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Environmental impact of potentially toxic elements accumulated in surface sediments of the Erikli Lagoon, Black Sea coast (Türkiye)

by

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Abstract

This study aims to (a) determine the concentration and distribution of elements in the surface sediments of the Erikli Lagoon, which are under natural and anthropogenic pressure, (b) determine possible effects on the environment using ecological indices, and (c) reveal possible sources. Multiple elements, total organic carbon and chlorophyll degradation products were analyzed in sediment samples. Enrichment factor (EF), contamination factor (CF), and geoaccumulation index (I_{geo}) were calculated to determine the sources of the elements. Modified hazard quotient (mHQ), ecological contamination index (ECI), contamination severity index (CSI) and potential ecological risk index (PERI) were calculated to determine ecological risks. It was found that Mn, Hg, As, Fe and Cd entering the lake are of anthropogenic origin. These elements pose a low to moderate ecological threat to the lake. Agricultural and domestic discharges and atmospheric deposition are the main sources of these elements. A moderate ecological risk with an average value of 194.89 was determined in the lagoon based on PERI and contamination levels of metals. The elements that pose this risk are Hg and Cd, due to their high toxicity. According to ECI and CSI, the ecological risk is low, with average values of 0.99 and 0.30, respectively.

Key words: metal contamination; risk assessment; sediment quality; ecotoxicological indices; Erikli Lagoon

1. Introduction

Coastal wetlands comprise mangroves, coastal lagoons, seagrass beds, microalgae and coral reefs that are temporarily or permanently submerged in fresh, saline or estuarine waters (Botello et al. 2018). Due to their tourism and ecological importance, these ecotones are receiving increasing attention worldwide. Although coastal environments are an important food source, significant changes are taking place in the biogeochemistry of coastal waters due to the fact that they are fragile ecosystems exposed to human activities such as agriculture, industry, dam construction, urbanization, fishing, aquaculture and harbor traffic (Maanan et al. 2015; Hu et al. 2018; Zonta et al. 2019)Cr, Cu, Pb, and Zn. Pollutants and wastewater generated by human activity around lagoons, which are mostly shallow bodies of water behind the shoreline, are often discharged into these areas without any treatment (Hu et al. 2018). In this regard, these biologically important ecosystems should be continuously monitored and evaluated, and the data obtained from these studies should provide the basis for local management and conservation strategies.

Metal pollution is an ongoing environmental problem that poses serious problems for both developing and developed countries (L. Zhang et al. 2007). Since metals do not degrade in nature, many of them cause toxic effects in organisms due to their ability to bioaccumulate in the food chain (Fernandes et al. 2008)Cu, Pb and Zn. Even at low concentrations, potentially toxic elements (PTEs) can cause serious damage to human health, including diseases of the nervous, skeletal, circulatory, endocrine, and immune systems, dermal lesions, kidney dysfunction and cancers (Pan et al. 2018). In the ecosystem, elements are generally adsorbed by particulate matter and eventually mixed with sediments (Chapman et al. 2003) some are essential, speciation affects bioavailability, and bioavailability is determined by both external environmental conditions and organism physiological/biological characteristics. Key information required for ERA of metals includes: emissions, pathways, and movements in the environment (Do metals accumulate in biota above background concentrations?, very few of which are water soluble (Hou et al. 2013). Therefore, more than 90% of elements are stored in the sediments (Liu et al. 2010). Pollutants stored in the sediment can be released back into the water column when oxidation-reduction conditions, dissolved oxygen, organic-inorganic carbon and pH concentration change (Çevik et al. 2009; Yi Wang et al. 2012; Hill et al. 2013; Y.-B. Wang et al. 2015;Yunqian Wang et al. 2015). Therefore, the sediments act as a secondary source of metal contamination, as metals can be desorbed due to changing biological and chemical conditions (Yunqian Wang et al. 2015; Monferran et al. 2016). Consequently, metals accumulated in the surface sediments always pose a potential risk to the ecosystem. Identification of these risks is important for a sustainable ecosystem and community health. Indices such as EF, CF, I_{geo}, mHQ, ECI, CSI, and PERI are frequently used tools for ecological risk assessment. Some indices (EF, CF, I geo) are useful for identifying possible sources of elements, while other indices are useful for identifying ecological risks. Multivariate statistical analysis allows interpretation of the source, transport and precipitation processes of the elements (Fural et al. 2021; Özkan et al. 2022; Varol et al. 2022; Aydın et al. 2023; Aykir et al. 2023).

The Erikli Lagoon is a shallow body of water that occupies part of İğneada Bay, which has rich geographical and biological features such as flood forests, lagoons, various types of coastlines, and important plant and animal biotopes. Despite these rich resources, both İğneada Bay and the Erikli Lagoon are under pressure from various environmental factors. There are two important natural processes that pose an ecological threat to the lagoon's waters and sediments. First, flood events occur in the region as a result of high humidity, saturation and precipitation characteristics in relation to the Black Sea climate prevailing in the region (Uludağ 2018). Flood waters transport materials into the lagoon. Second, the material resulting from landslides occurring in the upper basin of the streams supply sediment to the streams draining into the lagoon. Thus, the depth of the lagoon is rapidly decreasing (Uludağ 2018).

In addition to these natural processes, the Erikli Lagoon is under threat from serious anthropogenic pressure. Although there is a biological treatment facility currently serving the region, the lagoon has been used as a discharge area for wastewater from the surrounding settlements for many years. Sewage from many holiday camps (tent camps) in the floodplain is still discharged into the lagoon. The area near the lagoon where garbage is dumped using the 'wild dumping' method is also a serious source of pollution affecting the lagoon. Furthermore, the destruction of natural vegetation, especially the Erikli floodplain forests for the purpose of redeveloping İğneada Bay, is another important factor directly affecting the lagoon ecosystem in recent years (Uludağ 2018).

This study aims (a) to determine concentrations and distributions of PTEs in the surface sediments of the Erikli Lagoon, which are under natural and anthropogenic impact, (b) to determine possible environmental effects using ecological indices, and (c) to reveal possible sources using multivariate statistics.

2. Materials and methods

2.1. Study area

Lake Erikli is a lagoon lake located close to the Istranca Mountains in the Marmara Region, within the borders of the Demirköy district of the Kırklareli province. The lake is fed by the Efendi stream, which originates in the northwest, and by small streams that flow into the lake from a plateau in the north. The remarkably rich lithological features in the Erikli Lake basin include the variety of rocks encountered and their layering characteristics. Quaternary units in the basin are in the form of alluvium consisting of young fluvial sediments and beach sands on the shore. Tertiary units in the lake basin have the largest area of dispersion. They encompass the Trakya Formation (unconsolidated sand, gravel sand and mud stone) and the Mert Formation (thick layers of sandstone; Turoğlu 1997; Çağlayan and Yurtsever 1998). Mesozoic units are found northeast and north of the lake basin in the Istranca Mountains, consisting of volcanic sediments, schists and granites. The oldest rock group in the area are Paleozoic gneiss, quartzite and schist (Turoğlu 1997; Çağlayan and Yurtsever 1998; Uludağ 2018).

