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Evaluation of selected heavy metal and selenium pollution in water and sediments of Lake Eğirdir (Isparta/Türkiye) using statistical analysis and pollution indices

by

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Abstract

The purpose of this study is to assess heavy metal and selenium pollution in water and sediment of Lake Eğirdir using some indices. The water and sediments have the highest content of Fe. According to Water Quality Index (WQI) results, the lake water is in the good category, while the low pollution category depends on HPI and HEI values. The Enrichment Factor (EF) showed that the sediments contained very high, extremely high and significant levels of Pb, Cr, Cu, Mn, Ni and Fe. The Geoaccumulation Index (I_{geo}) revealed that Lake Eğirdir was not polluted with Cr, Cu, Fe, Mn, Mo, Ni and Zn. Based on the results of the Contamination Factor (CF), Cr, Cu, Fe, Mn, Mo, Ni and Zn were in the low contamination category. The results of The Pollution Load Index (PLI) for lake sediments indicated no contamination for all metals in all seasons. Sediment quality guidelines were used to determine the possible risk of heavy metal contamination of sediments, and the results show that Cd and Pb were at the minimal effect threshold (MET), while Cr, Cu, Ni and Zn were at the lowest effect levels (LEL). These results indicate that precautions should be taken to prevent an increase in metal pollution and reduce the existing pollution.

Key words: risk assessment, heavy metals, sediment, water, Türkiye

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1. Introduction

Ecologically, wetlands are among the richest biomes. In addition to being economically valuable, they serve as water storage reservoirs that reduce the severity of floods and improve water quality (Campbell & Reece 2008). Environmental pollution is one of the most important problems threatening our world. Our lakes, which are very important in terms of life and economy and have a rich ecological structure, are exposed to some irreversible changes as a result of conscious or unconscious interventions. The development of technology and industry, rapid population growth, irregular urbanization, increased agriculture and livestock activities, as well as an increase in domestic and industrial wastewater cause environmental pollution (Wetzel 2001; Kocataş 2008).

In the past, wetlands, especially lakes, were regarded as wastelands and people converted many wetlands into agricultural and development land, mostly by filling them with soil. In recent years, both private institutions and governments have attempted to protect the remaining wetlands through acquisitions, economic incentives and regulations (Campbell & Reece 2008).

Water pollution is one of the most important environmental problems today. Organic and inorganic substances, industrial wastes, pesticides, heavy metals, chemical fertilizers, detergents, petroleum and its derivates, microorganisms and oils, which enter aquatic systems in various ways, cause water pollution and deterioration of the water balance (Ellis et al. 1989; Wagner & Boman 2003; Uysal et al. 2009; Li et al. 2020).

Metals with a density greater than 5 g/cm^3 are called heavy metals, such as copper, zinc, iron, cadmium, nickel, etc. (Zhuang et al. 2016). Heavy metals originate from both natural sources and anthropogenic activities, such as erosion, forest fires, volcanic activities, mining, traffic, domestic, agricultural and industrial wastes, and spread in lakes, rivers and seas (Göksu 2014; Mostert et al. 2010; Islam et al. 2015; Yuan et al. 2019; Kumar et al. 2020a). Since 1960, heavy metals have been considered an important parameter in the systematic measurement of environmental pollution (Salomons 1993). Heavy metals are the major chemical pollutants in aquatic systems due to their non-degradability, high toxicity, persistence, ubiquity, easy accumulation and biomagnification (Vu et al. 2018; Xu et al. 2018; Ali et al. 2019; Fan et al. 2020). Metals are found in natural waters in the form absorbed by free ions, inorganic or organic compounds and particulate matter (Engel et al. 1981). When heavy metals are present in the aquatic environment as ions, their toxic effects increase (Türkmen & Türkmen 2004). Heavy metal concentrations in water and sediments depend on some physicochemical parameters, such as temperature, pH, dissolved oxygen, electrical conductivity etc. (Göksu 2014).

In fact, the concentration of heavy metals in water is lower than in sediments and aquatic organisms (Namminga & Wilhm 1976). Due to their high atomic weight and higher density compared to water, metals present in water are absorbed by sediment. The sediment acts as both a source and a sink. These toxic metals are released back into the water column with environmental changes such as pH, temperature, redox potential, salinity etc. in the dynamic water column above the sediment (Irabien & Velasco 1999; Soares et al. 1999; Laxmi Mohanta et al. 2020). The capacity of sediments to accumulate metals depends on several factors. These are divided into two groups: physical (grain size, surface area and surface charge) and chemical (composition and geochemical phases, and ion exchange capacity; Baker 1980).

While working on the water and sediments of Lake Eğirdir, Kaptan & Tekin-Özan (2014) analyzed some heavy metals and found that the metal with the highest concentration in water was Mn, and the metal with the lowest concentration was Cr. In the sediments, Fe occurred with the highest concentration and Cd with the lowest. Şener et al. (2014) determined some heavy metals in the sediments of Lake Eğirdir and reported significant enrichment of sediment samples with Pb, Cu, Ni, Fe and Zn.

Heavy metal pollution has been studied in various aquatic systems in Türkiye (Kayrak & Tekin-Özan 2018; Kankılıç 2019; Tokatlı & Ustaoğlu 2020; Güzel et al. 2022; Tokatlı & İslam 2022; Çomaklı, 2023; Yozukmaz & Yabanlı 2023) and other countries (Alahabadi & Malvandi 2018; Kumar et al. 2020b; Laxmi Mohanta et al. 2020; Qiao et al. 2020; Tian et al. 2020; Lipy et al. 2021; Karaouzas et al. 2021; Ehiemere et al. 2022; Seal et al. 2022; Tokatlı & İslam 2022; Çomaklı 2023; Yozukmaz & Yabanlı 2023).

Determination of metal levels alone does not provide information on their potential toxicity. For this reason, some indices such as the Water Quality Index (WQI), Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI) for water and the Enrichment Factor (EF), Geoaccumulation Index (I_{geo}), Contamination Factor (CF), and Pollution Load Index (PLI) for sediments have been used in recent years to determine the source of pollution and the degree of contamination, and to assess its ecological effects in water and sediment (Çevik et al. 2009; Li et al. 2015; Varol & Davraz 2015; Ustaoğlu & Tepe 2019; Tokatlı & Ustaoğlu 2020; Ustaoğlu 2021; Fındık & Aras

2023; Yozukmaz & Yabanlı 2023; Şener et al. 2023). In addition, various sediment quality guidelines (SQGs) have been developed to protect organisms living in freshwater ecosystems (MacDonald et al. 2000).

The most important objectives of this study are:

1. to determine some physicochemical parameters in water and the levels of Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in water and sediment, and the similarities and differences between the seasons;

2. to show the relationship between some physicochemical parameters and metals and Se in water;

3. to compare with permissible and standard limits of heavy metals and Se in water specified by the European Union (EU), the U.S. Environmental Protection Agency (EPA), the World Health Organization (WHO), the Ministry of Environment and Urban Planning, and Turkish Standardization Institute (TSE);

4. to evaluate the degree of contamination, water quality and sediment quality of Lake Eğirdir using the Water Quality Index (WQI), Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI), Enrichment Factor (EF), Geoaccumulation Index (I_{geo}), Contamination Factor (CF), Pollution Load Index (PLI) and Sediment Quality Criteria (SQGs).

Figure 1

Study area; Lake Eğirdir and sampling sites (source: Google map).

2. Materials and methods

2.1. Study area and sampling locations

Lake Eğirdir (Isparta) is the second largest (468 km^2) freshwater lake in Türkiye, located between latitudes 35°37′41″N and 38°16′55″N and longitudes 30°44′39″E and 30°57′43″E (Fig. 1). It was formed as a result of tectonic and karstic effects. It extends in a north–south direction north of the town of Eğirdir; its length is approximately 58 km and its width is approximately 15 km (Alp et al. 1994; Web 1 2021). The Hoyran Strait narrows in an east–west direction and divides the lake into two parts: Egirdir and Hoyran (Kesici & Kesici 2006).

