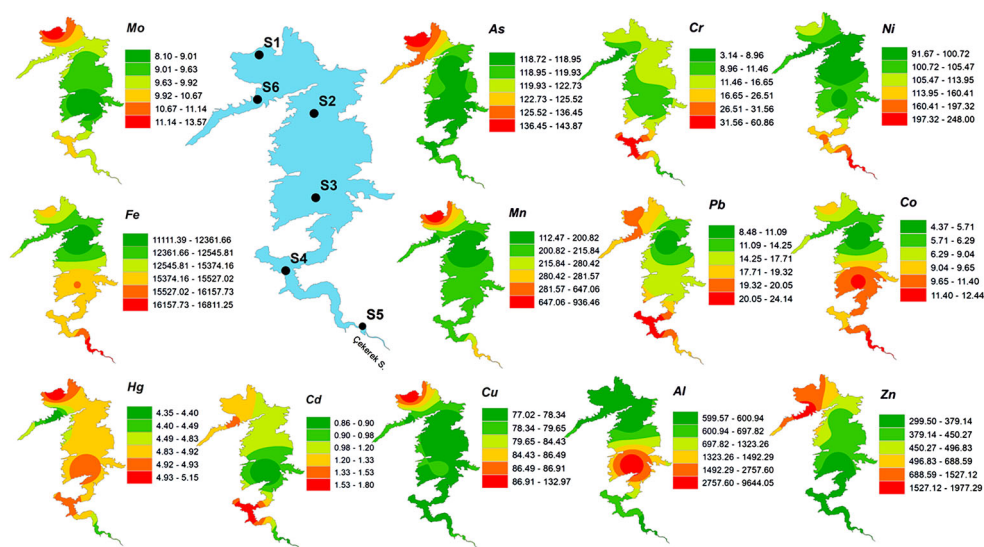


Figure 5. Water heavy metal concentrations (ppb) in sampling stations.

developed countries, modern agricultural applications, such as using excessively inorganic fertilisers, cause heavy metal pollution, and aquatic ecosystems are the final receiving environment for all types of pollutants [14]. For instance, differentiating concentrations of Cd, Cr, Ni, Pb, and Zn have been increased via using fungicides, phosphate fertilisers, and inorganic fertilisers [48]. Considering the river catchment of the Çekerek River, with is approximately 200 km long, and the main inlet of the Süreyyabey Dam Lake, the river passes mostly through agricultural areas and ends in Yozgat, whose economy is largely based on agriculture (600,533 ha) and animal husbandry.

The lowest concentrations of the investigated metals (Al, Fe, Mn, Cr, Co, Ni, Cu, Zn, and Pb) were recorded at the S2 station, which is the closest point to the dam. The concentration of As, Mo, Hg, and Cd was very close to each other in all sampling stations. In contrast to the current study, the lowest heavy metal values were determined at the close point of the river mouth [49]. The difference can be due to changes in hydrological regimes in dams through floods, and high water flow periods [50]. In another study, high heavy metal levels have been observed close to the dam because of the sluicing management [51]. Spatial variations in heavy metal levels in a reservoir may be associated with the sampling point being close to the urbanised area or far from the agricultural and urbanised area [52]. Thus, the decreased values of heavy metals in the S2 station can be explained with far away from urbanised and agricultural areas. The contribution of metals in sediment was Cr (16%), Mn (15%), Ni (13%), Al (11.2%), and Fe (16%), respectively according to the PCA results. The first two dimensions for sediment samples explained 56% of the total variance (Figure 6).

