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ECOLOGICAL RISK ASSESSMENT OF TOXIC METAL POLLUTION IN WETLANDS ECOSYSTEM; A CASE STUDY OF TORUL DAM LAKE, TÜRKİYE

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Abstract. In this study, the natural and anthropogenic toxic metal pollution together with the general characteristics in Torul Dam Lake sediments were investigated as a spatially and temporally. A sediment corer sampler was used to collect sediment samples at 6 different stations, from depths ranged between 10 to 50 m, in 2022. For this research four sampling campaigns were carried out which included effects of the two different climatic conditions, Spring and Autumn. Copper (Cu), Lead (Pb), Zinc (Zn), Nickel (Ni), and Arsenic (As) were determined as metals to be investigated in this study. Metal concentrations were determined by using an inductively coupled plasma-mass spectrometer (ICP-MS). A strong metal trend showing high metal concentration in Autumn was observed. The average metal concentrations (in dry weight) varied from 380.9±38.6 to 457.1±35.1 for Cu, 142.9±14.6 to 158.9±16.4 for Pb, 353.8±15.5 to 352.2±25.7 for Zn, 47.5±5.5 to 59.4±10.3 for Ni, 17.28±1.1 to 17.7±0.8 µg g^{-1} for As. With the purpose for determining the level of pollution, the methods of the factor of sediment enrichment factor (SEF) and geoaccumulation index (I_{GEO}) were applied. Since Cu and Pb SEF values are mostly determined in the range of $10<SEF<25$ (class 5), they are determined at severe enrichment pollution level. Zn values were determined in the range of $5<SEF<10$ (class 4) and the pollution risk level was determined as moderate-severe enrichment. Ni and As SEF values were determined in the range of $1<SEF<3$ (class 1), and the contamination risk is at the level of minor enrichment. According to I_{GEO}, Cu and Pb are classified in class 3 (moderately-heavily), Zn class 2 (moderately), Ni and As in class 0 (uncontaminated) pollution categories. These results show that toxic metal pollution in Torul Dam Lake Sediments poses a threat to this lake ecosystem.
Keywords: Dam Lake, Toxic metal, Pollution Index, Sediment, ICP-MS

1. INTRODUCTION

Unquestionably, water is the most important resource for all ecosystems. It is a very important component for all habitats. Although fresh water resources constitute 2.5% of the total water resources, resources such as lakes and surface water reservoirs are the most important ones. Fresh water resources such as lakes and surface waters provide us with drinking water as well as providing benefits in many areas of use such as agricultural irrigation and fish farming (Abdelali 2021). At the same time, reservoirs provide industrial water, hydroelectric power, and control of river waters. However, as in many ecosystems, dam lake ecosystems are under intense pollution pressure. The most important of these is toxic metal pollution (Najamuddin et al. 2016; Ozseker and Eruz 2017a). Toxic metals, such as cadmium (Cd), mercury (Hg), lead (Pb), copper (Cu), arsenic (As) and zinc (Zn), are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity, and ability to be incorporated into food chains (Dauvalter and Kashulin 2018; Nguyen et al. 2020; Karaouzas et al. 2021). More recently, with rapid urbanization and intensive industrial development, the toxic metal pollution of the lake environment has become a worldwide problem because these metals are indestructible and most have toxic effects on the aquatic environment (Nguyen et al.

2020; Yu et al. 2021). Metals entering aquatic ecosystems tend to accumulate in the sediment layer. Heavy metals are discharged into aquatic system through natural and anthropogenic pathways, including soil erosion, agriculture, industry, mining and smelting, transportation and energy production related activities, and then deposit in the sediments(Kang et al. 2017; Hu et al. 2019; Yu et al. 2021). Besides, sediments act as a sink of organic as well as inorganic pollutants (toxic metal) and provide a history of anthropogenic pollutant input. Sediments, which are the main elements of the limnological and ecotoxicology pollution studies, provide us with extensive information about the lake type and lake environment. Lake sediments can be considered as the ultimate density place of toxic metals. Over time, the sediment accumulating at the bottom of a lake is in contact with water and is in transition with the water column. Due to this transition, metals affect the benthic ecosystem such as absorbed by organisms (Jiang et al. 2021; Luo et al. 2021; Ozseker 2021; Akila et al. 2022; Erüz et al. 2022). Metals can accumulate in sediment by physical adsorption, chemical precipitation, and aquatic degradation, and this accumulation can pose a risk to human health through the food chain (Fan et al. 2017; Ding et al. 2020; Jiang et al. 2021). When environmental conditions change, the heavy metals in sediment can be released into the water body, causing secondary contamination (Jiang et al. 2023). Therefore, heavy metal analyzes of lake sediments are often used to monitor environmental pollution, and this can also be used to study the anthropogenic impacts on ecosystems and assess the health risks(Han et al. 2020; Luo et al. 2021). In this study, it was aimed to determine the spatial and temporal distribution of the current pollution potential of toxic metals in the Torul Dam Lake Ecosystem by using the sediment enrichment factor (SEF) and geoaccumulation indices I_{GEO}, which are widely used in the literature.