In 1996, the water area surrounded by the maximum water level of Lake Eğirdir was recognized as the 1st Degree Natural Protected Area and a 300-meter strip starting from the maximum water level was recognized as the 3rd Degree Natural Protected Area. Today, these areas have been given the status of "Natural Site–Qualified Natural Protection Area", "Natural Site-Sustainable Conservation and Controlled Use Area" and "Sensitive Area to be Strictly Protected". In addition, Lake Eğirdir is listed as "Class A Wetland", which can accommodate and feed more than 25,000 waterfowl (Web 1 2021; Web 2 2022).

Eight sites were selected in the lake, the coordinates of which are given in Table 1. In addition to these sites, two regions away from the coastal effect were selected as control sites. Only water samples were collected from the control sites. Some views from the study area are presented in Figure 2.

Site 1: The first site was located in the southwestern part of the lake and near the village of Beydere. It was determined that fishermen have cleared the *Phragmites australis* community to keep their boats. Bedre beach is located approximately 500 m west of this site.

Table 1

Coordinates of the sampling sites.

Site No.	North	East
1	37°55'26"	30°47'35"
2	38°1'26"	30°49'4"
3	38°9'57"	30°45'24"
4	38°12'30"	30°45'2"
5	38°15'60"	30°49'13"
6	37°58'26"	30°57'43"
7	37°53'10"	30°54'11"
8	37°50'51"	30°51'28"
Control site 1	38°13'19"	30°49'09"
Control site 2	37°56'31"	30°51'56"

Site 2: The second site is located in the south of the lake, near the village of Barla. The bottom is rocky. There is a forest 50 m from the site. The site is located 60 m from the city highway, and there is agricultural land on the other side of the road.

Site 3: This site is located in the north-west of the lake, near the village of Gencali. The site is located in the vicinity of a pasture with many livestock pens. During the field studies, animals were observed grazing in the region. The shores of the lake become muddy, especially in spring, when the water level in the lake rises.

Site 4: This site is located in the north of the lake. During the field studies, a nomadic group of people

Figure 2

Views of the study area.

was observed living in tents in summer and autumn. The water level is quite shallow and some parts are swampy.

Site 5: It is located in the north of the lake, near the village of Taşevi. There is agricultural land around this site. Approximately 300 m from the site, there is a water pumping station that pumps water to the agricultural land.

Site 6: The site is located in the western part of the lake, near the village of Mahmatlar. There are settlements at a distance of 50 m. The locals regularly cut macrophytes both to enter the lake with their boats and to prevent flies from breeding.

Site 7: It is located in the south of the lake, 2.3 km from the village of Sorkuncak. Its bottom is quite rocky.

Site 8: It is located in the south of the lake, near the Eğirdir District and approximately 40 m from the Isparta–Konya highway. There are apartments on the other side of the highway.

Control site 1 is located in the northern part of the lake, while control site 2 is located in the southern part of the lake. Both sites are located in the central part of the lake. Some macrophytes such as *Chara* sp, *Potamogeton pectinatus, Potamogeton lucens, Potamogeton perfoliatus, Utricularia australis, Nuphar lutea* can be found in the middle parts of the lake (Şener 2022) where these sites are located.

2.2. Sample collection and preparation

Water and sediment samples were collected from the sites seasonally (July 2019, October 2019, January 2020 and April 2020) to determine heavy metal concentrations. Water temperature, pH value, electrical conductivity and dissolved oxygen content were measured at each site using YSI multiparameter equipment. Water samples were collected 50 cm below the water surface, brought to the laboratory, filtered through a Whatman 0.45 μm glass fiber filter, transferred to a 500 ml polypropylene bottle, concentrated HNO_3 (65%, Merck, Germany) was added to reduce the pH below 2. Water samples were then stored at 4°C and analyzed directly (APHA 2005).

Sediment samples were collected at a depth of 30–50 cm using an Ekman grab sampler and brought to the laboratory. They were dried at room temperature for 7 days and sieved to obtain fractions smaller than 62 μm. These grain size fractions contain metals in higher concentrations and homogeneous distributions (Balkıs & Algan 2005). Then the sediment samples were dried in an oven to ensure complete drying. Approximately 1 g of the dried sediment samples was weighed and transferred to 50 ml glass bottles, added 5 ml HNO_3 and kept at room temperature for 24 h. The samples were heated at 120°C until their colored vapors disappeared and they were completely mineralized. After cooling, 1 ml of H_2SO_4 was added to bottles. Samples were transferred to polypropylene containers, and the solutions were made up to 25 ml with distilled water. Then 1–2 drops of HNO_3 were added and the solutions were stored at 4ºC until analysis (UNEP 1984).

2.3. Quality control and analytical method

Certified standard reference material HISS-1 (Marine Sediment Certified Reference Material for Trace Elements and Other Constituents, National Research Council Canada) was used for the sediment to determine the precision and accuracy of heavy metal analysis. A blank solution was used to determine the actual concentration of metals. Blanks and standard reference materials were prepared for heavy metal analysis as described above, and for more accurate results the blank, standard material and samples were analyzed in triplicate. All glassware and containers were soaked in 20% nitric acid overnight and rinsed with distilled water before use. Analyses were performed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Agillent 5110). The results are expressed as ppm. Replicate analysis of the reference material showed good accuracy, with recovery rates for metals between 91% and 106% for HISS-1 (Table 2).

Table 2

Concentrations of metals found in certified reference material HISS-1 from the National Research Council, Canada.

Metals	HISS 1 certified	HISS 1 observed	Recovery (%)
Cd	0.024 ± 0.009	0.023 ± 0.03	96
Cr	30.0 ± 6.8	27.95 ± 2.35	93
Cu	2.29 ± 0.37	2.13 ± 0.21	93
Fe	-	-	-
Mn	66.1 ± 4.2	59.91 ± 1.36	91
Mo	-	-	-
Ni	2.16 ± 0.29	2.3 ± 1.10	106
Pb	3.13 ± 0.40	3 ± 0.02	96
Se	0.050 ± 0.007	0.049 ± 0.1	98
Zn	4.94 ± 0.79	4.69 ± 0.25	95

2.4. Environmental quality standards

Physicochemical parameters, selected heavy metals and Se measured in the water of Lake Eğirdir were evaluated according to the Water Pollution Control Regulation (WPCR), which is the national legislation for lakes, and drinking water standards specified by the European Union (EU), the U.S. Environmental Protection Agency (EPA), the World Health Organization (WHO) and the Turkish Standardization Institute (TS 266; TSE 2005; Ministry of Environment and Urban Planning 2008; WHO 2017; EPA 2018; EU 2020).

2.5. Assessment of heavy metal pollution in water

The Water Quality Index (WQI), Heavy Metal Pollution Index (HPI) and Heavy Metal Evaluation Index (HEI) were used to assess metal contamination in the water of Lake Eğirdir.

2.5.1. Water Quality Index (WQI)

The Water Quality Index (WOI) is an important method for assessing drinking water quality; different water quality parameters are used to calculate it (Ustaoğlu 2020; Tokatlı & Ustaoğlu 2020).

Each parameter was assigned a relative weight value (wi) according to its effect on drinking water quality and human health on a scale from 1 to 5 (Varol & Davraz 2015). Relative weight (Wi) was calculated using the following formula (1):

$$Wi = \frac{wi}{\sum_{i=1}^{n} wi} \quad (1)$$

The following formula was used to calculate the quality grade (2):

$$Q_i = \left(\frac{C_i}{S_i}\right) \times 100 \quad (2)$$

where C_i is the concentration of heavy metals measured in water and S_i are standard values determined by WHO (2011).

The sub-index (SI_i) value was determined using the following formula (3):

$$SI_i = W_i \times Q_i \quad (3)$$

Finally, all sub-index (SI_i) values were summed to determine the water quality index (WQI) (4):

$$WQI = \sum SI_i \quad (4)$$

Yadav et al. (2012) defined five classes according to the results of the Water Quality Index (WQI): WQI < 50 (excellent); 50 ≤ WQI < 100 (good); 100 ≤ WQI < 200 (poor); 200 ≤ WQI < 300 (very poor); WQI ≥ 300 (undrinkable).