The geomorphological features of the Erikli Lake basin consist of high and low areas and slopes between them. The upper terrain, which is generally covered with populations of oak and beech trees, is intersected by the Efendi Stream, the Üvezli Stream, the Geyik Stream and their tributaries, which drain the higher land and feed Lake Erikli.

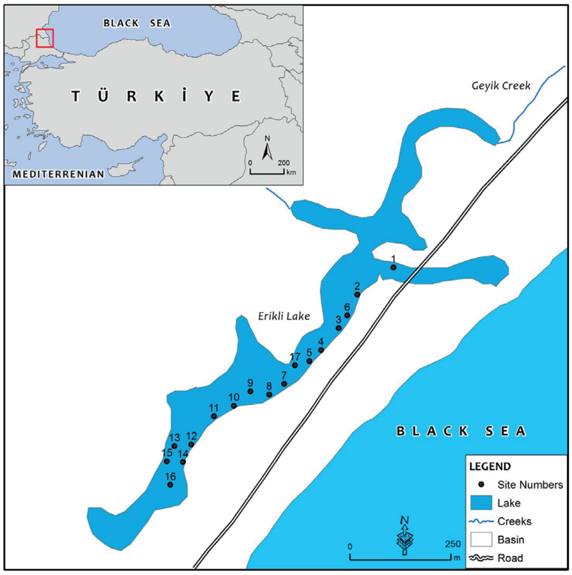

Figure 1

Location map of the study area.

In general, Lake Erikli and its surroundings exhibit features of the Black Sea climate. According to data from the İğneada Meteorological Station, annual precipitation is about 800 mm. However, data from the Demirköy Meteorological Station, representing the higher parts of the area, show that it receives more than 1000 mm of precipitation. Most of this precipitation falls in the autumn and winter months (Uludağ 2018). As a result of this precipitation, Lake Erikli is connected to the sea from autumn, and the connection is interrupted during the summer season, when precipitation is relatively low. According to the data of the İğneada Meteorological Station, the average of the coldest month is 3.7°C, whereas the average of the warmest month is 21.5°C in July (Uludağ 2018).

2.2. Analytical procedures

With the exception of the very shallow eastern part of the lake, samples of the surface sediment from 17 selected sites were collected with a Van Veen grab (Fig. 1). It is not possible to collect samples from the entire lake as some parts of the lagoon are covered with reeds. For this reason, sampling locations were randomly selected from the rest of the area. Samples were placed in plastic bags and transported to the laboratory. Wet sediment samples were used for chlorophyll degradation product (CDP) analysis. CDP was determined by spectrophotometry using the acetone extraction method (Lorenzen 1971). The samples were dried in an oven to use in all other analyses, and then ground in a mortar. Total organic carbon (TOC) was determined using the Walkley-Black method, which involves oxidation of organic matter with $K_2Cr_2O_7$ (Gaudette et al. 1974). Multiple element analyses were performed in the Bureau Veritas (Canada) laboratory using the ICP-MS method. Quality control and accuracy of the measurements were tested using a blank sample, duplicate reading and standard reference material (STD 11 from Bureau Veritas). Recovery rates for the elements in the standard reference material ranged from 93.79% to 101.34%.

2.3. Risk assessment methods

2.3.1. Enrichment factor (EF), contamination factor (CF) and geoaccumulation index (I_{geo})

The enrichment factor (EF), contamination factor (CF) and geoaccumulation (I_{geo}) index were calculated to determine whether the metals detected in the sediment reached their present concentrations as a result of natural accumulation or anthropogenic input.

These three indices show whether the origin of each metal is natural. The enrichment factor normalizes differences in grain size using lithophilic reference elements, such as Al, Fe and Ti, and was calculated according to the following formula (Çevik et al. 2009; Yilgor et al. 2012; Vrhovnik et al. 2013; Topaldemir et al. 2023):

$$EF = \frac{\left(\frac{C_i}{C_{ref}}\right)_{sample}}{\left(\frac{B_i}{B_{ref}}\right)_{background}} \tag{1}$$

where C_i is the concentration of the metal measured in the sediment sample, C_{ref} is the concentration of the reference element (Al) selected for normalization in the sediment sample, B^i is the regional background value of the metal, and B_{ref} is the background value of the reference element selected for normalization. Regional background values were obtained from Uludağ et al. (2018). EF results were evaluated according to Sutherland (2000): EF < 2 minimal or no enrichment; EF = 2–5 moderate enrichment; EF = 5–20 significant enrichment; EF = 20–40 very high enrichment; and EF > 40 extremely high enrichment.

CF is obtained by dividing the metal concentration in the sample by the background metal concentration (Hakanson 1980). The difference with EF is that it does not include grain size normalization. CF was evaluated according to the following scale: CF < 1 – low contamination; 1 ≤ CF <3 – moderate contamination; 3 ≤ CF <6 – high contamination; and CF > 6 – very high contamination.

I_{geo} was calculated based on the following formula (Muller 1969):

$$I_{geo} = \log_2 \frac{C_m}{(B_m \times 1.5)} \tag{2}$$

where C_m is the measured concentration of the metal and B_m is the background value of the metal. I_{geo} results were evaluated according to: $I_{geo} \leq 0$ – uncontaminated; $0 < I_{geo} < 1$ – uncontaminated to moderately contaminated; $1 < I_{geo} < 2$ – moderately contaminated; $2 < I_{geo} < 3$ – moderately to strongly contaminated; $3 < I_{geo} < 4$ – strongly contaminated; $4 < I_{geo} < 5$ – strongly to extremely contaminated; $I_{geo} \geq 5$ – extremely contaminated.