2. MATERIAL AND METHOD

2.1. Study area and sampling

This study was conducted in Torul Dam Lake as a reservoir lake at Southeastern Black Sea in 2014 (Figure 1). Torul Dam Lake; It is a dam located on Harşit Stream, within the borders of Gümüşhane province in the Eastern Black Sea Region, and was built between 2000-2007 for the purpose of generating energy.

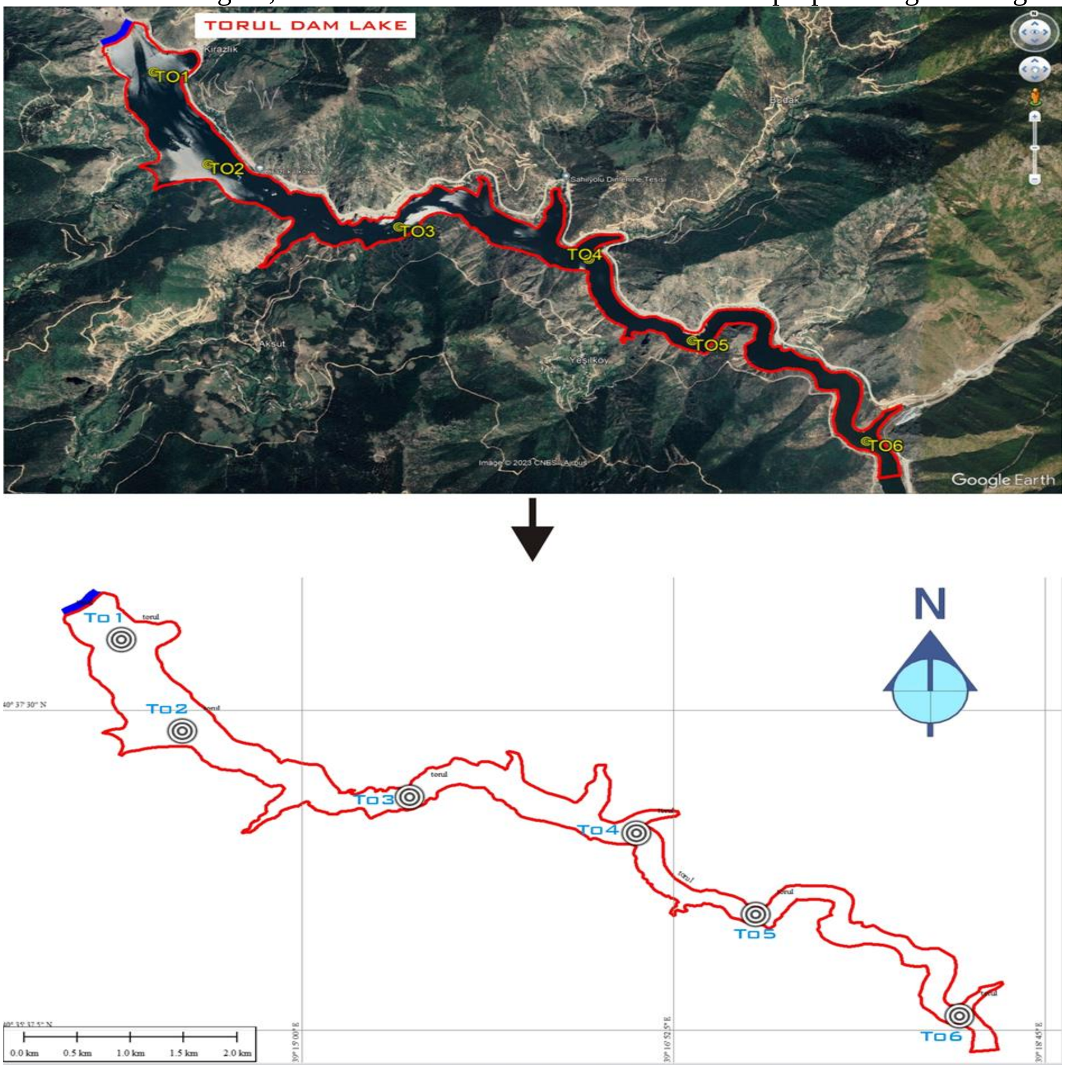


Figure 1. The map of study area

Six stations were sampled for sediment in both the autumn and spring seasons, with depths ranging from 10 to 50 meters. The selected stations were chosen to represent the anthropogenic source points entering the lake (Table 1).

Table 1. Coordinates of stations

Stations	Latitude	Longitude	Deepth (m)
TO1	40.632821˚	39.234760˚	50
TO2	40.624081˚	39.329166˚	35
TO3	40.617713˚	39.258862˚	24
TO4	40.614087˚	39.278520˚	20
TO5	40.606302˚	39.288455˚	16
TO6	40.595546˚	39.305527˚	10

Sediment samples from the study area were obtained using Ekman Grab (Zárate et al. 2021). The top layer of 0-5 cm of the obtained sediment samples was processed for analysis. Physicochemical parameters in sediment were measured in situ using a Hach Lange HQ4OD multimeter. To prevent any metal contamination during sampling, plastic equipment was used. The samples were kept at -18 ˚C prior to the laboratory analyses. The accumulation of metals in sediments is often associated with the presence of fine-grained fractions. Therefore, the classification of the sediments based on their grain size is a significant aspect that influences the sediments' ability to accumulate metals (Lanzerstorfer 2018; Chileshe et al. 2020; Özşeker et al. 2022a). For determining the general physical properties of the lake sediments, the samples were sieved using distilled water in an AS 200 vibratory sieve shaker (Retsch, Germany). The