2.5.2. Heavy Metal Pollution Index (HPI)

The Heavy Metal Pollution Index (HPI) is a widely used method for determining water quality in terms of selected parameters (Mohan et al. 1996). The formulas used are given below:

$$HPI = \frac{\sum_{i=1}^{n}(QiWi)}{\sum_{i=1}^{n} Wi}$$

$$Qi = \left(\frac{Ci}{Si}\right) \times 100$$

$$Wi = \frac{k}{Si}$$

Qi – sub-index of metals
Wi – unit weight of metals
Ci – measured values of metals
Si – standard values of the parameter given by WHO (2011)
k – constant value accepted as 1.
HPI < 100 indicates a low level of heavy metal pollution and no adverse health effects;
HPI = 100 indicates a threshold risk and may have adverse health effects;
HPI > 100 indicates that the water cannot be used for drinking and is not suitable for consumption (Saleh et al. 2019; Ustaoğlu 2020).

2.5.3. Heavy Metal Evaluation Index (HEI)

The Heavy Metal Evaluation Index (HEI) is used to evaluate water quality based on heavy metal content and is calculated according to the following equation (Al-Ani et al. 1987; Edet & Offiong, 2002; Ameh 2013; Kumar et al. 2019):

$$HEI = \sum \frac{H_c}{H_{MAC}}$$

H_C – monitored value of each parameter
H_{MAC} – permissible limit value for each parameter given by WHO (2011).

The HEI scale has the following levels: HEI < 10 (low contamination), 10 < HEI <20 (moderately contaminated), and HEI > 20 (high contamination; Saleh et al. 2019).

2.6. Assessment of heavy metal pollution in sediment

The Enrichment Factor (EF), the Geoaccumulation Index (I_{geo}), the Contamination Factor (CF) and the Pollution Load Index (PLI) were used to evaluate metal contamination in the sediments of Lake Eğirdir.

2.6.1. Enrichment Factor (EF)

It is used to determine the proportion of heavy metals of anthropogenic origin in sediments. The EF is used to normalize the heavy metal level relative to elements such as aluminum and iron (Din 1992). In this study, Al is used as a reference metal for normalization for the following reasons:

1. it is the most abundant metal of natural origin,
2. due to its high immobility, it is not significantly affected by diagenetic processes and strong redox reactions in sediments,
3. its content is generally unaffected by anthropogenic sources (Schropp & Windom 1988; Charlesworth & Service 2000).

The following formula (Buat-Menard & Chesselet 1979) was used to calculate the Enrichment Factor (EF):

$$EF = \frac{\left(\frac{C_n}{C_{ref}}\right)_{sample}}{\left(\frac{B_n}{B_{ref}}\right)_{reference}}$$

C_n – concentration of an element in the analyzed sample

C_{ref} – concentration of the reference element (Al) in the analyzed sample

B_n – average level of an element in shales according to Mason (1966)

B_{ref} – average level of the reference element (Al) in shales according to Mason (1966).

Yongming et al. (2006) divided the EF into five categories: EF < 2 (no or minimal enrichment), EF = 2–5 (moderate enrichment), EF = 5–20 (significant enrichment), EF = 20–40 (very high enrichment), and EF > 40 (extremely high enrichment).

2.6.2. Geoaccumulation Index (I_{geo})

The Geoaccumulation Index is a method developed by Müller (1969) for determining metal pollution by comparing metal levels in the sediment with the pre-industrial levels. The following formula is used to determine this index:

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

C_n – metal concentrations in the analyzed sediment

B_n – reference value of the measured metal.

Factor (1.5) is used as a basic matrix correction due to lithogenic variations. The range of the Geoaccumulation Index (I_{geo}) is divided into seven classes (Müller 1969; Müller 1981): $I_{geo} < 0$ (unpolluted), $0 < I_{geo} < 1$ (unpolluted–moderately polluted), $1 < I_{geo} < 2$ (moderately polluted), $2 < I_{geo} < 3$ (moderately–strongly polluted), $3 < I_{geo} < 4$ (strongly polluted), $4 < I_{geo} < 5$ (strongly–very strongly polluted) and $I_{geo} > 5$ (very strongly polluted).

2.6.3. Contamination Factor (CF)

The Contamination Factor proposed by Hakanson (1980) is used to determine the degree of heavy metal contamination in sediments. It was calculated using the following formula:

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

C_{metal} – metal concentration in sediments

C_o – average metal concentration in shales (Mason 1966).

The Contamination Factor (CF) is interpreted as follows: CF < 1 (low contamination); 1 < CF <3 (moderate contamination); 3 < CF < 6 (considerable contamination) and CF > 6 (very high contamination).

2.6.4. Pollution Load Index (PLI)

To determine the sediment quality relative to heavy metals, the Pollution Load Index (PLI) was calculated using the following formula (Tomlinson et al. 1980):

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times ... \times CF_n)}$$

CF is the Contamination Factor and n is the number of metals.

It has been reported that the ideal value is zero, which indicates no pollution in the environment, while PLI > 1 indicates progressive pollution (Suresh et al. 2011).

2.7. Sediment quality guidelines (SQG)

Sediment quality guidelines are used to protect organisms living in aquatic systems. MacDonald et al. (2000) classified the effects of heavy metals in sediments on the aquatic life. Four threshold values given by MacDonald et al. (2000) were used in this study:

1) lowest effect levels (LEL) and 2) minimal effect threshold (MET) – no effects on most sediment-dwelling organisms are expected below this level (EC & MENVIQ 1992; Persaud et al. 1993); 3) severe effect level (SEL) – sediments are considered to be heavily polluted; adverse effects on most sediment-dwelling organisms are expected above this level (Persaud et al. 1993); 4) toxic effect threshold (TET) – sediments are considered to be heavily polluted; adverse effects on sediment-dwelling organisms are expected above this level (EC & MENVIQ 1992).

2.8. Statistical analysis

SPSS version 22.0 for Windows was used for statistical analysis. The minimum, maximum, mean and standard deviation (SD) in tables were calculated based on the results of the analyses for each sampling season. One-Way ANOVA and Duncan's multiple comparison test were used to compare the concentrations of heavy metals and Se in water and sediments between the seasons (Fisher 1928; Duncan 1955). Duncan's test was also used to compare heavy metal and Se levels between the coastal and control sites (Duncan 1955). The Pearson test was conducted to determine the relationships between the physicochemical parameters and concentrations of heavy metals and Se in water (Pearson 1900). The relationship was considered statistically significant at $p < 0.05$.

3. Results

3.1. Physicochemical parameters of lake water

Physicochemical parameters of water samples per season are shown in Table 3. Mean water temperature ranged between 4.65°C (winter) and 26.29°C (summer). Mean pH varied between 7.15 (autumn) and 7.64 (summer). Dissolved oxygen was highest in winter (6.64 mg l^{-1}) and lowest in summer (3.8 mg l^{-1}). EC values ranged between 268.16 µs/cm (autumn) and 453.6 µs/cm (summer). The relationships between physical parameters were calculated using the Pearson test (Table 4). Significant positive correlations were found between temperature and EC and pH (< 0.05). Negative significant relationship was determined between temperature and dissolved oxygen (< 0.01).

3.2. Heavy metals and Se in lake water

The concentrations of nine metals (Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn) and Se in the four seasons are shown in Table 5. The analyzed metals were ranked as follows: Cr < Cd < Mo < Pb < Se< Mn < Cu < Ni < Zn < Fe. Of the analyzed metals, the highest concentration was determined for Fe, and the lowest for Cr.

Table 5 also shows seasonal variations in the content of heavy metals and Se. It was determined that Cr, Fe, Mn, Ni and Pb reached the highest concentrations in summer, Mo in winter, Se in autumn and Zn in spring. Cd occurred at the same concentrations in all seasons, Cr in all seasons except summer, and Cu in all seasons except autumn. Cu, Fe, Mn and Zn occurred at the lowest concentrations in autumn, Mo and Se in summer and Pb and Ni in spring. There is no significant relationships between seasons for any of the metals or Se (> 0.05).

To determine the effect of the coast (anthropogenic effect) on the levels of heavy metals and Se, the results

Table 3

Selected physicochemical parameters of Lake Eğirdir's water.