2.3.2. Modified degree of contamination (mCd) and pollution load index (PLI)

The integrated evaluation of the accumulation of metals in the sediment, the modified degree of contamination (mCd) proposed by Abrahim and Parker (2008), and the pollution load index (PLI) developed by Tomlinson et al. (1980) were calculated (n = number of PTEs) using the following equations:

$$mCd = \frac{\sum_{i=1}^{n} CF}{n} \tag{3}$$

$$PLI = \left(CF_1 \times CF_2 \times .....CF_n\right)^{\frac{1}{n}} \tag{4}$$

2.3.3. Modified hazard quotient (mHQ) and ecological contamination index (ECI)

The modified risk ratio (mHQ) was calculated to determine the risk caused by metal accumulation in the sediments of aquatic biota (Benson et al. 2018). The index is based on a comparison of metal concentrations in sediments with partially different threshold levels (reported by MacDonald et al. 2000) to determine adverse ecotoxicological effects and is formulated as follows:

$$mHQ = \left[C_i\left(\frac{1}{TEL} + \frac{1}{PEL} + \frac{1}{SEL}\right)\right]^{\frac{1}{2}} \tag{5}$$

where C_i is the measured metal concentration and TEL, PEL and SEL are the threshold effect level, probable effect level and severe effect level, respectively. The classification of mHQ is presented in Table 1. ECI, on the other hand, uses a source-specific factor derived from the principal component analysis/factor analysis to analyze the holistic ecological risks of metals with an empirical approach and is formulated as follows (Benson et al. 2018):

$$ECI = B_n \sum_{i=1}^{n} mHQ_i \tag{6}$$

where *Bn* is the reciprocal of the eigenvalue obtained from the analysis of the principal components only for metals. The ranking of the risks of PTEs to the ecosystem is evaluated according to Table 2.

Table 1

Classification of mHQ.

mHQ	Degree of risk
mHQ > 3.5	Extreme severity
3 < mHQ < 3.5	Very high severity
2.5 < mHQ < 3	High severity
2 < mHQ < 2.5	Considerable severity
1.5 < mHQ < 2	Moderate severity
1 < mHQ < 1.5	Low severity
0.5 < mHQ < 1	Very low severity
mHQ < 0.5	None to low severity

Table 2

Classification of ECI.

ECI	Degree of contamination
ECI > 7	Extremely contaminated
6 < ECI < 7	Highly contaminated
5 < ECI < 6	Considerably to highly contaminated
4 < ECI < 5	Moderately to considerably contaminated
3 < ECI < 4	Slightly to moderately contaminated
2 < ECI < 3	Uncontaminated to slightly contaminated
ECI < 2	Uncontaminated

2.3.4. Contamination severity index (CSI)

The CSI index, recently proposed by Pejman et al. (2015), is used to assess the severity of metal contamination in the sediments. The index is based on effects range low (ERL) and effects range median (ERM) reported by Long et al. (1995) to explain the limits of toxicity to biota, as well as the weight of metals obtained as a result of principal component analysis (PCA)/factor analysis (FA). CSI is formulated as follows:

$$CSI = \sum_{i=1}^{n} W_i \left[\left(\frac{C_i}{ERL_i} \right)^{1/2} + \left(\frac{C_i}{ERM_i} \right)^{2} \right] \tag{7}$$

$$W_i = \frac{(loading\ value_i \ \times\ eigen\ value)}{(\sum_i^n loading\ value_i \ \times\ eigen\ value)} \tag{8}$$

where W_i is the weight of metals, C_i is the concentration of the metal in the sediment, and n is the number of metals. In the W_i calculation, the eigenvalue value of the factor was found to be anthropogenic in PCA for metals only, and the loading values of the metals in that factor were used. CSI values were evaluated according to the scale presented in Table 3.

Table 3

Classification of CSI.

CSI	Degree of contamination
CSI ≥ 5	Ultra high severity of contamination
4 ≤ CSI < 5	Very high severity of contamination
3 ≤ CSI < 4	High severity of contamination
2.5 ≤ CSI < 3	Moderate to high severity of contamination
2 ≤ CSI < 2.5	Moderate severity of contamination
1.5 ≤ CSI < 2	Low to moderate severity of contamination
1 ≤ CSI < 1.5	Low severity of contamination
0.5 ≤ CSI < 1	Very low severity of contamination
CSI < 0.5	Uncontaminated

2.3.5. Potential ecological risk index (PERI)

The potential ecological risk index (PERI) proposed by Hakanson (1980) was calculated to determine the possible effects of metals both individually and in an integrated manner. The modified risk index (mRI) to determine the individual ecological risk of metals and PERI were used to determine the integrated risk, calculated as follows (Brady et al. 2015; Hakanson 1980; H. Zhang et al. 2017):

$$mRI = Ef_i \times Tr_i \tag{9}$$

$$PERI = \sum_{i=1}^{n} mRI \tag{10}$$

where Ef_i is the enrichment factor and Tr_i is the toxic liability coefficient. Tr_i values for the metals are as follows: Hg = 40, Cd = 30, As = 10, Cu = Pb = Ni = 5, Cr = 2, and Zn = 1 (Hakanson 1980). The calculated mRI and PERI values were evaluated according to the scale in Table 4.

Spearman's correlation test and factor analysis were used to determine possible sources of PTEs.

3. Results and discussion

3.1. Sediment characteristics and distribution of metals

Descriptive statistics of the variables are presented in Table 5 and surface distribution maps of the elements are shown in Figure 2. The average values of the metals, in descending order, are as follows: Fe (35176.5) > Al (20782.4) > Mn (452.2) > Zn (70.45) > Cu (36.05) > Cr (27.31) > Ni (24.05) > Pb (22.30) > As (6.17) > Cd (0.31) > Hg (0.10). When evaluated in

Table 4

Classification of mRI and PERI.

Individual ecological risk index (mRI)	Ecological risk level of single factor pollution	Integrated ecological risk index (PERI)	General level of potential ecological risk
$E^i_f < 40$	Low	PER < 150	Low
$40 \le E^i_f < 80$	Moderate	150 ≤ PER < 300	Moderate
$80 \le E^i_f < 160$	Considerable	300 ≤ PER < 600	Considerable
$160 \le E^i_f < 320$	High	600 ≤ PER	Very high
$320 \le E^i_f$	Very high		

terms of sampling sites, all metals except As reached a minimum value at S14. Fe and Al are two elements abundant in the Earth's crust, followed by Mn. Fe reached its highest value at S1, Al at S9, and Mn at S11. The average value of these three elements is above the regional background value obtained from the core samples. Zn reached its maximum value at S1, closely followed by S9. Values at other sites do not show great fluctuations, except for S13 and S14. The average value of Zn in surface sediments is also above the regional background value. Cu reaches its maximum value at S9, followed by S5, S4, S3 and S1, respectively. The average Cu value on the surface is below the background value. The Cr concentration was quite high at S1 compared to other sites, followed by S9 and S5. The average Cr value is below the background value. The highest concentration of Ni was found at S5, followed by S9, S9, S3, S4 and S11, respectively. There are no large differences between these sites.

The average Ni concentration in surface sediments is slightly above the regional background and reached its highest value at S9, followed by S1, S3–S5, and S10–S11 sites, with similar values. The average Pb content is just above the background value. As reaches its maximum concentration at S8, followed by S11 and S10, with a minimum value at S1. It is also worth noting

Table 5

Descriptive statistics.