concentrations of trace elements in sediment depend on the sediment grain size (Vanapalli et al. 2021); therefore, the samples were separated into grain-size fractions for analyzing the trace elements. The sediment samples were then sieved using a <63.0 µm mesh because metals usually exhibit a higher affinity to small grains (Ozseker 2021). Cu, Pb,Zn, nickel (Ni), and arsenic (As) were investigated to determine any serious pollution of the ecosystem. Cu, Pb, Zn, nickel (Ni), and arsenic (As) were investigated to determine in the lake ecosystem. Metal concentrations were analyzed using inductively coupled plasma MS in the ACME Laboratory (Vancouver, BC, Canada). The accuracy of the analysis ranged from 95.81 to 130.50%. Two-way analysis of variance (ANOVA), followed by Duncan's test, was used to identify the significance ($p<0.05$) of local and seasonal differences. In this study, region and season were used as independent variables and metal values were used as dependent variables. Statistical analyses were performed using SPSS 23.0. (IBM, Armonk, NY, USA).

2.2. Sediment Pollution Indexes

The Sediment Enrichment Factor (SEF) is used to assess the degree of contamination caused by each element individually (Kowalska et al. 2018). Metal concentrations in the upper continental crust (UCC) were used as background reference values. Although there is no definite agreement about the selection of the element to be used in normalization, elements that are geochemically inactive and easily found in fine-grained materials such as aluminum, iron, zircon, and titanium are generally used(Rudnick et al. 1985; Migaszewski et al. 2014). Because of its resemblance to the metal concentration in silicate crustal rocks, Al was chosen for geochemical normalization (Faměra et al. 2018). SEF was estimated using the following equation (3);