	Temperature (°C)	pH	Dissolved Oxygen (mg l^{-1})	Electrical Conductivity (µg cm^{-1})
Summer	24.38 – 29.42 26.29 ± 1.90	6.29 – 8.36 7.64 ± 0.71	2.94 – 5.65 3.86 ± 0.90	355.6 – 502.6 453.6 ± 48.53
Autumn	16.82 – 22.51 19.61 ± 2.26	6.89 – 7.57 7.15 ± 0.21	4 – 4.71 4.31 ± 0.27	244.8 – 288.7 268.16 ± 14.83
Winter	2.72 – 6.37 4.65 ± 1.40	6.31 – 7.95 7.25 ± 0.49	6.2 – 6.95 6.64 ± 0.26	276.8 – 402.4 303.38 ± 41.82
Spring	17.04 – 21.81 20.11 ± 1.93	7.17 – 8.14 7.53 ± 0.29	3.99 – 4.8 4.32 ± 0.30	237.1 – 289 269.93 ± 18.57

Table 4

Pearson correlation matrix showing the correlation coefficients between physicochemical parameters of water and metal levels.

	Temp. (°C)	pH	DO (mg l^{-1})	EC (µs cm^{-1})	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Zn
Temperature (°C)	1	0.412*	–0.845**	0.402*	–0.139	0.279	–0.011	0.106	0.266	–0.364*	0.015	0.031	–0.211	0.030
pH		1	–0.289	0.159	0.207	0.164	–0.220	–0.087	0.139	–0.226	–0.061	0.124	0.142	0.022
Dissolved oxygen (mg l^{-1})			1	–0.333	0.217	–0.278	0.004	–0.170	–0.287	0.297	–0.082	–0.073	0.165	–0.058
Electrical conductivity (µs cm^{-1})				1	–0.020	0.224	0.016	0.337	0.241	–0.174	0.056	0.080	–0.168	0.060
Cd					1	0.328	0.236	0.074	0.351*	–0.119	0.447*	0.159	0.072	0.297
Cr						1	0.324	0.277	0.944**	–0.354*	0.312	–0.089	–0.105	0.162
Cu							1	–0.005	0.251	–0.091	0.442*	0.103	–0.215	0.676**
Fe								1	0.543**	–0.521**	0.160	–0.085	–0.025	–0.069
Mn									1	–0.459**	0.305	–0.105	–0.086	0.092
Mo										1	–0.198	–0.169	0.152	0.077
Ni											1	0.073	0.023	0.573**
Pb												1	–0.069	–0.006
Se													1	–0.013
Zn														1

*significant at 0.05; **significant at 0.01

Table 5

Concentrations (ppm) of selected heavy metals in the water of Lake Eğirdir.

	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Zn
Summer	0.002 – 0.003 0.002 ± 0.0004^{a*}	0.001 – 0.032 0.0047 ± 0.011^a	0.031 – 0.051 0.039 ± 0.008^a	0.15 – 2.9 0.772 ± 0.937^a	0.007 – 0.372 0.071 ± 0.125^a	0.003 – 0.006 0.004 ± 0.001^a	0.007 – 0.103 0.047 ± 0.04^a	0.003 – 0.080 0.015 ± 0.026^a	0.003 – 0.024 0.011 ± 0.008^a	0.031 – 0.112 0.064 ± 0.032^a
Autumn	0.002 – 0.003 0.002 ± 0.0004^a	0.0004 – 0.002 0.001 ± 0.0004^a	0.026 – 0.049 0.037 ± 0.007^a	0.1 – 0.57 0.253 ± 0.179^a	0.005 – 0.035 0.016 ± 0.011^a	0.004 – 0.006 0.005 ± 0.001^a	0.015 – 0.088 0.046 ± 0.031^a	0.003 – 0.060 0.014 ± 0.019^a	0.009 – 0.03 0.016 ± 0.006^a	0.041 – 0.08 0.059 ± 0.015^a
Winter	0.002 – 0.003 0.002 ± 0.0004^a	0.0001 – 0.002 0.001 ± 0.0005^a	0.027 – 0.049 0.039 ± 0.007^a	0.14 – 1.55 0.471 ± 0.484^a	0.007 – 0.051 0.02 ± 0.015^a	0.003 – 0.01 0.006 ± 0.002^a	0.009 – 0.124 0.045 ± 0.037^a	0.0005 – 0.07 0.013 ± 0.023^a	0.004 – 0.028 0.015 ± 0.008^a	0.048 – 0.093 0.061 ± 0.016^a
Spring	0.001 – 0.003 0.002 ± 0.0004^a	0.00002 – 0.001 0.001 ± 0.001^a	0.03 – 0.053 0.039 ± 0.007^a	0.11 – 2.15 0.41 ± 0.706^a	0.006 – 0.108 0.023 ± 0.034^a	0.004 – 0.007 0.005 ± 0.001^a	0.006 – 0.012 0.036 ± 0.03^a	0.003 – 0.12 0.007 ± 0.003^a	0.007 – 0.021 0.013 ± 0.005^a	0.044 – 0.16 0.067 ± 0.038^a

*Means with the same superscript in the same row are not significantly different according to Duncan's multiple range test ($p < 0.05$)

from the two control sites and eight coastal sites were compared seasonally and presented in Table 6. It was determined that mean concentrations of Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn were higher at the coastal sites than at the control sites, and the Se level was higher at the control sites in summer. Levels of Cd, Cr, Mo, Pb and Se in autumn were higher at the control sites, while levels of Cu, Fe, Mn, Ni and Zn were higher at the coastal sites. Levels of Cd, Cu and Ni were higher at the control sites, while levels of other metals were higher at the coastal sites in winter. Levels of Cd, Cr, Cu, Fe, Mn, Mo and Zn were higher at the coastal sites than at the control sites. Levels of Fe, Mn and Zn varied significantly (< 0.05) between the coastal and control sites, while levels of other metals and Se did not vary significantly (> 0.05).

The relationships between the levels of metals and Se in water and selected physicochemical parameters were determined using Pearson's correlation matrix (Table 4). Negative correlations were determined between water temperature and Cd, Cu, Mo and Se, between pH and Cu, Fe, Mo, Ni and Zn, between dissolved oxygen and Cr, Fe, Mn, Ni, Pb and Zn, between EC and Cd, Mo and Se. As shown in Table 4, negative correlations were found between Cd and Mo ($r = -0.119$), Mo and Pb ($r = -0.169$), Cu and Fe ($r = -0.005$), Fe and Mo ($r = -0.521$), Mn and Mo ($r = -0.459$), Pb and Se ($r = -0.069$), Mo and Ni ($r = -0.198$), Mo and Pb ($r = -0.169$), Pb and Zn ($r = -0.006$), Se and Zn ($r = -0.013$). Significant correlations at < 0.05 were found between EC and Mo, Cd and Mn, Cd and Ni, Cr and Mo, Cu and Ni. Significant correlations (< 0.01) were determined between Cr and Fe, Cr and Mn, Cu and Zn, Fe and Mn, Fe and Mo, Mn and Mo, Ni and Zn.

3.3. Assessment of the contamination degree

To determine the degree of heavy metal pollution in water, the Water Quality Index (WQI), the Heavy Metal Pollution Index (HPI) and the Heavy Metal Evaluation Index (HEI) were calculated.

3.3.1. Water Quality Index (WQI)

WQI values were calculated for Lake Eğirdir. Table 7 shows the standard values provided by WHO (WHO 2011) and Wi values (Xiao et al. 2014; Kurt et al. 2022). The lowest WQI was determined in spring at 52.12, and the highest WQI was determined in summer at 80.76 (Table 8). According to these results, WQI values in all seasons were $50 \leq WQI < 100$, i.e. indicating the good category.

Table 6

Concentrations (ppm) of heavy metals in water at the coastal and control sites of Lake Eğirdir.