	Unit	Average	Standard error	Minimum	Maximum	Background value
Cu	µg g^{-1}	36.05	2.62	6.71	49.49	44.53
Pb		22.30	1.64	4.18	32.39	21.4
Zn		70.45	4.95	18.6	103.0	60.7
Ni		24.05	1.46	7.0	29.5	23
Mn		454.24	18.48	265.0	575.0	125
Fe		35176.5	1608.31	18200	42900	18400
As		6.17	0.26	4.2	8.4	3.4
Cd		0.31	0.03	0.03	0.46	0.15
Cr		27.31	1.65	12.8	45.3	31.4
Al		20782.4	1319.96	5900	27700	20400
Hg		0.102	0.01	0.016	0.169	0.041
CDP		171.1	22.20	8.19	372.45	-
P (%)	%	0.042	0.003	0.022	0.066	-
S		2.79	0.22	0.24	3.98	-
OC		8.96	0.52	3.66	11.19	-

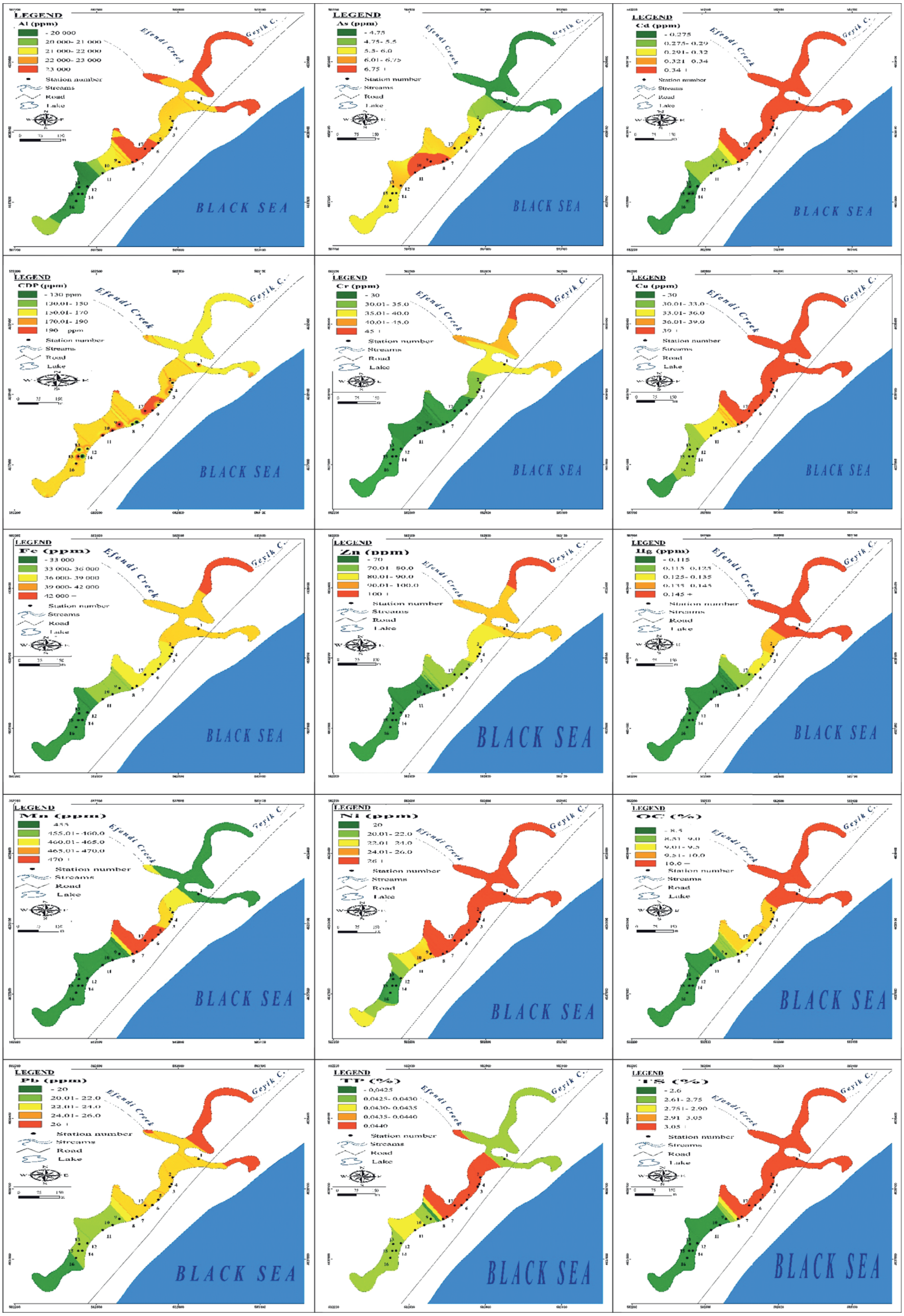

Figure 2

Spatial distribution maps of variables.

that the distribution of As differs from other elements, which is related to different sources and transport processes. Elements can have different sources such as terrestrial, wastewater, atmospheric deposition and transport routes such as ligands, colloidal particles, and particulate matter (Berg and Steinnes 2005; Sigg and Behra 2005). The mean content of As is higher than the background value. Cd, one of the elements known to be highly toxic to the ecosystem, reached the highest values at S2, followed by site S5. Cd content significantly varied between the sites. Values at S13 and S14 were extremely low. The average content of Cd on the surface is about twice the background value.

Hg, another important element in terms of damage to the ecosystem, shows significant differences in distribution between the sampling sites and reached its maximum level at S2. The first three sites also represent the highest values. Distinctly different minimum values were determined at S13 and S14. The similarity in the distribution between Hg and Cd is remarkable. This similarity may be due to their shared transport processes. Hg and Cd correlate very strongly with TS (0.95 and 0.87, respectively, $p < 0.05$). Therefore, it is highly likely that these two elements were carried by insoluble sulfides. As explained in the following sections, since these two elements pose a high ecological risk, their presence in the same area in large quantities increases their effects on the ecosystem.

TOC, CDP, TS and TP are important variables that affect the transportation and precipitation processes of metals. Therefore, their concentrations and distribution were also evaluated in the study. The TOC concentration has generally high values. The highest value was determined at sites S1 and S2, followed by S10 and S13. The minimum TOC value was determined at S14. In terms of low values, S13 and S14 clearly stand out from other sites. CDP values representing primary production reached the highest level at S9, followed by S7. These two values are quite high compared to other sites. S9 and S7 are followed by S10, S15 and S11. Values at other sites varied significantly. CDP shows the largest decrease at S14, but TS concentration showed a maximum value at S2 and a minimum value at S14. TP concentration also reached quite high values at S9 (maximum) and S17 compared to other sites. The smallest values were determined at S14 (minimum) and S13. In general, the values at other sites are more or less similar.