$$SEF = (C_M/C_{Al})_{Sample} / (C_M/C_{Al})_{Earths\ crust} \quad (3)$$

where $(C_M/C_{Al})_{Sample}$ is the ratio of the measured metal concentration and Al (C_{Al}) in the sediment sample, and $(C_M/C_{Al})_{Earth's\ crust}$ is the ratio of the measured metal (C_M) and the reference ratio of Al in the Earth's crust (Sinem Atgin et al. 2000). The geoaccumulation index (I_{GEO}) was used to estimate the contribution level of anthropogenic effects to the toxic metal abundance by using following equation (4) (Feng et al. 2019):

$$I_{GEO} = \log_2^{[Cn/(1.5Bn)]} \quad (4)$$

where C_n is the measured concentration of the toxic metal n in the sediment, Bn is the geochemical background concentration for element n which is either directly measured in un-impacted sediment of the area or taken from the literature (Turekian et al. 1961). Classification and definition values of the pollution indexes are given in Table 2.

Table 2. Classification and definition values of Pollution indices

SEF			I_{GEO}		
Class	Factor	Pollution	Class	Factor	Pollution
1	1-3	Minor enrichment	0	≤1	Uncontaminated
2	3-5	Moderate enrichment	1	0-1	Uncontaminated-Moderately
3	5-10	Moderate-severe enrichment	2	1-2	Moderately
4	10-25	Severe enrichment	3	2-3	Moderately-Heavily
5	25-50	Very severe enrichment	4	3-4	Heavily
6	>50	Extremely Severe enrichment	5	4-5	Heavily-Extremely
			6	≥5	Extremely

3. RESULT AND DISCUSSION

The physicochemical properties and sediment grain size are given in detail in Table 3. The sand fractions were found to be dominant (>70 %) in the sediment layer. TOC concentration, another important factor affecting metal mobility, were between 0.65% and 0.96%. When the physicochemical parameters related to the mobility of metals were examined, a difference was observed between the stations depending on the depth. Also, values of pH and oxygen in the stations ranged between 7.95 to 8.67, and 6.89 to 8.60 mg/L, respectively.

Table 3. Physicochemical properties of the dam lake sediments in the present study

Season	General Properties	TO1	TO2	TO3	TO4	TO5	T06
Autumn	≤ 0.63 μm %	16	27	39	9	23	31
	≥0.63 μm %	84	73	61	91	77	69
	pH	7,95	8,21	8,54	8,1	7,98	8,4
	O2 mg/L	6,2	6,28	6,98	7,12	7,24	7,3
	TOC mg/L	0,71	0,79	0,9	0,87	0,79	0,92
Spring	≤ 0.63 μm %	12	19	33	19	28	41
	≥0.63 μm %	88	81	67	81	72	59
	pH	8,24	8,51	8,37	8,67	8,44	8,11
	O2 mg/L	6,18	5,9	6,1	6,21	6,14	6,2
	TOC mg/L	0,65	0,74	0,86	0,89	0,93	0,96

Spatial concentrations of toxic metals (Cu, Pb, Zn, Ni, and As) in the dam lake sediment samples were given in Figure 2. Toxic metal concentrations in dam lake sediments in autumn varied from 414.15 to 498.46 µg g^{-1} for Cu, from 141.15 to 185.6 µg g^{-1} for Pb, from 320 to 389 µg g^{-1} for Zn, from 46.47 to 76.11 µg g^{-1} for Ni, and from 16.41 to 18.74 µg g^{-1} for As. In the spring season, metal concentrations were ranged from 340.11 to 432.37 µg g^{-1} for Cu, from 120.31 to 159.84 µg g^{-1} for Pb, from 324 to 367 µg g^{-1} for Zn, from 38.63 to 54.10 µg g^{-1} for Ni, and from 15.38 to 18.24 µg g^{-1} for As.