	Sites	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Zn
Summer	Control 1	0.0023^{a*}	0.0005^{a}	0.0344^{a}	0.11^{a}	0.0043^{a}	0.0035^{a}	0.0196^{a}	0.0045^{a}	0.0127^{a}	0.0389^{a}
	Control 2	0.0020^{a}	0.0005^{a}	0.0342^{a}	0.25^{a}	0.0109^{a}	0.0029^{a}	0.0146^{a}	0.0097^{a}	0.0095^{a}	0.0412^{ab}
	Coast	0.0022^{a}	0.0051^{a}	0.0392^{a}	0.7718^{b}	0.0708^{b}	0.0044^{a}	0.0475^{a}	0.0153^{a}	0.0105^{a}	0.0644^{b}
Autumn	Control 1	0.0022^{a}	0.0012^{a}	0.0321^{a}	0.1^{a}	0.0043^{a}	0.0063^{a}	0.0435^{a}	0.08^{a}	0.0171^{a}	0.0527^{a}
	Control 2	0.0024^{a}	0.0012^{a}	0.0355^{a}	0.17^{a}	0.0067^{a}	0.0062^{a}	0.019^{a}	0.0064^{a}	0.0165^{a}	0.0563^{ab}
	Coast	0.0021^{a}	0.0007^{a}	0.0367^{a}	0.2525^{b}	0.0161^{b}	0.0052^{a}	0.0457^{a}	0.0136^{a}	0.0157^{a}	0.0588^{b}
Winter	Control 1	0.0026^{a}	0.0003^{a}	0.0384^{a}	0.11^{a}	0.004^{a}	0.0048^{a}	0.0208^{a}	0.0024^{a}	0.0059^{a}	0.0424^{a}
	Control 2	0.0026^{a}	0.0003^{a}	0.0476^{a}	0.19^{a}	0.0066^{a}	0.0049^{a}	0.053^{a}	0.0003^{a}	0.0098^{a}	0.0668^{ab}
	Coast	0.0024^{a}	0.0007^{a}	0.0393^{a}	0.4713^{b}	0.0202^{b}	0.0058^{a}	0.0447^{a}	0.0125^{a}	0.0153^{a}	0.0607^{b}
Spring	Control 1	0.0021^{a}	0.0003^{a}	0.037^{a}	0.09^{a}	0.0041^{a}	0.0032^{a}	0.0395^{a}	0.0084^{a}	0.0184^{a}	0.0506^{a}
	Control 2	0.0014^{a}	0.0004^{a}	0.0364^{a}	0.11^{a}	0.0064^{a}	0.0038^{a}	0.0592^{a}	0.0119^{a}	0.0209^{a}	0.054^{ab}
	Coast	0.0022^{a}	0.0006^{a}	0.0394^{a}	0.41^{b}	0.0231^{b}	0.0054^{a}	0.0361^{a}	0.0072^{a}	0.0133^{a}	0.0675^{b}

*Means with the same superscript in the same row are not significantly different according to Duncan's multiple range test ($p < 0.05$)

3.3.2. Heavy Metal Pollution Index (HPI)

The Heavy Metal Pollution Index (HPI) was also calculated to evaluate the degree of heavy metal pollution in Lake Eğirdir. The minimum HPI value was determined in spring at 62.65, the maximum HPI value was recorded in summer at 80.03 (Table 8). The results indicate that the level of heavy metal pollution is low and there is no harmful effect on health.

3.3.3. Heavy Metal Evaluation Index (HEI)

The Heavy Metal Evaluation Index (HEI) was calculated. The lowest HEI value was recorded at 3.69 in spring and the highest value was recorded in summer at 5.99. According to the HEI results, the water in Lake Eğirdir is in the low contamination category in all seasons (Table 8).

Table 7

Weight value of each parameter.

Parameter	WHO (2011)	Weight wi (Xiao et al. 2014; Kurt et al. 2022)
pH	6.5–8.5	4
Cd	3	5
Cr	50	5
Cu	2000	2
Fe	300	4
Mn	400	4
Ni	70	1
Pb	10	5
Se	40	3
Zn	3000	1
$\sum wi = 34$		

3.4. Heavy metals and Se in lake sediments

The concentrations of heavy metals and Se in sediments (arithmetic mean, minimum, maximum and standard deviation) are shown in Table 9. All metals were determined in all seasons. The total levels of metal concentrations in sediment samples were in the order: Fe > Mn> Pb > Zn > Ni > Cr > Cu > Se > Mo > Cd. Fe, Pb, Se and Zn reached the highest levels in summer, while Cd and Mo in autumn, Cr, Cu, Mo and Ni in winter. The lowest levels of Cr, Cu, Fe and Ni were determined in spring, Cd and Mo in summer, Zn in autumn and Mn, Pb and Se in winter. Only Cd levels varied significantly (< 0.05) by season, while other metals did not vary significantly (> 0.05).

3.5. Ecological risk assessment

The Enrichment Factor (EF), the Geoaccumulation Index (I_{geo}), the Contamination Factor (CF) and the Pollution Load Index (PLI) were calculated to determine heavy metal pollution in the sediment.

3.5.1. Enrichment Factor (EF)

As shown in Table 10 and Figure 3, Pb was at a very high enrichment level (EF = 20–40) in summer and spring, and at an extremely high enrichment level (EF > 40) in autumn and winter. Cr was at a minimum

Table 8

WQI, HPI and HEI values for Lake Eğirdir and each season.

	Summer	Autumn	Winter	Spring
WQI	80.76	56.60	63.68	52.12
HPI	80.03	77.09	75.41	62.65
HEI	5.99	4.06	4.66	3.69

Table 9

Concentrations (mg kg^{-1}) of selected heavy metals in Lake Eğirdir's sediment.

	Summer	Autumn	Winter	Spring
Cd	0.38 – 0.81 0.54 ± 0.16[a*]	0.61 – 0.95 0.77 ± 0.14[b]	0.39 – 0.74 0.57 ± 0.11[a]	0.45 – 0.85 0.56 ± 0.15[a]
Cr	4.78 – 28.85 14.57 ± 8.3[a]	5.88 – 35.96 15.78 ± 10.1[a]	5.95 – 39.68 16.96 ± 11.73[a]	3.85 – 24.71 10.42 ± 6.66[a]
Cu	4.85 – 32.66 14.51 ± 9.26[a]	5.88 – 22.01 13.64 ± 4.77[a]	6.16 – 23.99 15.59 ± 7.34[a]	6.41 – 21.46 13.08 ± 6.38[a]
Fe	3009.71 – 20203.12 11453.5 ± 6045.03[a]	4038.23 – 15602.46 10899.78 ± 3595.2[a]	2285.71 – 19559.37 11412.96 ± 5654.004[a]	2079.38 – 17399.72 7665.29 ± 4878[a]
Mn	95.87 – 607.91 351.76 ± 182.41[a]	86.76 – 547.87 355.79 ± 183.07[a]	78.82 – 503.97 298.66 ± 150.41[a]	86.49 – 673.16 316.16 ± 192.02[a]
Mo	0.37 – 2.51 0.91 ± 0.74[a]	0.11 – 1.71 0.96 ± 0.65[a]	0.23 – 2.65 1.32 ± 0.66[a]	0.47 – 1.45 1.15 ± 0.3[a]
Ni	5.98 – 52.88 25.01 ± 19.36[a]	5.88 – 82.19 26.04 ± 25.75[a]	4.93 – 92.59 28.41 ± 29.13[a]	6.41 – 74.13 22.5 ± 22.46[a]
Pb	12.14 – 108.17 48.24 ± 37.51[a]	16.18 – 61.32 38.68 ± 13.75[a]	16.67 – 60.61 35.78 ± 15.53[a]	19.23 – 98.9 42.81 ± 30.33[a]
Se	0.87 – 4.83 2.98 ± 1.57[a]	0.66 – 4.01 2.38 ± 1.13[a]	1.04 – 5.73 2.02 ± 1.6[a]	0.91 – 2.91 2.12 ± 0.83[a]
Zn	22.44 – 73.32 39.83 ± 16.63[a]	20.59 – 42.55 33.11 ± 7.87[a]	22.17 – 46.3 36.27 ± 8.68[a]	21.33 – 46.7 34.27 ± 8.37[a]

*Means with the same superscript in the same row are not significantly different according to Duncan's multiple range test ($p < 0.05$)

Table 10

Enrichment Factor (EF), Geoaccumulation Index (I_{geo}) and Contamination Factor (CF) of Lake Eğirdir's sediment by seasons.

