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RESEARCH ARTICLE

Assessment of Potentially Toxic Element Pollution in Tributaries of Mogan Lake, Türkiye

Serap Pulatsü[1]*, Dijar Latifi[2]

[1]Ankara University, Faculty of Agriculture Department of Fisheries and Aquaculture, 06100, Ankara, Türkiye https://orcid.org/0000-0001-5277-417X
[2]Ankara University, Graduate School of Natural and Applied Sciences, 06100, Ankara, Türkiye https://orcid.org/0009-0008-7301-5912

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Abstract: In this study, four tributaries (Başpınar, Gölcük, Sukesen and Yavrucak Creeks) of Mogan lake under anthropogenic pressure and declared as a Special Environmental Protection Area were investigated with the following goals: a) Determination of the variations in potentially toxic element concentrations (Cr, Ni, Cu, Zn, As, Cd, Hg, Pb) in the creek waters between different months (December 2002, February 2023, April 2023), b) Calculation of potentially toxic elements indexes (Heavy Metal Pollution Index-HPI and Heavy Metal Evaluation Index-HEI) in terms of irrigation water quality, based on international and national values, c) Determination of the potential ecological risk (PER) status of the creeks in terms of irrigation water quality, d) Comparison of potentially toxic element concentrations with the environmental quality standard values specified in the current "Turkish Surface Water Quality Regulation". According to the findings; a) In terms of overall potentially toxic element levels, the creeks are ranked as follows: Başpınar Creek> Sukesen Creek>Gölcük Creek>Yavrucak Creek. The heavy metal As was identified as having the highest contribution to metal pollution and the potentially toxic element concentrations in all creeks in February and April were found to be higher compared to that in December, b) The HPI value was found to be less than 15 for all months and creeks, with the highest HPI value of 13.21 calculated in Başpınar Creek in February, c) The HEI values were found to be less than 10 (ranging from 0.02 to 0.84), indicating a low level of potentially toxic element pollution according to this index, d) In terms of irrigation water quality, all creeks exhibited a low level of PER, with the highest PER value of 13.54 belonging to Başpınar Creek, e) The detected potentially toxic element concentrations in all four creeks did not exceed the maximum EQS values provided. In this context, it has been determined that the potentially toxic element levels in creek waters, due to anthropogenic activities, are not currently causing significant pollution. However, it is noted that Başpınar Creek is at a higher risk compared to other creeks. Furthermore, because of the ongoing anthropogenic activities in the basin, long-term metal monitoring studies are important in terms of the sustainability of Lake Mogan.

Anahtar kelimeler:

Potansiyel toksik elementler
Kirlenme
Yüzey suları
Dereler
Mogan Gölü

Mogan Gölü'nü (Türkiye) Besleyen Derelerde Potansiyel Toksik Element Kirliliğinin Belirlenmesi