Values of metal concentrations determined for Lake Erikli compared with other lakes in Turkey and different regions of the world are presented in Table 6. These comparisons are intended to provide a global understanding of the relative status of problematic and/or uncontaminated lakes in various countries.

Table 6

Comparison of elemental concentrations in Erikli Lagoon with values obtained from lakes in Turkey and elsewhere in the world.

Lake	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Al	Hg	References
Lake Sera, Turkey	26.27	13.41	45.58	9.69	867.66	25704.1	3.80	0.22	14.39	27958	0.03	Ustaoğlu, Islam et al. 2022
Eğirdir, Turkey	14.85	8.62	38.75	43.84	484.36	15200	16.83	-	-	-	-	Şener et al. 2014
Salda, Turkey	3.03	6.57	16.06	442.61	205.18	12690.75	1.24	0.07	77.72	-	-	Çaldirak et al. 2017
Havasu, USA	3.28–45.6	2.88–18.6	11.7–52.5	3.42–22.4	78.1–646	3360–12600	2.38–9.20	BDL–0.24	2.79–26.1	1940–14800	-	Wilson 2018
Boyukshor, Azerbaijan	14.7	28.5	86.8	-	355	-	-	1.7	25.1	-	0.0085	Khalilova and Mammadov 2016
Geneva, Switzerland	21–1166	63–3977	175–8586	45–226	-	20374–61856	-	0.32–23.2	18–265	-	0.040–11.4	Gascón Díez et al. 2017
Bourget, France	3.86	4.47	42.89	8.21	-	-	-	0.09	37.6	-	-	Lécrivain et al. 2018
Aygır, Turkey	19.34	12.51	38.84	24.38	386	13740	4.18	0.25	19.18	13960	0.04	Kükrer 2018
Küçükçekmece, Turkey	67.68	30.18	183.91	92.76	436.98	26800	9.16	0.45	74.62	26500	0.09	Kükrer et al. 2019
Erikli	36.05	22.30	70.45	24.05	452.24	35176.5	6.17	0.31	27.31	20782.4	0.10	This study

Accordingly, while the average Cu value in the sediments of Lake Erikli is higher than in lakes Eğirdir, Salda, Boyukshor, Bourget and Aygır, it is lower than in Lake Küçükçekmece and is within the minimum–maximum range of Geneva and Havasu lakes. It was determined that Pb and Zn concentrations were higher than in lakes Eğirdir, Salda, Havasu, Bourget and Aygır but lower than in lakes Boyukshor, Geneva and Küçükçekmece. While the average Ni value calculated for Lake Erikli is lower than for lakes Eğirdir, Salda, Geneva, Aygır and Küçükçekmece, it is higher than Ni values for lakes Havasu and Bourget. While Mn concentration is higher than that determined for lakes Salda, Boyukshor, Aygır and Küçükçekmece and lower than in Lake Eğirdir, it is in the minimum–maximum range of Lake Havasu. As for Fe concentration, the average value for Lake Erikli is in the minimum–maximum range of Lake Geneva, while it is higher than in the other lakes surveyed. While As values are lower than those of lakes Eğirdir and Küçükçekmece and higher than those of lakes Salda and Aygır, they are within the minimum–maximum values of Lake Havasu. It was determined that Cd concentration was higher than in lakes Salda, Havasu, Bourget and Aygır, but lower than in lakes Boyukshor, Geneva and Küçükçekmece. As for Cr values, the average content in Lake Erikli is lower than in lakes Salda, Bourget and Küçükçekmece, but higher than in lakes Havasu, Boyukshor and Aygır, and within the minimum–maximum range of Lake Geneva. The Al concentration is higher than the values measured in lakes Havasu and Aygır and lower than the average value for Lake Küçükçekmece. As for Hg, values were above the average values for lakes Boyukshor, Aygır and Küçükçekmece. To conclude, we found that the elemental values of Lake Erikli were higher than those of Lake Sera for all elements except Mn and Al.

3.2. Contamination level assessment

Various indices are used to evaluate the levels of contamination with potentially toxic elements in aquatic systems with the objective of assessing the advantages and disadvantages of the indices in a holistic approach to provide a broad perspective on contamination (Pejman et al. 2015; Ustaoğlu 2020; Ustaoğlu and Islam 2020)heavy metals contamination in surface sediments of northwest Persian Gulf was investigated and a new index was formulated for assessing severity of heavy metal pollution in aquatic environments. The surface sediment samples were collected from 45 stations. The concentrations of 8 metals (Fe, Cu, Zn, Cr, Ni, Pb, Cd and V. One of the most frequently used indices related to metal accumulation is the enrichment factor (EF). According to the data obtained from this index, the average enrichment values of the metals in descending order are as follows: Mn> Hg> As> Fe> Cd> Zn> Ni> Pb> Cr> Cu. In terms to average values, Mn, Hg and As show moderate enrichment, while enrichment in other elements is minimal. A box and whisker graph based on the EF values calculated for the metals is presented in Figure 3, showing minimal enrichment of Cu, Pb, Zn, Ni and Cr at all sites. Mn showed significant enrichment at S14 (7.33) and moderate enrichment at S7 (2.69). Hg showed moderate enrichment, except at sites S6, S7, S13, S14 and S17, where enrichment was minimal. It was determined that Fe increased to a moderate level of enrichment at some sites (S1, S2, S11, S13–15), while it showed minimal accumulation at other sampling sites. Although Cd showed minimal enrichment on average, it reached a medium level at sites S1–S5, S10–S12 and S17. Moderate enrichment was determined at sites S8, S11 and S13 and significant enrichment only at site S15.

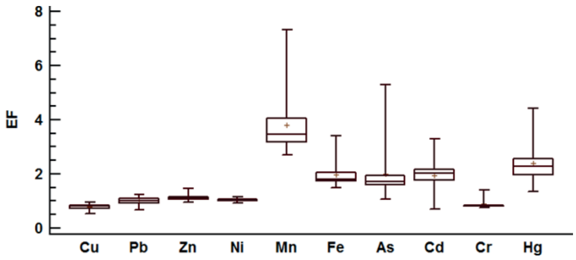

Figure 3

Box and whisker plot of EF.

According to the calculated average values of the contamination factor, Cu and Cr show low contamination, Pb, Zn, Ni, Fe, As, Cd, Al and Hg show moderate contamination, and Mn shows a significant degree of contamination. Pb, Zn, Ni and Al are among the elements showing a medium level of contamination, very close to the lower limit (Fig. 4). The order of the metals according to the average contamination values is as follows: Mn> Hg> Cd> Fe> As> Zn> Ni> Pb> Al> Cr> Cu.