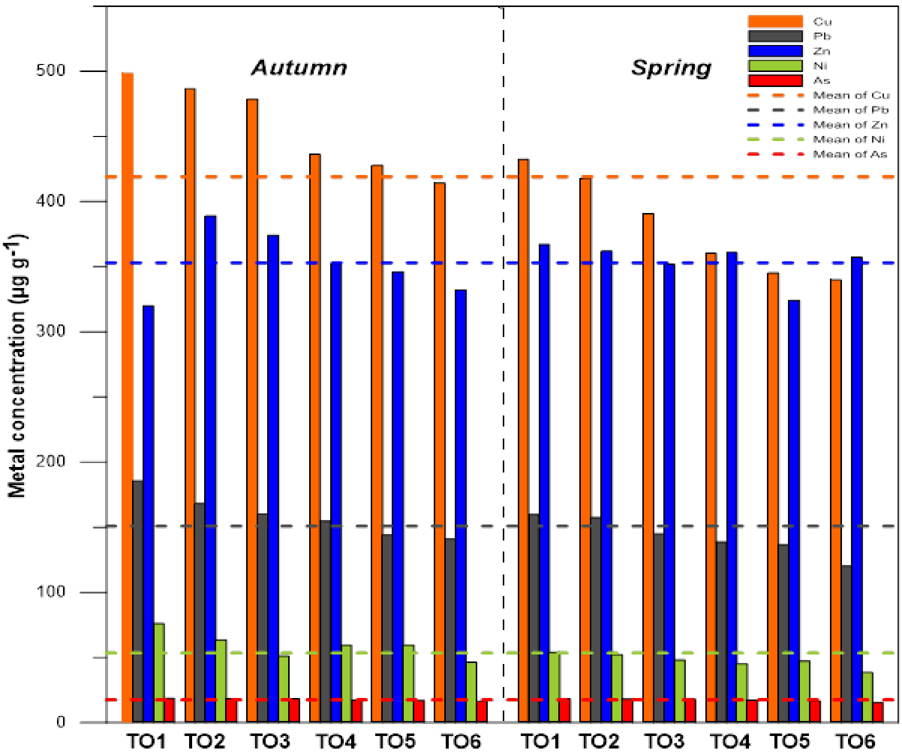


Figure 2. Change in metal concentrations according to stations

Metal concentrations were higher in the autumn season. It was observed that the results were above the threshold values except for Ni and As elements in both autumn and spring seasons.

When the metal concentrations were examined temporally, it was determined that it was higher in the autumn season. It was observed that the results were above the threshold values except for Ni and As elements in both autumn and spring seasons. These results reveal that the studied regions are rich in terms of geochemical structure, as well as anthropogenic input in the region, and the studied elements exceed the current concentrations in the region.

When the metal concentrations were analyzed spatially, it had been determined that the highest concentrations are at TO1 and TO2 stations in the outlet part of the dam lake (body part) where the sediment accumulates the most. The lithogenic material fraction of the sediment samples at these stations consists of clayey material, which is generally smaller than 63 µm. As it is known, metals tend to accumulate in the thinnest fraction material structure of the sediment. In addition, according to the stations, metal concentrations were ranked according to their densities TO1>TO2>TO3>TO4>TO5>TO6. Metal concentrations were listed according to their densities as Cu>Pb>Zn>Ni>As.

The static two-way ANOVA analysis was used to determine whether an interaction existed between the two independent variables (region and season) and the dependent variables (metal values). The results revealed significant differences in Cu and Pb values according to season (($F=824.402$; $p<0.05$), ($F=256.736$; $p<0.05$)). Zn, Ni, and As values showed no significant difference (($F=0.651$; $p>0.05$), ($F=0.673$; $p>0.05$), ($F=1.886$; $p>0.05$)).

Principal component analysis (PCA) was used to determine the main drivers of the seasonal distribution of the toxic metals. The first two components with eigenvalues >1 was used to construct the PCA biplot. The cumulative contribution of the first two principal components was 70.1% (51.4% and 21.9% for PC1 and PC2, respectively). The variance on the PC 1 (x-axis) was mainly driven by Cu, Pb, and As. Besides, the variance on the PC 2 (y-axis) was highly contributed by Zn and Ni (Figure 3). The stations were segregated into two clusters determined by the k-means clustering method (Figure 3). Cluster 1 was mainly affected by Cu, Pb, and As, concentrations, on the other hand, cluster 2 was found to be affected by Zn and Ni. A significant difference between the seasons was determined in terms of metal compositions (PERMANOVA, $F = 7.81$, $p < 0.05$). A pairwise PERMANOVA revealed that the toxic metal composition in autumn was significantly different from spring.