Öz: Bu çalışmada. antropojenik baskı altındaki bir havzada konumlanan ve Özel Çevre Koruma Bölgesi olarak ilan edilen Mogan Gölü'nü besleyen dere (Başpınar, Gölcük, Sukesen ve Yavrucak Deresi) sularında; a) Potansiyel toksik elementlerin (Cr, Ni, Cu, Zn, As, Cd, Hg, Pb) dereler ve aylar (Aralık-2002, Şubat 2023, Nisan-2023) arası farklılığının belirlenmesi, b) Sulama suyu kalitesi açısından ağır metal indekslerinin (Heavy Metal Pollution Index-HPI and Heavy Metal Evaluation Index-HEI) uluslararası ve ulusal değerler esas alınarak hesaplanması, c) Derelerin sulama suyu kalitesi açısından potansiyel ekolojik risk (PER) durumunun tespit edilmesi, d) Potansiyel toksik element konsantrasyonlarının yürürlükte olan -Yerüstü Su Kalitesi Yönetmeliği- kapsamında belirtilen çevresel kalite standard değerleri ile karşılaştırılması amaçlanmıştır. Bulgular doğrultusunda, a) Tüm potansiyel toksik element düzeyleri açısından dereler; Başpınar Creek>Sukesen Creek>Gölcük Creek>Yavrucak Creek olarak sıralanmıştır. Derelerdeki metal kirliliğinde payı en çok olan ağır metal As iken, tüm derelerde şubat-nisan ayı ağır metal konsantrasyonları, aralık ayına göre daha yüksek bulunmuştur, b) Tüm ay ve derelerde HPI değeri 15'den küçük bulunurken, en yüksek HPI değeri 13.21 olarak Başpınar Deresi'nde şubat ayında hesaplanmıştır, c) HEI değerleri ise 10'dan küçük (0.02-0.84) saptandığından bu indis açısından da düşük düzeyde ağır metal kirliliği belirlenmiştir, d) Tüm derelerde sulama suyu kalitesi açısından düşük düzeyde PER söz konusu olup, en yüksek PER değeri 13.54 ile yine Başpınar Deresi'ne aittir, e) Dört derede de tespit edilen ağır metal konsantrasyonları, Max.-EQS için verilen sınır değerleri aşmamıştır. Bu bağlamda, antropojenik faaliyetlerden dolayı dere sularındaki ağır metal seviyelerinin şu an için ciddi boyutlarda kirlilik yaratmadığı ancak özellikle Başpınar Deresi'nin diğer derelere göre daha fazla risk altında olduğu belirlenmiştir. Ayrıca havzadaki antropojenik faaliyetlerin süregelmesi nedeniyle, uzun-dönemli metal izleme çalışmaları Mogan Gölü'nün sürdürülebilirliği açısından önem arz etmektedir.

*Corresponding author: spulatsu@agri.ankara.edu.tr

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Introduction

Anthropogenic activities limit the use of surface water resources for irrigation, domestic fishing, and industrial purposes by deteriorating water quality. The main causes of potentially toxic element pollution in water and sediment include discharge of untreated waste from the mining industry and other industrial activities. Additionally, the contamination of water bodies can occur through various pathways, such as the introduction of heavy metal-containing chemical pesticides used in agricultural practices (Pulatsü et al., 2014). In this context, recommended thresholds for potentially toxic element concentrations in water used for drinking, irrigation, domestic use, as well as for the protection of aquatic life have been provided by different sources (FAO, 1994; Goher et al., 2014; Mollo et al., 2022).

Determining various pollution indices is one of the most common methods for assessing environmental pollution in surface waters, soils and sediments. The Heavy Metal Pollution Index (HPI) is widely used to assess the cumulative impact of various metals on the quality of surface waters. On the other hand, the Heavy Metal Evaluation Index (HEI) is extensively employed to indicate the overall surface water quality in terms of metal levels. HPI is considered a reliable technique for assessing water quality based on potentially heavy metal concentrations. On the other hand, HEI is defined as a rating that reflects the compound effect of different dissolved heavy metals (Edet and Offıong, 2002; Rahman et al., 2014). Moreover, the potential ecological risk (PER) index can be evaluated considering the toxicity factor of a specific metal, making it possible to enumerate the contamination status of any given metal in an ecosystem (Hakanson, 1980).

The increasing number of industrial facilities (such as aluminum coating factories, brick factories, and machinery factories) due to its proximity to Ankara and efficient road transportation are among the main anthropogenic factors in the Mogan Lake basin (Karaaslan, 2009). Additionally, unplanned urbanization due to increasing human population around the lake, increasing number of hobby gardens and the transportation of waste from andesite and stone quarries to the lake through tributaries can also be counted as contributing factors. In this context, certain rehabilitation efforts have been conducted within the lake basin (Anonymous, 2022). It appears inevitable that negative interventions on tributaries will lead to further reduction in the already limited water flows and increase pollution.