Sediment quality guideline

There have been many quality guidelines exist for freshwater sediments [38], however, there is no such a national quality guideline for sediment in Turkey yet. Therefore, in

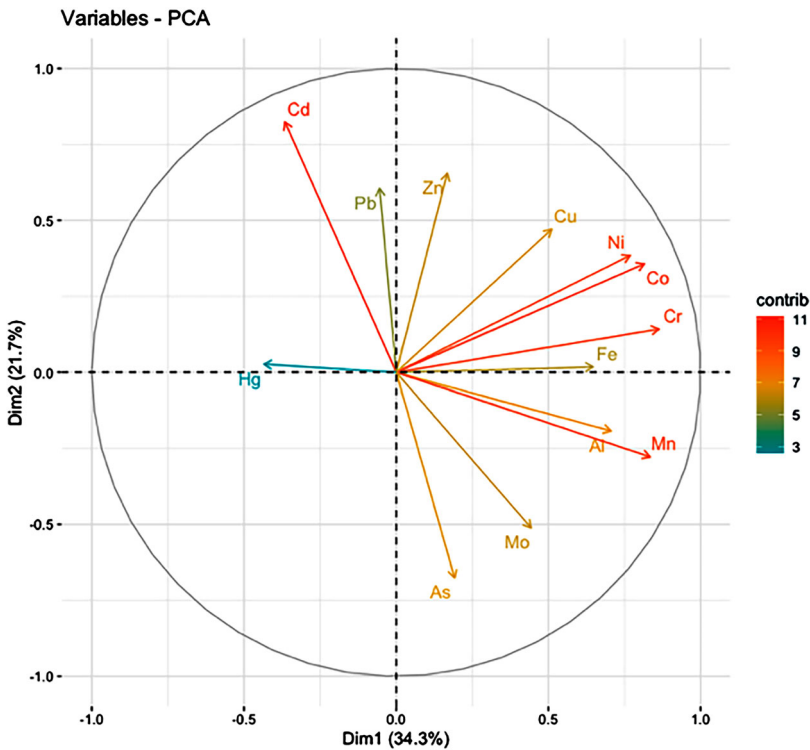


Figure 6. PCA plot for sediment heavy metals concentrations.

the current study, the heavy metal concentrations were compared with TEC and PEC values [38]. The mean concentrations of Cr and Ni were higher than the PEC value (Table S1), which may therefore suggest a potentially harmful effect on sediment-dwelling organisms. However, the concentration of Cu, Zn, and As was found to be between TEC and PEC values. Therefore, the toxic or nontoxic effects of these metals could not be predicted [38]. Since the Cd, Hg, and Pb concentrations were lower than the TEC value, adverse effects were not expected.

Contamination indices

Contamination factor (CF) and pollution load index (PLI)

According to the mean CF index values, Al (0.58), Cr (0.33), Fe (0.50), Mn (0.44), Co (0.39), Cu (0.28), Zn (0.42), and Hg (0.74) were classified in low degree contamination class in all stations (Figure 7(a)), suggesting that contaminations of these metals were not a major concern. The concentration of Ni was only detected moderate level in S4 (2.23) and S5 (1.47) stations. The primary sources of Ni in reservoirs are metallurgical industries, fossil fuel combustion, municipal wastewater, groundwater and geological weathering [53,54]. In our case, the stations where the contamination is observed are close to the main inlet (Çekerek River), suggesting the possibility of the point source of the pollution originates from the river (Figure 1). The lack of intense industry and urbanisation around these stations (except for small villages) strengthens the possibility of pollution caused by

the Çekerek River. Mean CF values for As, Mo and, Cd were 2.91, 2.50, 2.63, respectively. According to the values, the contamination classes were stated as low to moderate for all stations. Pb (mean CF value 8.66) contamination was highest in relatively all stations and this can be classified as a very high degree contamination class (Figure 7(a)). The observation of contamination in most of the sampled stations indicates non-point contamination based on the basin rather than a point source. The usage of fertilisers in agricultural areas around the reservoir may cause the contamination of these heavy metals. After fertiliser application Cd, Pb, and As concentrations were also increased in the cultivated soils [55]. Inorganic fertilisers and organic fertilisers or sewage sludge also contain heavy metals and lead to a considerable amount of heavy metals increase in agricultural areas [56].