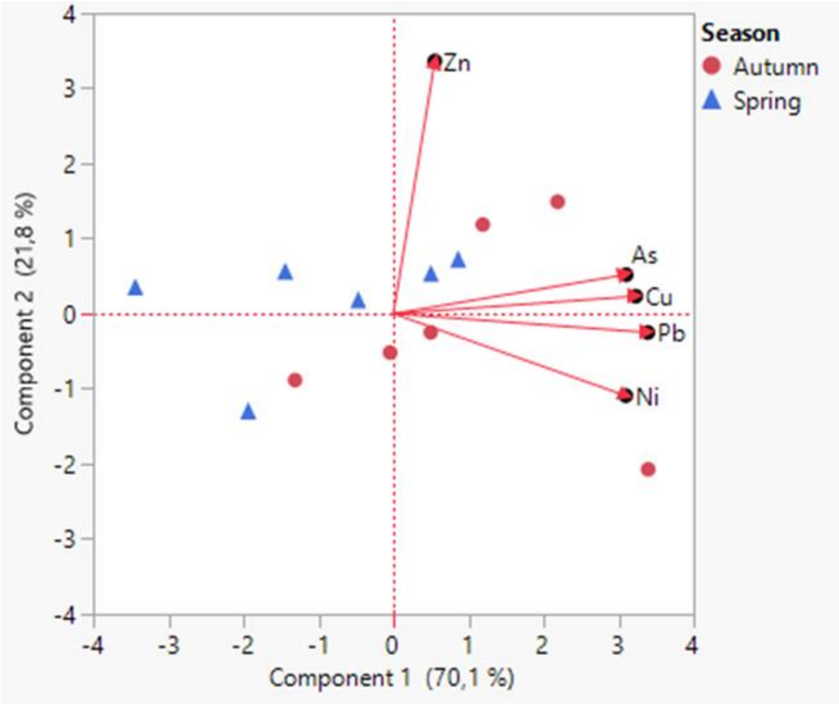
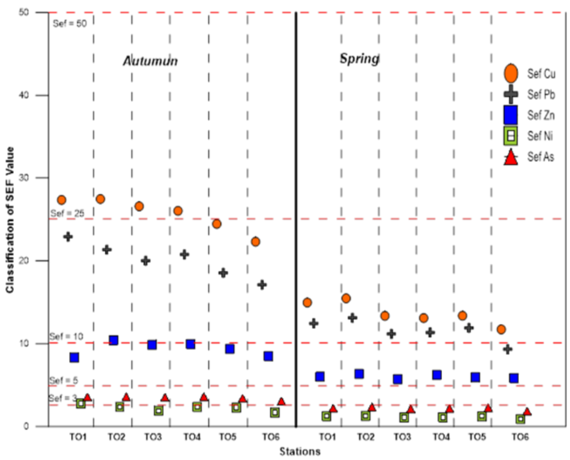


Figure 3. Principal component analysis (PCA) biplot for metal concentration in the Dam Lake sediments

In this study, sediment enrichment factor (SEF) and geoaccumulation index (I_{GEO}), which are widely used in the literature, were used to evaluate the extent of metal pollution (Xia et al. 2018; Han et al. 2020; Özşeker et al. 2022b).

The values of SEF and I_{GEO} were given in Figure 4 and Figure 5. The SEF and I_{GEO} of toxic metals in the Torul Dam Lake were Cu > Pb > Zn > As > Ni. The highest SEF and I_{GEO} values were determined in autumn season (Figure 4-5).

In the autumn season, the SEF value of Cu was found to be in the range of 25–50 (very severe enrichment); Pb was found to be in the range of 10-25 (severe enrichment), Zn was found to be in the range 5-10 (moderate-severe enrichment), As was found to be in the range of 3-5 (moderate enrichment), and Ni was found to be in the range 1-3 (minor enrichment) for all the stations. In the spring season, Cu and Pb were found to be in the range 10-25 (severe enrichment), Zn was found to be in the range 5-10 (moderate-severe enrichment), Ni and As were found to be in the range 1-3 (minor enrichment) for all the stations (Figure 4).