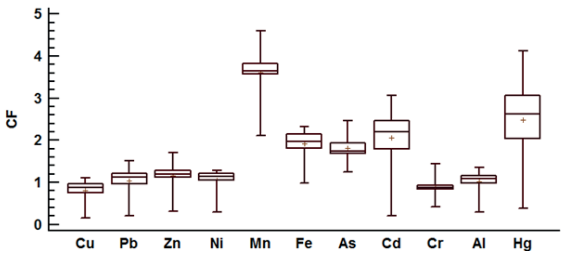

Figure 4

Box and whisker plot of CF.

The average values calculated from the geoaccumulation index indicate moderate contamination for Mn, an 'uncontaminated–moderately contaminated' level for Fe, As, Cd, and Hg, and an 'uncontaminated' level for Cu, Pb, Zn, Ni Cr and Al (Fig. 5). The geoaccumulation indices of the metals in descending order are as follows: Mn> Hg> Fe> Cd> As> Zn> Ni> Al> Pb> Cr> Cu.

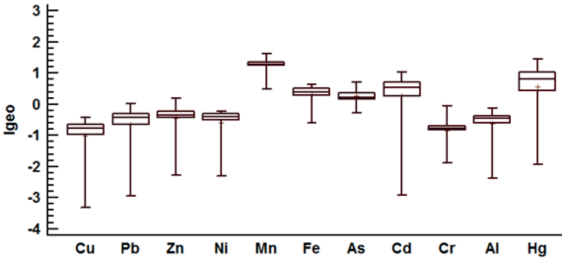

Figure 5

Box and whisker plot of I_{geo}.

The element with the highest contamination in the calculated indices is Mn, which occurs naturally in sediments and soil due to weathering of bedrock (Boudissa et al. 2006). In addition to natural processes, human activities also play an important role in Mn accumulation. The use of biosolids and similar organic materials in agricultural areas, mining and metal smelting activities is the main source of anthropogenic Mn enrichment (Li et al. 2014). Iron, another element at a high contamination level, is found in various fertilizers and sewage (Shuman 1998; Ustaoğlu et al. 2022). Artificial fertilizers and pesticides also contain high concentrations of Cd, As, Pb, Ni and Cu (Sönmez et al. 2014). Although agricultural activity is not very intensive in the Erikli Lake basin, fruit growing, sapling cultivation and non-commercial agricultural activities are carried out in the area, and fertilizers are used. Mn and phosphorus are two important elements for plant growth, and the fact that these two elements are included in the same factor of the factor analysis indicates an agricultural origin.

The mCd index used for the integrated assessment of contamination in the sediment indicates values ranging from 0.63 to 1.98. These results show that the level of contamination ranges from none or very low to low. The average mCd value was 1.62, indicating that the average contamination in the lake is low. It was determined that S13 and S14 showed markedly low contamination, whereas high contamination was found at S1–S5, S9 and S11.

The values of the PLI index, which assesses integrated accumulation, ranged from 7.36×10^{-6} to 57.43, with an average value of 15.14. Sites with the highest accumulation were S1–S5, S9 and S11. These data are consistent with the mCd data.

3.2.2. Overall assessment of the contamination level

Although the three indices used for contamination assessment employ basically the same logic, there are minor nuances between them. EF normalizes variations in grain size, while Igeo takes into account the variation in background values. CF does not account for any variation. Although there are differences in the rankings of the metals in these three indices due to variations in calculations, the results are similar. In general, it can be said that Mn, Hg, As, and Cd deposited in sediments have anthropogenic sources. The low number of elements with anthropogenic accumulation and the low contamination factors of other elements result in low values of integrated indices such as PLI and mCd.

3.3. Assessment of ecological and ecotoxicological risks

Various indices have been developed to assess the potential damage that toxic metals can cause to the ecosystem. While some of these indices (e.g. PERI) are based on the level of contamination, other indices developed in recent years (mHQ, ECI, CSI, etc.) have been designed based on values obtained from ecotoxicological laboratory studies.

In our study area, mRI calculations carried out to determine individual ecological risks of the metals show a descending order of Hg > Cd > As > Ni > Pb > Cu > Mn > Cr > Zn. According to average mRI values, Hg poses a considerable, Cd a moderate and other elements a low potential risk. Among the 17 sites, Hg reached the highest risk value at S2 (high) and the lowest risk value at S14 (moderate). Similarly, Cd had the highest value at S2 (considerable) and the lowest risk value at S14 (low; Fig. 6). The PERI data calculated to assess the potential integrated risks of metals ranged from 139.74 to 317.84, with an average value of

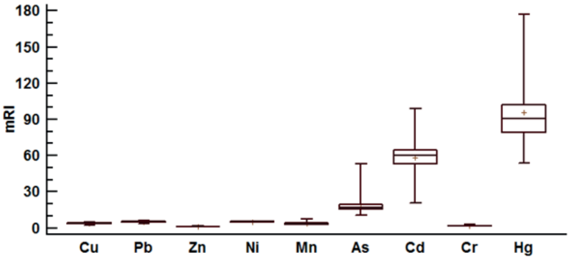

Figure 6

Box and whisker plot of mRI.

194.89. According to these results, the total ecological risk in the lake ranges from low to considerable (Fig. 7).

The mHQ index, obtained using threshold values derived from ecotoxicological studies of TEL, PEL and SEL, was calculated separately for each metal. The average mHQ values of the metals are in the following order: Ni> As> Cu> Cr> Pb> Zn> Hg> Cd. Accordingly, a low severe risk was detected for Ni, As, Cu and Cr, and a very low severe risk was detected for other elements. The mHQ values were very low to moderate for Ni. Values for As were distributed throughout the lake in the low contamination range. The mHQ values for Cu, Pb, Zn, Cr and Hg indicate very low to low contamination at the 17 sites. For Cd, very low to severe contamination was detected at all the sites (Fig. 8). According to the results of the ECI obtained by adding up the values derived for metals from mHQ and multiplying them by the eigenvalue obtained from the factor analysis, Lake Erikli is in the 'uncontaminated' class (0.56–1.12). Ecological contamination reaches the highest values at sites S9, S1, S5, S3, S4 and S11, whereas the risk of ecological contamination at S13 and S14 was determined to be at the lowest levels (Fig. 9). These data are consistent with the distribution of data from PLI and mCd.

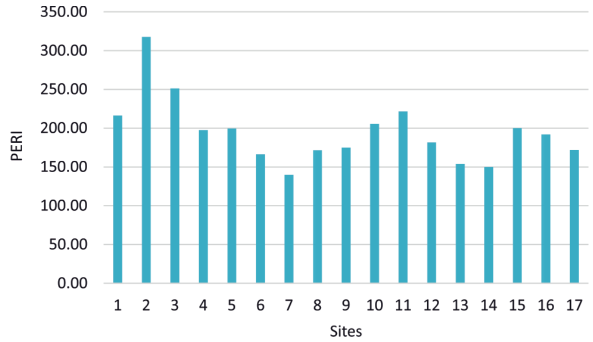

Figure 7

Distribution of PERI values.