According to PLI results, S4 and S5 stations are above the pollution limit value of 1 due to the high Ni concentrations thus, these stations can be classified as polluted. While, S1, S2, S3, and S6 can be classified as unpolluted due to the low values (Table 1).

Enrichment factor (EF)

In the present study, the mean EF values for heavy metals are ordered as follows: Pb (15.5), As (5.13), Cd (4.87), Mo (4.47), Ni (1.88), Hg (1.35), Mn (0.77), Zn (0.74), Co (0.69), Cr (0.58) and Cu (0.49) that in line with the other studies (Figure 7(b)). According to EF results, no

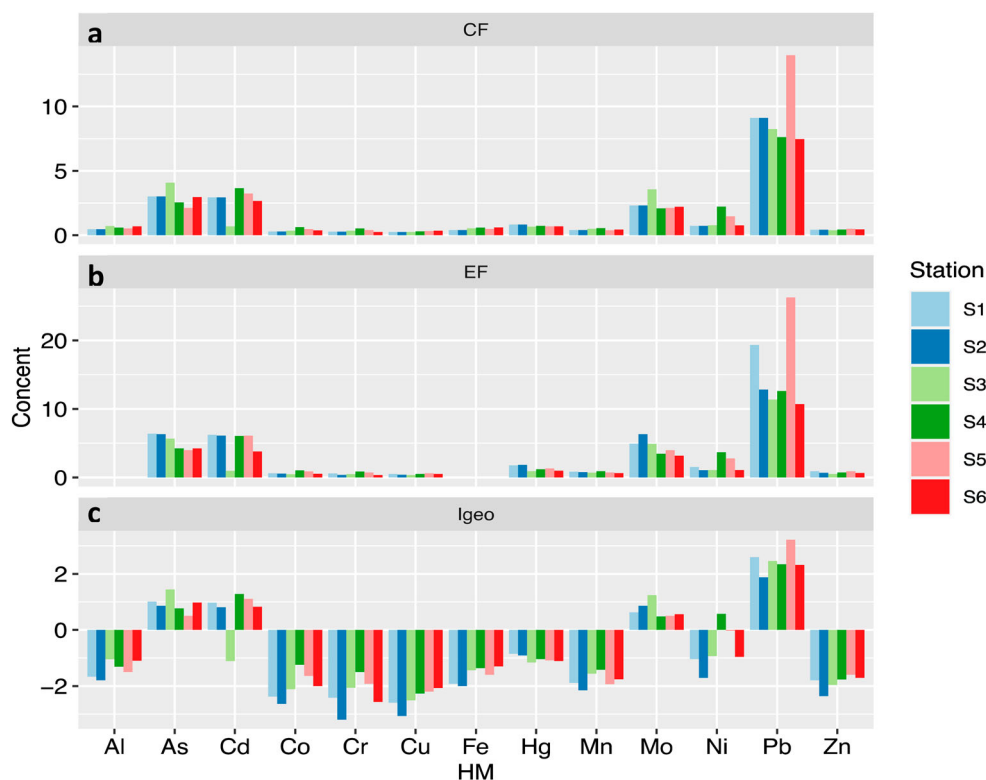


Figure 7. Different accumulation index for heavy metals, a) Contamination Factor, b) Enrichment Factor, c) Geoaccumulation index values.

Table 1. PLI indice results for each station.