The "Regulation on Surface Water Quality" in effect in Turkey establishes priority substances and environmental quality standards for surface water resources. Within this framework, the arithmetic mean of one year's monitoring results of specific pollutants and priority substances for each water body category (rivers/lakes, coastal and transitional waters) is compared to the annual average environmental quality standard (Mean-EQS). Alternatively, for any specific pollutant and/or priority substance, the individual monitoring data is compared to the maximum allowable environmental quality standard (Maximum-EQS). As a result of the assessment, if the monitoring data is lower than both the Mean-EQS and the Maximum-EQS values, the environmental quality standard values for the receiving environment are considered to be met (TSWQR, 2016). In the Gölbaşı Special Environmental Protection Area Management Plan, covering the period from 2015 to 2019 and issued by the General Directorate of Protection of Natural Assets under the Ministry of Environment and Urbanization, the objective of achieving compliance with the standard values of the Surface Water Quality Regulation (Water Framework Directive) is set for Mogan-Eymir Lakes and the creeks that feed these lakes by the end of the fifth year (Anonymous, 2022).

Despite the potentially toxic element studies conducted on the water-sediment of Lake Mogan (Yüksel and Arica, 2018; Küçükosmanoğlu and Filazi, 2020; Binici et al., 2021; Binici and Pulatsü, 2022a, 2022b), no previous studies has been found regarding the determination of potentially toxic element levels in tributaries of Lake Mogan. The aim of this research is to assess the following aspects in tributaries receiving both point and non-point sources of pollution that reach Lake Mogan: a) Determination of variations in potentially toxic element levels (Cr, Ni, Cu, Zn, As, Cd, Hg, Pb) among different creeks and months, b) Calculation of metal pollution indices such as Heavy Metal Pollution Index (HPI) and Heavy Metal Evaluation Index (HEI) in the context of irrigation water quality, c) Identification of the potential ecological risk (PER) status of the creeks in terms of irrigation water quality, d) Comparison of potentially toxic element concentrations with the environmental quality standard values specified in the "Turkish Surface Water Quality Regulation”, e) Statistical evaluation of possible sources of heavy metals. The findings of this study are important for revealing the current status of heavy metals in the surface waters of tributaries and for establishing a preliminary database in this regard.

Material and Methods

Study area

Lake Mogan is located within the boundaries of the Gölbaşı Special Environmental Protection Area and is also considered as one of the significant wetlands in our country nominated for Ramsar designation. The groundwater recharge of Lake Mogan is relatively low and water input during summers primarily occurs through irregularly flowing creeks that tend to dry up. The most important creeks are Sukesen, Başpınar, Gölova, Yavrucak, Çolakpınar, Tatlım, Kaldırım, and Gölcük, located in the eastern-northwestern parts of the basin (Anonymous, 2017). In this study, water samples were taken from four selected creeks that represent the sources of pollution for Lake Mogan and contribute to its inflow (Figure 1). The coordinates of the creeks and potential pollutant sources related to them are presented in Table 1.