	Enrichment Factor (EF)				Geoaccumulation Index (I_{geo})				Contamination Factor (CF)			
	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring
Cd	_	_	_	_	0.263	0.774	0.333	0.310	1 < CF < 3	1 < CF < 3	1 < CF < 3	1 < CF < 3
Cr	1.7773	5.6303	6.9398	1.3925	−3.211	−3.095	−2.989	−3.699	CF < 1	CF < 1	CF < 1	CF < 1
Cu	3.0025	9.5875	11.7035	3.29	−2.218	−2.308	−2.114	−2.366	CF < 1	CF < 1	CF < 1	CF < 1
Fe	2.3576	7.1612	8.1071	1.7172	−2.626	−2.699	−2.635	−3.211	CF < 1	CF < 1	CF < 1	CF < 1
Mn	4.7851	14.0514	12.9645	4.6293	−1.857	−1.842	−2.095	−2.012	CF < 1	CF < 1	CF < 1	CF < 1
Mo	_	_	_	_	−2.120	−2.023	−1.565	−1.761	CF < 1	CF < 1	CF < 1	CF < 1
Ni	4.0631	11.8465	14.8123	3.6289	−2.029	−1.971	−1.842	−2.178	CF < 1	CF < 1	CF < 1	CF < 1
Pb	21.2792	61.1107	63.8503	23.2818	0.685	0.366	0.255	0.513	1 < CF < 3	1 < CF < 3	1 < CF < 3	1 < CF < 3
Se	_	_	_	_	1.727	1.401	1.163	1.233	3 < CF < 6	3 < CF < 6	3 < CF < 6	3 < CF < 6
Zn	_	_	_	_	−1.842	−2.108	−1.977	−2.053	CF < 1	CF < 1	CF < 1	CF < 1

enrichment level (EF < 2) in summer and spring, and at a significant enrichment level (EF = 5–20) in autumn and winter. Cu, Mn and Ni were at a moderate enrichment level (EF = 2–5) in summer and spring, while at a significant enrichment level (EF = 5–20) in autumn and winter. Fe was at a minimum enrichment level (EF < 2) in spring, at a moderate enrichment level (EF = 2–5) in summer, and at a significant enrichment level (EF = 5–20) in autumn and winter.

3.5.2. Geoaccumulation Index (I_{geo})

The Geoaccumulation Index (I_{geo}) showed that Lake Eğirdir was not polluted with Cr, Cu, Fe, Mn, Mo, Ni and Zn ($I_{geo} < 0$) in all seasons (Table 10). Cd and Pb levels fell in the unpolluted–moderately polluted class ($0 < I_{geo} < 1$), and Se in the moderately polluted class ($1 < I_{geo} < 2$) in all seasons.

3.5.3. Contamination Factor (CF)

The Contamination Factor (CF) is shown in Table 10. Cr, Cu, Fe, Mn, Mo, Ni and Zn were found in the low contamination category (CF < 1), Cd and Pb were in the moderately contaminated category (1 < CF < 3), and Se was in the considerably contaminated category (3 < CF < 6) in all seasons.

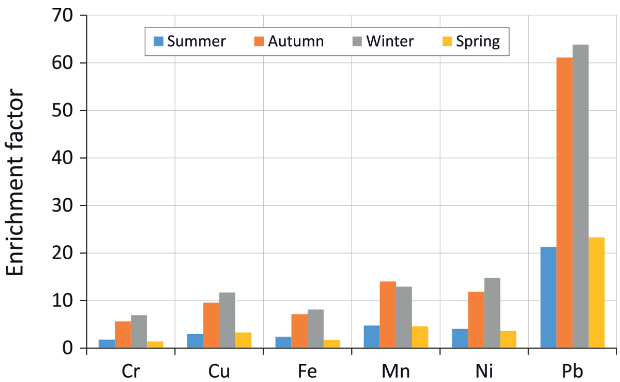

Figure 3

Enrichment Factor (EF) of Lake Eğirdir's sediments.

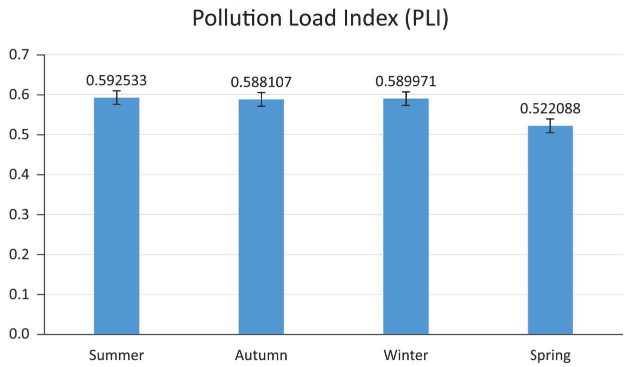

Figure 4

Pollution Load Index (PLI) for sediments of Lake Eğirdir by seasons.

3.5.4. Pollution Load Index (PLI)

According to Figure 4, which shows the results of the Pollution Load Index (PLI), lake sediments showed no pollution (PLI < 1) for any of the metals in all seasons.

4. Discussion

Water temperature affects physical, chemical and biological activities in water and changes the concentrations of many substances (Atıcı et al. 2005). During the study period, the water temperature varied between 2.72°C and 29.42°C. It was highest in summer and lowest in winter. In lakes, pH is one of the most important parameters affecting the toxicity of some compounds (Boyd et al. 2016). The pH value in lakes varies between 6 and 9. As a result of photosynthesis and evaporation, pH increases in summer (Tanyolaç 2011). The pH of Lake Eğirdir varied between 6.29 and 8.36. Şener et al. (2013) reported that water pH values in Lake Eğirdir ranged between 9.40 and 9.67, and were higher compared to other similar lakes, which may be due to the geochemical structure of the lake basin with carbonate rocks. It has been reported that the high pH of Lake Eğirdir's water is caused by the limestone around the lake, which is highly alkaline and raises the pH of the aquatic environment when dissolved in water (Bulut & Kubilay 2019). The fact that pH is higher in summer compared to other seasons can be attributed to the following causes: (i) due to the karstic structure of Lake Eğirdir (Şener et al. 2013), increasing chemical dissolution with temperature increases the amount of carbonates in the lake and this increase causes the pH level to rise (ii); as evaporation increases in summer, the amount of alkaline substances in the lake increases, making the lake water alkaline. Dissolved oxygen is very important for aquatic life and a major indicator of ecological health (Mutlu et al. 2016; Ustaoğlu & Tepe 2019). The amount of dissolved oxygen in the water of Lake Eğirdir was found to be high in winter and low in summer. It ranged from 2.94 mg l^{-1} to 5.65 mg l^{-1}. Wetzel (2001) reported that as water temperature increases, the amount of dissolved oxygen in water decreases and chemical and biochemical reactions accelerate. A significant negative correlation was found in Pearson correlation analysis between temperature and dissolved oxygen ($r = -0.845$, $p < 0.01$). The electrical conductivity of surface water can vary depending on geological structure, water temperature, dissolved matter in water and amount of precipitation (Tepe & Boyd 2003). The electrical conductivity in Lake Eğirdir varied between 502.6 μs cm^{-1} (in summer) and 237.1 μs cm^{-1} (in spring). When water temperature increases, the electrical conductivity decreases (Ustaoğlu & Tepe 2019). The results of Pearson correlation analysis confirm this relationship with a significant positive correlation between electrical conductivity and temperature ($r = 0.402$, $p < 0.05$) and a negative correlation between electrical conductivity and dissolved oxygen ($r = -0.333$, $p > 0.05$). The electrical conductivity was minimal in spring and this may be due to melting snow water and spring rains (Tepe & Boyd 2001).

Based on the temperature values and according to the Water Pollution Control Regulation (WPCR; Ministry of Environment and Urban Planning 2008), the lake's water can be classified as water quality class III in summer and as water quality class I–II in other seasons. According to the Water Pollution Control Regulation (WPCR; Ministry of Environment and Urban Planning 2008), pH values for the water of Lake Eğirdir indicate water quality class I–II, and electrical conductivity values indicate water quality class I in all seasons. According to the Water Pollution

Control Regulation (WPCR; Ministry of Environment and Urban Planning 2008), dissolved oxygen values for Lake Eğirdir's water indicate water quality class I in winter and water quality class II in other seasons. Temperature, pH, electrical conductivity and dissolved oxygen values were found to be below the limits set for drinking water by the European Union (EU; 2020), the U.S. Environmental Protection Agency (EPA; 2018), the World Health Organization (WHO; 2017) and the Turkish Standardization Institute (TS 266; 2005). It was reported that pH values for Lake Eğirdir's water were above and dissolved oxygen values were below the eutrophication control limit values set by the Water Pollution and Control Regulation in Türkiye (Şener et al. 2013).