PLI					
S1	S2	S3	S4	S5	S6
0.8	0.7	0.8	1.1	1.0	0.9

enrichment was observed for Cr, Mn, Co, Cu, and Zn elements for all stations. On the other hand, Ni concentrations for all stations were classified as a minor enrichment class; only the S4 (3.69) station showed moderate enrichment. Enrichment factors for As ranged from moderate (S4 (4.24), S5 (3.98), S6 (4.24)) to moderately severe classes (S1(6.39), S2 (6.31), S3 (5.64)). Mo concentrations for all stations also revealed similar enrichment values (moderate enrichment), except for the S2(6.33) station (moderately severe enrichment). For the Cd, S3 (0.96) and S6 (3.81) stations were pointed out as minor and moderate enrichment; however, all other stations were classified in a moderately severe enrichment class. Among all elements, the highest EF value was observed for Pb in all the stations and classified as a severe enrichment class (Figure 7(b)). Hg concentrations pointed out minor enrichment for all stations except for the S3 (0.93) station which was classified as no enrichment class in the CF index. However, the average EF index value for Hg is 1, which is the limit value for the “no enrichment” and “minor enrichment” classes. The observed low Hg pollution rate can explain the Hg reserves in Turkey. Because, it is well known that Turkey is not rich in Hg reserves, and the main Hg deposits are located in Western Anatolia which is far from the study area [57]. However, Hg is widely used in many industries and can be transported to different ecosystems in many different ways such as air [58], rain [59], and leaching to groundwater [60]. Compared to the other studies from Turkey, the mean EF value of Hg in this study (1.32) was lower than that of Çıldır lake 1.8 [61] and higher than that of Uzunçayır dam, 0.07 [62]. Since there is no previous heavy metal analysis in the study area, it is challenging to make a retrospective comparison, but the findings in the present study are consistent with the previous studies for dams and lakes in Turkey (Table 2).

Geoaccumulation index

The geo-accumulation index values for Al, Co, Cr, Fe, Hg, Mn, and Zn were below zero (Figure 7(c)), which can be interpreted as “no pollution” in all stations. On the other hand, Ni concentrations for all stations were classified as unpolluted except for S4 (0.57) which can be classified as unpolluted to moderately polluted class (Figure 7(c)). Although there is no industrial area close to the dam, it may be possible for industrial wastes to reach the dam via the inlet [63]. Similarly, As, Cd, and Mo are classified as unpolluted to moderately polluted or moderately polluted. Among others, Pb was classified into moderately to strongly polluted (S1, S2, S3, S4, S6) and strongly polluted class (S5) (Figure 7(c)). Unlike the Ni pollution and also in line with the other index results, As, Cd, Mo, and Pb pollution were detected as moderate/unpolluted to moderately polluted. The diffusion of these metals throughout the dam sediment indicates non-point pollution rather than point source pollution. The levels of As, Cd, Mn, and Pb can be explained as the transport of chemicals (fertiliser or pesticide) used for agricultural purposes from the basin to the dam or the surrounding geological environment. Atmospheric transportation of moderate or severe enrichment of heavy metals might also be another reason for the

Table 2. The mean heavy metals concentrations in sediment (ppm)/water (ppb) from Sureyyabey dam and other dams of the world.