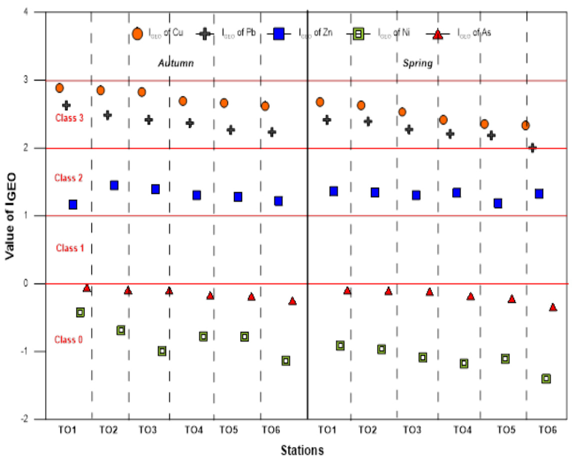


Figure 4. Overall comparison of SEF values Figure 5. Overall comparison of I_{GEO} values

The sediment samples were considered moderately- heavily contaminated by I_{GEO} since Cu and Pb were between the range of $2 < I_{GEO} < 3$. Zn was between the range of $1 < I_{GEO} < 2$ as a moderately. Besides, Ni and As were considered uncontaminated because $I_{GEO} < 0$ was determined for the Torul Dam Lake (Figure 5).

Many studies have been conducted on the current situation of toxic metal pollution, both nationally and internationally. The comparison of the results of our study with the studies in the literature is given in Table 4.

Table 4. Comparison of metal values obtained in the study with both international and national some studies

Location	Cu	Zn	Pb	Ni	As	Reference
Present study	457	352.2	158.9	59.4	17.7	Autumn
Present study	380.9	353.8	142.9	47.6	17.3	Spring
Bafa Lake Türkiye (autumn)	25.28	36.52	13.75	175.97	-	(Algül and Beyhan 2020)
Bafa Lake Türkiye (spring)	19.55	29.10	10.12	152.40	-	(Algül and Beyhan 2020)
Sera Lake, Türkiye	76.9	390	156.5	130.3	8.7	(Ozseker and Eruz 2017b)
Uzungöl Lake, Türkiye	307.2	259	155.9	24.7	8.5	(Ozseker and Eruz 2017b)
Borçka Dam Lake, Türkiye	446.5	356	154.6	56.6	17.8	(Ozseker and Eruz 2017a)
Gökçekaya Dam Lake, Türkiye	108.9	265.8	74.4	125.7	19.4	(Akin and Kırmızıgül 2017)
Küçükçekmece Lake, Türkiye	67.7	266.9	40.2	84.1	9.2	(Kükrer et al. 2019)
Hazar Lake, Türkiye	55.2	87.8	18.1	126.7	19.6	(Varol et al. 2020)
Houguan Lake, China	38.6	90.7	39.3	-	30	(Rao et al. 2021)
Emerald Lake, Indian	611.3	174.4	34.1	154.2	-	(Karthikeyan et al. 2020)
Ashtamudi Lake, Indian	53.1	112.2	113.3	115	-	(Hussain et al. 2020)
Inle Lake, Myanmar	79.2	18.8	9.6	11.4	6.6	(Aung et al. 2019)
Sochagota Lake, Colombia	104	85	21	53	36	(Cifuentes et al. 2021)
Pilvelis Lake, Latvia	12.3	93	7.2	8.1	-	(Stankevica et al. 2020)
Respomuso Lake, Spain	42.5	117.3	33.1	38.6	87.3	(Lavilla et al. 2006)

4. CONCLUSION

In this study, the spatial and temporal distribution of the existing toxic metal pollution of Torul Dam Lake within the borders of Gümüşhane province in the Southeastern Black Sea Region of Turkey was evaluated using different pollution indices. For this purpose, 6 sampling points that may be affected by toxic metal sources around the dam lake were evaluated. The highest metal concentrations were detected at TO1 and TO2 stations, which represent the outlet part of the lake and where clay fractionated material is concentrated in the sediment structure. The autumn season draws attention as the season in which the highest concentrations are observed. It is noteworthy that Cu, Pb and Zn metals pose a risk for the ecosystem in the evaluations made according to the pollution indices. Therefore, regular pollution monitoring studies should be conducted over an extended period in the Torul Dam Lake to assess and control toxic metal pollution levels. Additionally, effective implementation of laws and regulations should be ensured for all institutions and organizations in the basin that can impact the resources.

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