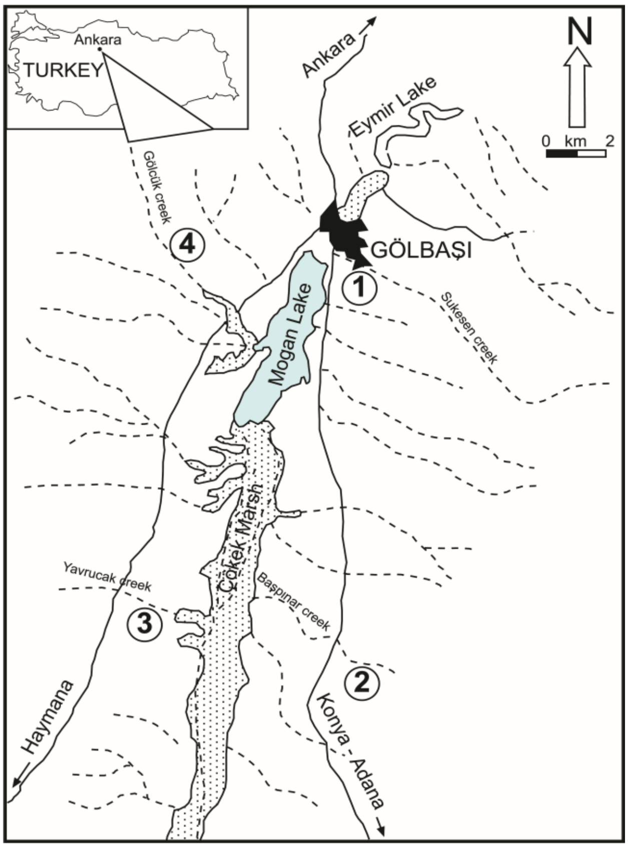

Figure 1. Map of the study area and selected creeks

Table 1. Characteristics of selected creeks

Creeks	Pollution sources	Coordinates
Sukesen Creek	Quarries and settlements	39°47,350"N, 32°48,266"E
Başpınar Creek	Settlements and agricultural activities	39°46,616"N, 32°48,149"E
Yavrucak Creek	Agricultural activities	39°47,542"N, 32°48,205"E
Gölcük Creek	Agricultural activities	39°45,436"N, 32°45,568"E

Methods

In this study, three sampling periods (December 2022, February 2023, and April 2023) were conducted on the selected creeks that feed Lake Mogan. . The sampling periods were chosen due to the increased likelihood of heavy rainfall based on previous meteorological data. The water samples were transported to the laboratory in a dark and cool environment. Potentially toxic element analyses (Hg, As, Cd, Cr, Pb, Ni, Cu, Zn) were performed on the water samples in an accredited laboratory according to TS EN ISO 17294-1.24 standards, with four replicates for each analysis.

a) Pollution evaluation indices

In the present study, eight metals (Cr, Ni, Cu, Zn, As, Cd, Hg, Pb) were assessed for the calculation of HPI, HEI and PER. Regarding HPI, HEI and PER values; Data I: FAO (1994), Data II: TSWQR (2015) were calculated separately (Table 2) based on the potentially toxic element concentration values reported for the irrigation water class regarding the quality of creek surface waters are also presented.

Heavy Metal Pollution Index (HPI)

Heavy Metal Pollution Index (HPI), which characterizes the pollution status of the creeks in terms of heavy metals, is calculated according to the following formula:

$HMPI=\sum(Q_i \times W_i)/\sum W_i$

$Q_i = C_i / S_i \, x100$

Where, Qi is the sub-index of the ith parameter; Wi is the unit weightage of the ith parameter (=k/ Si); k: Proportionality constant for metal (=1); Ci is the monitored value of potentially toxic elementsof ith parameter; Si is the standard value of the ith parameter (µg/L).

To assess the contamination level, HPI values are divided into three groups: (i) Low (HMPI value < 15), (ii)

Moderate (HMPI value = 15-30), and (iii) High (HMPI value > 30) (Edet and Offiong, 2002).

Heavy Metal Evaluation Index (HEI)

The HEI value, which provides information about the overall water quality in terms of heavy metals, is calculated using the following equation (Zakir et al., 2020):

$$HEI = \sum_{i=1}^{n} M_i / MAC_i$$

M_i: The monitored value of the ith metal (μg/L)

MACi: Maximum admissible concentration of the ith metal (μg/L) (The standard permissible value of the ith metal (μg/L)

The classifications of surface water quality based on HEI are as follows: <10 for low pollution, 10-20 for moderate pollution, and >20 for high pollution (Kumar et al., 2019).

b) Risk assessment

Potential ecological risk (PER) assessment

The potential ecological risk assessment of potentially toxic element contamination was proposed as a diagnostic tool for identifying and managing water pollution problems associated with increasing levels of heavy metals in surface water (Rahman et al., 2014). Based on Hakanson (1980) method, the potential ecological risk index has been calculated:

$$PER = \sum_{i=1}^{n} T_i \times C_i / S_i$$

Ci: The monitored value of the ith metal (μg/L)

Si: The standard permissible value of the ith metal (μg/L) (Table 2)

Ti = The individual metal's biological toxicity factor.

The toxicity factor values are: 5 for Ni, Cu, Pb; 2 for Cr; 1 for Zn; 10 for As; 30 for Cd; 40 for Hg (Hakanson, 1980).