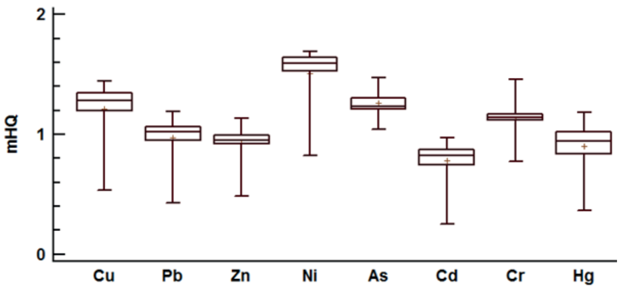

Figure 8

Box and whisker plot of mHQ.

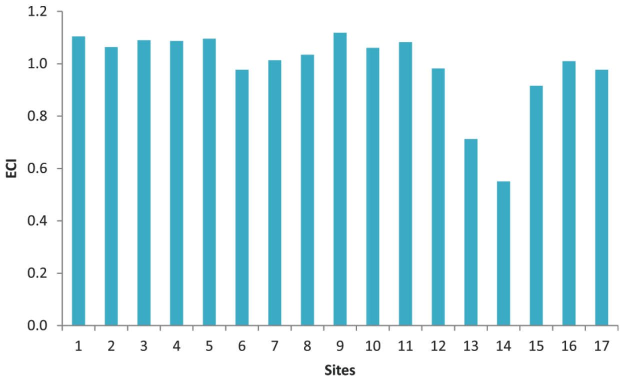

Figure 9

Distribution of ECI values.

CSI is another index based on ecotoxicological thresholds and is calculated by considering the weight of metals derived from factor analysis. The index provides an integrated assessment of potentially toxic elements that accumulate in the sediments. CSI values ranged between 0.15 and 0.38, with an average value of 0.30. Since all values are < 0.5, the level of contamination in the lake was determined to be 'uncontaminated'.

3.3.1. Overall assessment of ecological and ecotoxicological risk levels

The mRI and PERI indices are calculated according to EF values. mHQ, ECI and CSI are based on threshold values obtained from toxicity studies performed in the laboratory on certain benthic species. These differences in calculation sometimes cause inconsistencies between the indices. However, using all indices and conducting comprehensive assessments provides the opportunity to obtain a more holistic evaluation. Due to high Hg and Cd enrichment, mRI values were higher than for other elements. As an overall assessment for all indices, although there are no irreversible problems in the region, Hg and Cd enrichments should be carefully examined and monitored.

3.4. Determination of possible sources and transportation processes of PTEs

Spearman's rank correlation test and cluster and factor analysis were applied to the dataset to determine possible sources and migration processes of the PTEs. The correlation matrix is given in Table 7. Organic material is one of the main carriers of metals due to its high capacity to bind to metals (Bai et al. 2011; G. Zhang et al. 2016)Cd, Cr, Pb, Ni, Cu, and Zn in order to study spatial distribution characteristics based

Table 7

Descriptive statistics.

	CDP	OC	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Al	Hg	TP	TS
CDP															
OC	0.43														
Cu	0.31	**0.57**													
Pb	0.31	**0.73**	**0.94**												
Zn	0.38	**0.75**	**0.82**	**0.92**											
Ni	0.30	0.47	**0.95**	**0.90**	**0.79**										
Mn	**0.82**	**0.53**	0.42	0.41	0.38	0.37									
Fe	**0.50**	**0.80**	**0.75**	**0.86**	**0.88**	**0.74**	**0.53**								
As	-0.17	0.16	0.37	0.31	0.10	0.40	0.19	0.08							
Cd	0.28	**0.81**	**0.75**	**0.82**	**0.87**	**0.72**	0.39	**0.84**	0.29						
Cr	0.34	0.42	**0.85**	**0.86**	**0.79**	**0.88**	0.34	**0.67**	0.33	**0.56**					
Al	0.27	0.41	**0.84**	**0.84**	**0.80**	**0.90**	0.33	**0.62**	0.40	**0.62**	**0.95**				
Hg	0.40	**0.88**	**0.73**	**0.81**	**0.80**	**0.66**	**0.56**	**0.89**	0.13	**0.85**	**0.50**	0.48			
TP	**0.87**	0.41	0.40	0.34	0.32	0.31	**0.77**	0.35	-0.01	0.15	0.42	0.30	0.35		
TS	0.39	**0.81**	**0.66**	**0.72**	**0.73**	**0.63**	**0.57**	**0.85**	0.21	**0.87**	0.42	0.42	**0.95**	0.25	

on Kriging method and assess their ecological risks posed by these heavy metals. Results showed that the mean concentrations of these heavy metals were lower than potential effect levels. Patches of higher heavy metal concentrations occurred in the inflow area of the Cheng River and northeast area nearby the road and railway. The higher concentrations of As and Cr also appeared in the east area (lake outlet. There is a strong correlation between TOC and Pb, Zn, Fe, Cd and Hg and a relatively weak correlation between Cu and Mn, indicating that Pb, Zn, Fe, Cd, Hg, Cu and Mn were attached to organic material and therefore transferred to the sediment.

There is a strong relationship between CDP and Mn and a relatively weak relationship between CDP and Fe. This indicates that plant biomass plays a role in the transport of these two elements. Mn and Fe are two important micronutrients for the aquatic ecosystem (Sanders et al. 1998). For this reason, they are used in plant metabolism. When the concentration of metals increases in their environment, algae accumulate metals in their tissues due to bioaccumulation (Muslu and Gökçay 2020). In addition to the essential elements necessary for their own metabolism, plants can also accumulate elements that have no biological function (Memon et al. 2001).

In addition, the strong relationship between CDP and TP shows that phosphorus inputs are associated with increased plant biomass. Cu, Pb, Zn, Ni, Mn, Fe, Cd and Hg show significant correlations with TS, and these elements have strong correlations with each other. The high correlation between TS and some metals may indicate the formation of insoluble sulfides (Bai et al. 2016; G. Zhang et al. 2016). Cu, Zn, Ni, Pb, Fe, Cd, Cr and Al also appear to be interrelated. This group, which contains lithophilic elements such as Al, is likely to be of lithogenic origin due to weathering. Hg has correlations with all other elements except As and Al. The fact that Hg does not appear to be associated with Al, despite its high correlation with Fe, may indicate a mixed source. Hg appears to come from both natural and anthropogenic sources.