Study area	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Mo	Cd	Hg	Pb	Reference
	Sediment (mg/kg)													
Süreyyabey Reservoir, Turkey	8455.3	201.5	721.4	52651.4	105.5	628.6	61.7	182.8	19.2	0.3	0.1	0.2	12.4	This study
Keban Reservoir, Turkey		144.0	588.0	61700.0	24.0	107.0	34.0	77.0	15.0		0.2		11.0	Varol 2020
Uzunçayır Reservoir, Turkey		97.3	631.6	31740.0		237.8	29.5	62.8	9.1		0.2	0.0	11.3	Kutlu 2018
Kapulukaya Reservoir S1, Turkey	3.2	394.4	550.4	2.5	25.6	81.3	17.5	43.7	20.0	3.4	1.0	1.4	19.5	Kankılıç et al. 2013
Kapulukaya Reservoir S2, Turkey	3.7	327.0	542.3	2.6	23.7	65.8	19.2	45.8	19.4	3.7	0.9	1.3	21.4	Kankılıç et al. 2013
Kapulukaya Reservoir S3, Turkey	3.7	559.2	713.3	2.4	23.3	68.1	16.3	66.2	31.2	3.5	0.8	1.2	22.6	Kankılıç et al. 2013
Karakaya Reservoir, Turkey		0.1	6.9		0.0	0.0	0.2			nd	nd			Ural et al. 2012
Beyler Reservoir, Turkey	21055.6	19.4	346.1	20468.7		13.2	17.5	39.7			0.2		5.6	Findık and Turan 2012
Three George Reservoir, China		140.3				35.2	97.7	177.0	10.1		0.3	0.1	114.1	Shui et al. 2020
Miasto Reservoir, Poland		0.3				2.7	1.7	10.1		0.3			3.2	Sojka et al. 2018
Wadi Al-Aqiq Reservoir, Saudi Arabia		50.6	481.8	22670.1	14.2	30.0	50.3	37.1					6.8	Alghamdi et al. 2018
Furnas Reservoir, Brazil		2.5		6450.0			10.8	6.6			0.3			Qudra et al. 2019
Treshold Impact Concentration		43.4	–	–	–	22.7	31.6	121.0	9.79	–	0.99	0.18	35.8	Macdonald et al. 2000
Probable Impact Concentration		111.0	–	–	–	48.6	149.0	459.0	33.0	–	4.98	1.06	128.0	Macdonald et al. 2000
	Water (µg/L)													
Süreyyabey Reservoir, Turkey	2814.6	25	425.3	15052.1	9.1	155.5	91.9	916.1	128.3	10.5	1.3	4.8	17.7	This study
Keban Reservoir, Turkey	23.2	0.4	3.7	17.8	0.1	1.5	1.0	3.1	3.1				0.1	Canpolat et al. 2020
Krakkızı Reservoir, Turkey		22.1		59.0		15.8	2.8	5.0	2.4		0.0		2.6	Varol 2013
Three George Reservoir, China		0.5				1.2	13.0			0.0		0.0		Lin et al. 2020
Bratsk reservoir, Russia	12.1	0.2	22.1	22.4	0.8			3.8	0.4		0.0	0.0	0.1	Poletaev et al. 2021
Surface Waters of World	32.0	0.7	34.0	66.0			1.5	0.6	0.6		0.1		0.1	Gaillard et al. 2013
WHO		50.0				70.0	2000.0		10.0		3.0	6.0	10.0	WHO 2011
Toxicity Reference Values (Acute)		16	–	–	–	470	–	120	340	–	1.8	1.4	65	USEPA 2021
Toxicity Reference Values (Chronic)		11	–	1000	–	52	–	120	150	–	0.7	0.77	2.5	USEPA 2021
Water Quality Class, Turkey		i	iii	ii	lv	i	iii	iii	iii	iv		i	iv	iii

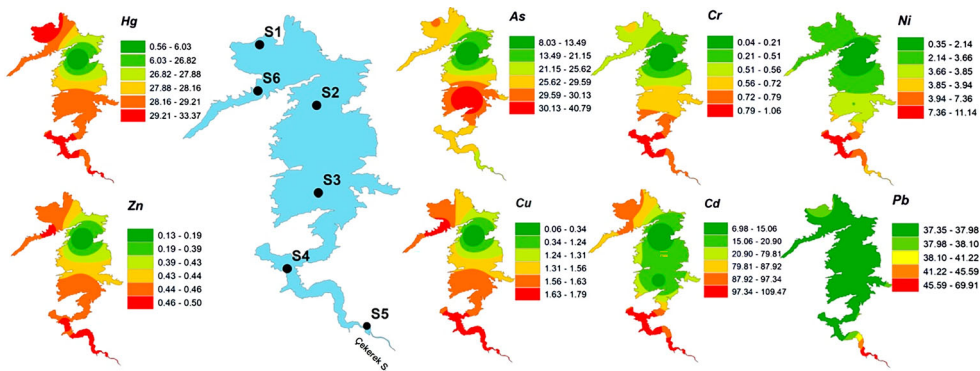


Figure 8. Ecological risk index values.