All analyzed metals and Se were determined in water samples in all seasons. Fe has the highest levels among the analyzed metals, followed by Zn, Ni and Cu. Cr had the lowest concentration. Similar results were determined for Lake Karataş (Başyiğit & Tekin-Özan 2013), the Ganga River (Kumar et al. 2020b), Oymapınar Dam (Tekin-Özan 2021), Lake Işıklı (Gülcü-Gür & Tekin-Özan 2017), and Lake Yeniçağa (Saygı & Yiğit 2012). Iron generally occurs in water with the highest concentration, as it is one of the most abundant metals in the Earth's crust and in other resources (Usero et al. 2004). Overall, heavy metal levels have increased compared to the results of analyses carried out in October 2009 and May 2009 by Şener et al. (2013) and between September 2011 and February 2012 by Kaptan & Tekin-Özan (2014). During this 10-year period, heavy metals may have entered the water from various sources, such as domestic, agricultural and anthropogenic sources.

In general, the levels of metals increase in summer and decrease in the wet season. Tekin-Özan (2008) studied levels of heavy metals in water of Lake Beyşehir and reported that the metals reached the highest concentrations in the hot season and the lowest in the warm season. There is no significant relationships between seasons for any of the metals (> 0.05).

The increase in Cr, Cu, Fe, Mn, Ni and Se levels in summer can be due to increasing air temperature and evaporation (Gülcü-Gür & Tekin-Özan 2017). Cd, Cu, Mo and Se levels decrease in summer due to increasing biological activities of macrophytes, fish and other living organisms. Melting snow and heavy rain can cause heavy metal levels to drop (Gülcü-Gür & Tekin-Özan 2017).

Two control sites were selected to determine the anthropogenic effect on heavy metal levels. Fe, Mn and Zn varied significantly (< 0.05) between the coastal and control sites, while other metals and Se did not vary significantly (> 0.05). The fact that all metals (except Se) at the coastal sites in summer were at higher levels than at the control sites can be attributed to the following reasons: (i) the presence of pesticides and fertilizers that were used in agricultural operations during the summer season; (ii) the increase in domestic wastewater in the lake dependent on the population growth due to the tourist nature of Eğirdir; (iii) the lack of water circulation in the lake due to summer stagnation. It was determined that Se, Cd, Cr, Mo and Pb values were higher at the control sites in autumn. It can be assumed that this is due to the fact that autumn circulation is observed with a decrease in air temperature. It was observed that the levels of Cr, Fe, Mn, Mo, Pb, Se and Zn were higher at the coastal sites in winter. The runoff of pesticides used to control pests in apple orchards around the lake may have led to an increase in heavy metal levels at the coastal sites. The high values of Cd, Cr, Cu, Fe, Mn, Mo and Zn at the coastal sites in spring may be due to the mixing of pollutants entering the lake with precipitation.

Changes in physicochemical parameters of water ensure the transition of heavy metals from sediment to water or from water to sediment (Şener & Şener 2015; Metin Dereli et al. 2017). Kaptan & Tekin-Özan (2014) found negative correlations between temperature and Cd, Cr, Cu, Fe, Mn, Mo and Se, between pH and Cd and Mn, between dissolved oxygen and Fe, Mn and Zn, between electrical conductivity and Cr, Mo, Cu and Ni in water of Lake Eğirdir. According to Table 4, when the temperature increases, Cr, Fe, Mn, Ni, Pb and Zn levels increase and Cd, Cu, Mo and Se levels decrease. This decrease in summer may be due to the use of Cu, Mo and Se by some organisms due to their increasing biological activities. In this study, when pH values increased, Cu, Fe, Mo, Ni and Zn levels decreased (Table 4). The solubility of metal compounds in water depends on pH and oxidation-reduction potential of water. In general, the solubility of heavy metals decreases with increasing pH (Weiner 2008). Cu toxicity is affected by pH. When pH is low, Cu is soluble in water and its toxicity increases (Kruger 2008). Negative correlations were found between dissolved oxygen and Cr, Fe, Mn, Ni, Pb and Zn (Table 4). The ferro form of iron turns into the ferric form in oxygenated environments (Tanyolaç 2011). Zinc acts similarly to iron and manganese in water (Tanyolaç 2011). It can be said that the content of Mn and Zn tends to decrease as dissolved oxygen increases, as does Fe. Negative correlations were determined between electrical conductivity and Cd, Mo and Se, and similarly for temperature. In general, metals have high toxicity in acidic and soft waters, and low toxicity in basic and hard waters (Uruç et al. 2008). Negative correlations were found between Mo and Cd, Pb, Se, Fe, Pb, Ni, Mn, between Pb and Se, Zn, between Cu and Fe, between Se and Zn. Kar et al. (2008) found a significant negative correlation between Fe and Cr, and a positive correlation between Ni and Mn, as well as between Ni and Zn in surface waters in India, and concluded that these relationships would help us understand the nature of these metals and their species speciation in the aquatic environment.

According to the Water Pollution Control Regulation (WPCR; Ministry of Environment and Urban Planning 2008), Cd, Mn and Zn values indicate that the lake's water can be classified as water quality class I in all seasons and class III based on Se values, and class II based on Cr, Cu and Ni values. Fe levels indicate that Lake Eğirdir can be classified as water quality class II in summer, winter and spring, and class I in autumn (WPCR; Ministry of Environment and Urban Planning 2008). Based on Pb concentrations, Lake Eğirdir's water can be classified as water quality class I in spring and class II in other seasons (WPCR; Ministry of Environment and Urban Planning 2008). Metal concentrations were compared with water quality standards for drinking water (TSE 2005; WHO 2017; EPA 2018; EU 2020). There is no drinking water standard value for Mo. According to these standards, Cu, Fe, Mn and Ni results were higher than the permissible levels for drinking water in all seasons (TSE 2005; EPA 2018; EU 2020), Pb in summer, autumn, winter (TSE 2005; WHO 2017) and spring (EU 2020), and Se in all seasons (TSE 2005). Bulut (2015) evaluated Hg, Pb, As, Ni, Cd, Cu, Cr, Mn and Zn levels in the water of Lake Eğirdir according to drinking water standards set by TSE-266, WHO, EPA and EU and declared that As levels exceeded the limit values in summer and autumn, while other metals did not exceed the limit values. According to another study carried out in Lake Eğirdir, Co, Cu, Mn, Ni and Zn levels were below WHO and TS 266 drinking water limits, while Al, Fe and Pb concentrations were above the permissible limits (Şener et al. 2013).

In all seasons, the WQI value was $50 \leq WQI < 100$. Thus, it was a good category. In a study carried out by Ustaoğlu & Aydın (2020), WQI values ranged from 14.26 (Yağlıdere Stream) to 21.57 (Aksu Stream), and they belong to the excellent water category. In the work on Karaçomak Dam (Türkiye), WQI values were between 12.27 and 56.78 (Imneisi & Aydın 2016). According to the HPI values, the water in Lake Eğirdir was in the low-level category in all seasons. Şener et al. (2023) reported that HPI values for Lake Beyşehir (Türkiye) ranged from 15.64 to 20.38 and declared that the lake water samples were suitable for use as drinking water. It was reported that HPI values for the Boğaçayı River (Türkiye) were between 7.81 and 43.97, which fell into the low pollution category (Cengiz et al. 2017). According to the HEI values, the lake's water can be classified in the low pollution category in all seasons. The HEI values for Lake Beyşehir ranged between 0.165 and 0.397 (Şener et al. 2023), which indicates that the lake's water can be classified in the low pollution class.