The classifications of surface water quality based on PER are as follows: <110 for low risk, 110-200 for moderate risk, 200-400 for considerable risk, and >400 for very high risk. (Sharafi et al., 2016).

c) Comparison based on EQS values

The Mean-EQS and Max. EQS values specified under the "Turkish Surface Water Quality Regulation" (TSWQR, 2016) for heavy metals in Table 2.

Table 2. Standard permissible value (S_i) or maximum admissible concentrations (MAC_i) of metals for irrigation water and national surface water quality standard values (EQS)

Metals	Concentrations (μg/L)			
	Irrigation water		EQS (TSWQR, 2016)	
	FAO (1994)	TSWQR (2015)	Mean-EQS	Max. EQS
Cr	100	50	1.6	142
Ni	200	50	4	34
Cu	200	50	1.6	3.1
Zn	2000	500	5.9	231
As	100	50	53	53
Cd	10	5	0.08	0.45
Hg	2	0.5	1.2	0.07
Pb	5000	20	1.2	14

d) Statistical analyses

The Kruskal-Wallis test was used to determine if there was a significant difference in the concentration values of heavy metals among different months. The Tukey test, a post hoc multiple comparison test, was used to identify which months had significant differences. The Spearman correlation coefficient was used to determine whether there was a significant relationship among the concentration values of heavy metals. In this study, Principal Component Analysis/Factor Analysis (PCA/FA) with varimax rotation was conducted to identify potential sources of heavy metals. To determine the appropriate dataset for PCA, the Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity tests were performed. The KMO is a measure of the acceptability of sampling since it indicates the common variance that might be induced by underlying factors. If the KMO value is close to 1, it suggests that the samples are acceptable or PCA might be more effective (Kolassa, 2020). All statistical analyses were performed by using SPSS 22.

Results

Potentially toxic element concentrations in creeks

In Table 3, the variations of the eight heavy metals (Cr, Ni, Cu, Zn, As, Cd, Hg, Pb) for each creek according to the months, as well as the variations of each potentially toxic element across the creeks for each month are presented. It was determined that the concentrations of all heavy metals vary according to the months for each creek. Cr, Ni, and As levels in Başpınar Creek in December showed a statistically significant difference compared to those of other two months ($p<0.05$). In Gölcük Creek, while the levels of Ni, Cd, and Hg did not show a statistically significant difference between February and April ($p>0.05$), there was a significant difference ($p<0.05$) between the values of Cr, Cu, Zn, As, and Pb for the same months. For Sukesen Creek, the As values showed a statistically significant difference across all months. In December, the Cr value differed significantly from those of February and April, while the Ni concentrations in April showed a significant difference compared to those of December and February ($p>0.05$). In Yavrucak Creek, there were no statistically significant differences ($p>0.05$) between the concentrations of As and Hg during the months of February and April. In all creeks, the concentrations of Cu, Cd, Hg, and Pb were below the detection limits in December, while the Cr concentrations were below the detection limits in Gölcük and Yavrucak Creeks (Table 3).

As seen in Table 2, the monthly concentration values of each potentially toxic element also varied depending on the creeks. In Başpınar Creek, the concentration of Cr reached its maximum value in April (2.41 µg/L), while the concentration of Zn reached its maximum value in February (1.64 µg/L), showing a statistically significant difference compared to other creeks ($p<0.05$). In Sukesen Creek, it was determined that the concentration of Ni in February (3.51 µg/L) and the concentration of Cu in April (1.54 µg/L) showed a statistically significant difference compared to those of other creeks ($p<0.05$). The concentration of As was found to be high in Başpınar Creek in all months. Based on the concentration data of As, the ranking of the creeks was as follows: Başpınar Creek > Sukesen Creek > Gölcük Creek > Yavrucak Creek. The difference in As levels between Gölcük and Sukesen Creeks in February was not statistically significant ($p>0.05$). In Başpınar Creek, while the Cd (0.39 µg/L) and Hg (0.07 µg/L) concentrations showed a statistically significant difference compared to other creeks in February ($p<0.05$), the difference in Pb concentration between February and April among the creeks was not statistically significant ($p>0.05$).