water and sediment contamination in the Süreyyabey Dam Lake. Although we have no data related to this assumption, several studies showed that frequent usage of fossil fuels and gas emissions from industry causes an increase in heavy metal concentration in the atmosphere [64]. Consequently, these heavy metals can be transported to long distances by wind and re-enter aquatic ecosystems via precipitation over broad spatial scales [65]. For instance, a study showed that average annual wet deposition concentrations of Pb, Cu, As, and Cd in Kazakhstan's natural ecosystems were estimated to be 3.8 ± 1.52 , 16.11 ± 1.48 , 0.96 ± 0.84 , and 0.88 ± 0.44 $\mu\text{g/L}$, respectively [66].

Assessment of ecological risk (ER)

The ER results revealed that the Cr (0.66), Ni (5.37), Cu (1.40), Zn (0.42), Hg (29.55), and As (29.07) (except for S3: 40.79-moderate ecological risk) has low ecological risk. Cd (79.03) were classified as three ER classes as follow; low (S3:20.90), moderate (S2: 78.75; S6: 79.81) and considerable (S1: 87.92; S4: 109.47; S5: 97.34). For the Pb (43.29) concentration, ER results showed differences among stations between low (S2: 27.60; S4: 38.1; S6: 37.35) to moderate (S1: 45.5; S3: 41.22; S5: 69.91) states (Figure 8).

According to the PERI results, all stations were classified as “moderate” except for the S3 which was classified as a low ecological risk class. The main reason for the moderate Ecological Risk Value is due to the high relative toxicity of Cd, Pb, and As in the system. Many heavy metals pose a risk to aquatic organisms and through the food web via bioaccumulation thereby they might also affect human health at certain concentrations [67–69].

Conclusion

In this study, seasonal concentrations of 13 metals (Al, Fe, Mn, Cr, Ni, Zn, Co, As, Pb, Cu, Mo, Hg, and Cd) in both sediment and water samples were determined in the Süreyyabey Dam Lake. Moreover, contamination indices, sediment quality and ecological risk parameters were calculated. Heavy metal concentrations in sediment and water column were significantly different in Süreyyabey dam Lake. Higher heavy metal concentrations were observed in sediment as reported in several studies (Table S1). The contamination risk of heavy metals was not the same extent for Al, Cr, Mn, Fe Co, Cu, Zn, and Hg.

Nevertheless, As, Mo, Cd, and Ni are generally moderately contaminated. The most prevailing contamination was observed for Pb in all stations. The enrichment factor (EF), contamination factor (CF), geoaccumulation index (Igeo), and pollution load index (PLI) revealed that sediments were considerably polluted by Pb and moderately polluted by As, Mo, Ni, Cd. Although there are no industrial facilities exist close to the basin, the main contamination source of heavy metals can be originated from the agricultural area. According to the high results of Igeo, CF, EF, and PLI indices for Ni pollution would because of the proximity to the main inlet, indicating heavy metal transport to the dam by the Çekerek River. In general, heavy metal concentrations were high in the water in comparison to the previous studies. The study also has some drawbacks. First, the sampling period covers only one year. Precipitation amount, water holding capacity or discharge amount are important parameters specially to determine heavy metal concentration in the water column, and long-term data will give more reliable results. Second, the Dam covers a large area and increasing the number of background samples will provide more detailed and reliable results. In this study, the number of samples and the sampling period had to be limited due to financial limitations. Considering the anthropogenic activities, heavy metal concentration has a high potential to increase in the near future. Thereby, further studies are needed to reveal the heavy metal pollution for a broader range in the region to develop management plans for public authority[70]. In particular, the extent to which fish species produced for commercial purposes in the dam ecosystem are affected by heavy metals and the amount of bioaccumulation in fish species should be investigated in detail in the future. Furthermore, regular monitoring should be considered urgently to take early warning precautions.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability statement

Data will be made available on reasonable request.

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