The concentrations of heavy metals and Se in the sediments are summarized in Table 9. The average concentrations of Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se and Zn in summer in the present study were respectively 13.5, 5.51, 2.00, 8.3, 3.07, 4.13, 3.74, 32.37, 1.69 and 1.43 times higher than their previous values reported by Kaptan & Tekin-Özan (2014) for the sediment of Lake Eğirdir; similar results were obtained for other seasons. These results indicate that metal levels in Lake Eğirdir have increased due to various reasons, such as domestic wastewater, agriculture and tourism. Şener et al. (2011) concluded that the high accumulation of metals in the sediments of Lake Eğirdir may be due to both geological origin and anthropogenic effects. The Fe content in the sediments was the highest, while Cd content was the lowest. Similar results were obtained for Lake Işıklı (Gülcü-Gür & Tekin-Özan 2017), Lake Karataş (Başyiğit & Tekin-Özan 2013), Lake Uluabat (Barlas et al. 2005) and Lake Kovada (Sancer & Tekin-Özan 2016). Usero et al. (2004) reported that Fe is found in high concentrations in lake, river and marine sediments, as it is one of the most abundant elements in the Earth's crust. Kerrison et al. (1988) stated that Cd accumulates slowly in sediments.

Fe, Pb, Se and Zn reached the highest levels in summer, while Cd and Mo in autumn, Cr, Cu, Mo and Ni in winter. The levels of Cr, Cu, Fe and Ni were the lowest in spring, Cd and Mo in summer, Zn in autumn, and Mn, Pb and Se in winter. Only Cd levels varied significantly (< 0.05) from season to season, while other metals did not vary significantly (> 0.05). Kankılıç et al. (2013) reported that the content of Fe, Mn, Cu, Hg, Pb and As reached the highest level in summer. Fe, Zn, Al, Cu, Mn and B reached high values in summer in the sediments of the Beyler Reservoir (Fındık & Turan 2012). Kumar et al. (2020a) reported that heavy metal levels in sediments were higher in summer and winter than in rainy seasons. Due to the evaporation in summer, the metal levels in sediment may have increased. With summer stagnation, metals precipitated from the water column into the sediment.

EF values (Table 10) were calculated to determine the metal pollution by comparing the metal levels in the sediment with the pre-industrial levels. Pb was at a very high enrichment level (EF = 20–40) in summer and spring, and at an extremely high enrichment level (EF > 40) in autumn and winter. Cr was at a minimum enrichment level (EF < 2) in summer and spring, and at a significant enrichment level (EF = 5–20) in autumn and winter. Cu, Mn and Ni were at a moderate enrichment level (EF = 2–5) in summer and spring, while at a significant enrichment level (EF = 5–20) in autumn and winter. Fe was at a minimum enrichment level (EF < 2) in spring, at a moderate enrichment level (EF = 2–5) in summer, and at a significant enrichment level (EF = 5–20) in autumn and winter. Şener et al. (2014) calculated EF values for the sediment of Lake Eğirdir and found that Pb, Ni, Zn and Fe were at a significant enrichment level, while Cu and Mn were at a moderate enrichment level. Transport events from ophiolitic rocks, such as Co, can cause Cu and Ni enrichment in a lake (Bamba 1974; Ramp 1978; Foley 1991).

The results of the Geoaccumulation Index (I_{geo}) indicate that the sediments of Lake Eğirdir are not contaminated with heavy metals, except for Cd and Pb, which were in the unpolluted–moderately polluted class ($0 < I_{geo} < 1$), and Se, which was in the moderately polluted class ($1 < I_{geo} < 2$) in all seasons. Binici & Polatsü (2022) reported that Pb in Lake Mogan (Türkiye) was at high levels, while Cu and Cd were at moderate levels based on the value of the Geoaccumulation Index (I_{geo}). In the study conducted on Lake Beyşehir, Tunca (2016) found that the sediment was moderately contaminated with Cr, Ni, Zn and Mn.

Cr, Cu, Fe, Mn, Mo, Ni and Zn were found in the low contamination category (CF < 1), Cd and Pb were in the moderately contaminated category (1 < CF < 3), and Se was at the considerably contaminated category (3 < CF < 6) in all seasons. In the study carried out by Binici & Polatsü (2022) in Lake Mogan, heavy metals were ranked as Cu > As > Cd > Pb > Hg > Cr > Zn > Ni, according to the values of the Contamination Factor (CF).

The results of the Pollution Load Index (PLI) for lake sediments suggest no pollution (PLI < 1) for all metals in all seasons. Binici & Polatsü (2022) reported that PLI values for Lake Mogan were > 1, and this result indicates heavy metal contamination of the sediment.

The calculated values of the index indicate that Cd, Pb and Se accumulated at high levels in Lake Eğirdir. Füge (2013) reported that some heavy metals, such as Cd and Pb, entered the soil and groundwater with fertilizers and pesticides. Se entered the water as a result of processing metal mines and agricultural activities (Hamilton 2004). Şener et al. (2014) found that the high Zn value was caused by clayey-silty sediments at the lake shore. The use of fertilizers and pesticides in agricultural activities around Lake Eğirdir can cause increased levels of Cd, Pb and Se.

In this study, sediment quality guidelines were used to determine the possible risk of heavy metal contamination in sediments (MacDonald et al. 2000). The results show that Cd and Pb were at the minimal effect threshold (MET), while Cr, Cu, Ni and Zn were at the lowest effect levels (LEL). These results show that heavy metals generally do not cause any potential threat to aquatic organisms, and most sediment-dwelling organisms are not adversely affected by these levels of metals.

5. Conclusions

Lake Eğirdir is the second largest lake in Türkiye and is very important for the region due to its high potential for fisheries and its use for irrigation, drinking water, tourism and being an important nesting and visiting area for birds. The concentrations of the selected heavy metals and Se in water and sediments of Lake Eğirdir were determined seasonally. The possibility of anthropogenic effects was assessed using selected ecological indices, such as EF, I_{geo}, CF and PLI, and multivariate statistical analysis techniques. In addition, water temperature, pH, electrical conductivity and dissolved oxygen levels were measured. The analyzed metals were ranked as follows: Cr < Cd < Mo < Pb < Se< Mn < Cu < Ni < Zn < Fe. In general, metal levels increase in summer and decrease in the wet season. According to the Water Pollution Control Regulation (WPCR) by the Ministry of Environment and Urban Planning (2008) and based on the physicochemical values, the water in Lake Eğirdir was classified as category I–II and, based on the levels of heavy metals, as water quality class II. Temperature, pH, electrical conductivity and dissolved oxygen values were below the limits for drinking water set by the European Union (EU 2020), the U.S. Environmental Protection Agency (EPA 2018), the World Health Organization (WHO 2017) and the Turkish Standardization Institute (TS 266 2005). Cu (EU 2020), Fe (TSE 2005; EPA 2018; EU 2020), Mn (TSE 2005; EU 2020), Ni (TSE 2005; EU 2020) and Se (TSE 2005) in the lake's water exceeded the permissible levels for drinking water in all seasons. According to the Water Pollution Control Regulation for the quality of inland surface waters and based on summer temperature values and Se levels in all seasons, Lake Eğirdir falls into the "contaminated water category". According to the HPI and HEI results, the water in Lake Eğirdir can be classified in the low pollution class. The water was in the good category with respect to WQI. Based on these results, the water of Lake Eğirdir can be used for industrial purposes after proper treatment, except for industries that require high quality water, such as the food and textile industries. The total levels of metal and Se concentrations in the sediment samples were in the following order: Fe > Mn > Pb > Zn > Ni > Cr > Cu > Se > Mo > Cd. Only Cd levels varied significantly (< 0.05) by season, while other metals did not vary significantly (> 0.05). The EF, I_{geo}, CF and PLI values for Lake Eğirdir showed that the lake is exposed to Pb, Se and Cd pollution. This pollution can be caused by anthropogenic sources such as agricultural activities, pesticides, tourism, municipal waste and fishing activities. In addition, the geogenic effect of the lake may cause the metal pollution.

The following suggestions can be made to reduce pollution and protect the lake: (1) the use of pesticides and fertilizers in agricultural land around the lake should be reduced, and organic farming should be implemented to the greatest extent possible; (2) the town of Eğirdir is a preferred destination for camping tourism, so it is necessary to protect the lake from being polluted by the waste of campers staying on the lake shore; (3) the discharge of domestic and industrial wastewater into the lake should be prevented; (4) navigation and fishing boats on the lake should use high-quality fuels; (5) protecting the lake is no enough. At the same time, similar measures should be taken for water resources feeding the lake.

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