Atmospheric deposition is considered the likely source of this element. Pacyna and Pacyna (2001) suggest that 66% of Hg in the atmosphere comes from fossil fuel use. The fact that As does not show any significant correlation with any other variable indicates that this element has a different source and/or transport mechanisms than other elements. Although it is believed that the contribution of metals in household washing products to total wastewater is low, this rate can increase to 13% for As (Jenkins and Russell 1994). For As, which does not correlate with any other metal, the source may be wastewater from settlements and camp sites around the lagoon. The relationship between Mn and CDP and OC and TP suggests that the enrichment of this element may be of agricultural origin. The fact that Mn is the element with the highest enrichment and is associated only with Fe and Hg supports the idea that it comes from different sources.

Another method to determine the source is factor analysis. Three factors with eigenvalues > 1 were identified and these factors explain 91.87% of the total variance. While the first factor accounts for 74.96% of the total variance, it mainly consists of TOC, Cu, Pb, Zn, Ni, Mn, Fe, As, Cd, Cr, Al, Hg and TS. This factor mostly represents mixed sources. Although there are moderate levels of their enrichment according to EF values, the weighted source is considered to be terrestrial. The second factor accounts for 9.17% of the variance and consists of CDP, TP and Mn. The fact that Mn has nearly close loads to CDP and TP indicates that this element has two different sources. While the first source relates to terrestrial transport, the second source is considered agricultural. Mn is a component of fertilizers (Shuman 1998), and the presence of TP and CDP in this factor supports the view that it is of agricultural origin. Phosphorus is also known to be a limiting nutrient in freshwater ecosystems and is associated with the trophic state (Doolittle et al. 2018). The third factor consists of As, accounting for 7.74% of the total variance. This shows that As has different sources and movement processes, thus supporting the correlation analysis (Table 8).

Another analytic tool applied to the dataset was cluster analysis (Fig. 10). The results from this analysis are consistent with those obtained from correlation and factor analyses. As is not in the same set as any of the other variables. Similarly, Mn also appears to have different transport processes and sources. The high similarity between CDP and TP moderates the relationship between the plant biome and phosphorus. The close relationship of Hg with TOC shows that organic complexes play an important role in the transfer of this element to sediments. The group consisting of Cu, Pb, Ni, Al, Zn and Fe refers to elements of terrestrial origin. The proximity between Cd and TS indicates the compounds of this element with S.

Table 8

Factor loading matrix after varimax rotation for Erikli Lagoon.

	Factor 1	Factor 2	Factor 3
CDP	0.23	**0.95**	–0.08
OC	**0.89**	0.28	0.10
Cu	**0.87**	0.39	0.21
Pb	**0.89**	0.38	0.16
Zn	**0.88**	0.41	–0.12
Ni	**0.87**	0.34	0.25
Mn	**0.64**	**0.63**	0.33
Fe	**0.92**	0.35	0.05
As	0.10	0.00	**0.98**
Cd	**0.94**	0.16	0.13
Cr	**0.79**	0.31	–0.20
Al	**0.82**	0.39	0.20
Hg	**0.92**	0.13	–0.01
TP	0.35	**0.92**	0.06
TS	**0.90**	0.21	0.20

4. Conclusions

The Erikli Lagoon is an ecosystem with rare geographical and biological features. However, the basin of this ecosystem is under natural and

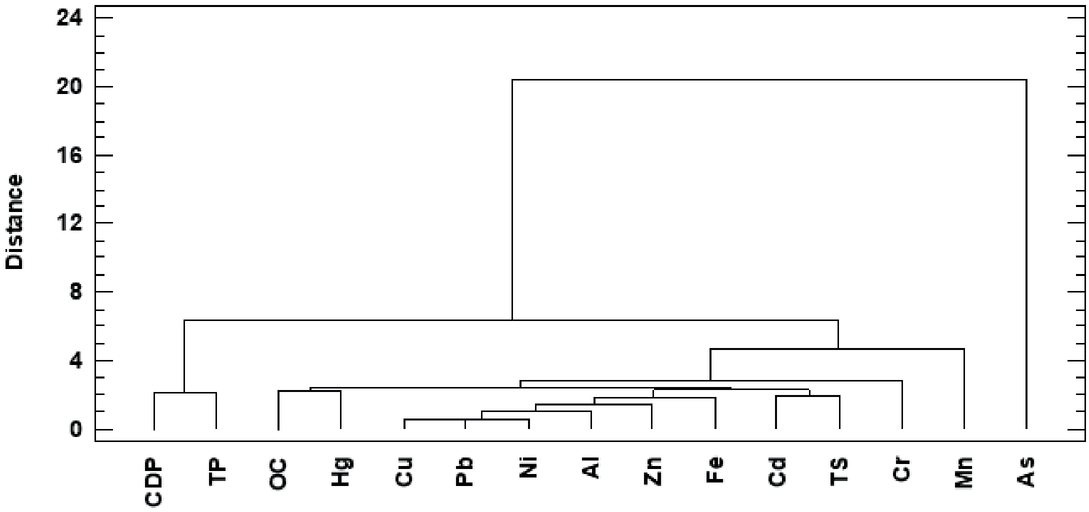

Figure 10

Dendrogram of cluster analysi.

anthropogenic pressure from floods, landslides, sewage discharge, and proximity to a landfill. In this study, a comprehensive risk and source assessment of the surface sediments accumulated in the bottom of the lagoon was carried out using different ecological indices. The accumulation of Mn, Hg, As, Fe and Cd detected in the sediments was determined to be of anthropogenic origin. Among these human-induced accumulations, only Hg and Cd exceeded the levels that would pose an ecological risk. These elements come from various sources, such as domestic and agricultural discharges and atmospheric deposition. According to the integrated PERI, which is based on the contamination levels of metals, a moderate ecological risk was determined in the lagoon. The elements that pose this risk are Hg and Cd, which results from their high toxicity. According to mHQ, ECI and CSI, derived from ecotoxicological laboratory studies, the ecological risk is low. The difference in risk levels between PERI and other indices is due to the different calculation formula of each index. Calculation of PERI is based on the EF value, while calculations of other indices are based on threshold values derived laboratory experiments. Thus, even if an element does not show anthropogenic enrichment, it can be dangerous if it exceeds the threshold value. When used together, these indices reduce the possibility of errors in assessment and provide a comprehensive understanding. Although risk factors such as holiday camps around the lagoon and agriculture and landfills in the basin lead to metal enrichment in the lake, it is understood that the risk at current levels is not irreversible. However, the lagoon's ecosystem will gain a healthier structure by controlling the discharges and implementing a sustainable environmental policy.

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Declarations

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Conflicts of interest

The authors declare no conflict of interest.

Availability of data and material

Not applicable

Code availability

Not applicable

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