Potentially toxic element pollution status in creeks

The variations of the calculated HPI-I and HPI-II and HEI-I and HEI-II values based on the months and creeks are shown in Figure 2, according to the criteria reported by the International (FAO, 1994) and national (TSWQR, 2015) standards, respectively. In this study, when HPI-I and HPI-II values are considered together, the range of variations were as follows: for Başpınar Creek: 0.29-13.21; for Gölcük Creek: 0.03-3.94; for Sukesen Creek: 0.01-1.60; and for Yavrucak Creek: 0.01-0.91 (Figure 2). As seen in the figure, the HPI value was less than 15 for all months and creeks, indicating a low level of pollution. The maximum HPI value was determined for Başpınar Creek (13.21) and the main contributors to pollution, as evaluated by HPI, were As, Cr, Ni, and Cu. When considering the HEI values within the scope of the study, it was found that they were less than 10 (ranging from 0.02 to 0.84) for all creeks on a monthly basis (Figure 2). Therefore, with respect to HEI,, there is a low level of potentially toxic element pollution in the irrigation water.

Ecological risks of potentially toxic elements in creeks

When considering the PER-I and PER-II values together for the creeks, the range of variations are determined as follows: for Başpınar Creek: 1.81-13.54; for Gölcük Creek: 0.53-6.46; for Sukesen Creek: 0.91-5.52; and for Yavrucak Creek: 0.16-2.64. Although the PER values for February and April were found to be higher compared to that in December, overall, there was a low risk in terms of irrigation water quality for all creeks (Figure 2-5). According to the potential ecological risk values, the creeks were ranked as follows: Başpınar Creek > Sukesen Creek > Gölcük Creek > Yavrucak Creek.

Within the scope of the study, for all creeks examined, As, Ni, and Cr were identified as significant components of potential ecological risk in December, while Hg, As, and Cd were identified as important heavy metals in February and April, which are key contributors to a potential ecological risk. Moreover, the highest PER value of 13.54 belonged to Başpınar Creek in February.

Possible sources of potentially toxic elements in creeks

Principal component analysis was performed to identify the types and contributions of heavy metals from pollution sources in selected tributaries. Başpınar Creek had two factors with eigenvalues greater than 1. In the first factor, Ni, Cr, As, Pb, and Cu metals were grouped together, explaining 56% of the variance. In the second factor, Cd, Zn, and Hg were grouped, explaining 29% of the variance (Table 4). It was determined that the concentration values of the 5 heavy metals that contributed significantly to the pollution in Başpınar Creek were generally higher than those of other creeks (Table 3). In this context, the proximity of the tributary to residential areas and intensive agricultural activities supported the varying levels of contribution and high concentrations of heavy metals. In Gölcük Creek, it was determined that the first principal component, which explained 53% of the total variance, exhibited stronger positive loadings for Cr (0.987), Cu (0.981), Zn (0.957), Hg (0.751), and Ni (0.700) compared to other metals, while the second factor grouped Pb (0.941), As (0.919), and Cd (0.884), explaining 40% of the variance (Table 4). It was observed that particularly in February, the concentrations of Cu and Ni in these creek waters were higher compared to the other two months. The waters of both creeks, influenced by residential and agricultural activities, seemed to be responsible for the increase in potentially toxic element concentrations, especially with respect to Ni and Cr.

Table 3. Levels of potentially toxic element concentrations according to months and creeks

Creeks	Metals	December Mean ± SD (µg/L)	February Mean ± SD (µg/L)	April Mean ± SD (µg/L)
Başpınar	Cr	0.29 ± 0.04^{aA*}	2.18 ± 0.23^{bA}	2.41 ± 0.18^{bA}
	Ni	0.37 ± 0.28^{aA}	1.57 ± 0.00^{bA}	2.00 ± 0.68 ^{bA}
	Cu	-	0.63 ± 0.21^{aAB}	0.49 ± 0.31^{aA}
	Zn	0.53 ± 0.24^{aA}	1.64 ± 0.42^{bA}	0.33 ± 0.05^{aA}
	As	17.94 ± 1.45^{aA}	26.39 ± 1.85^{bA}	27.41 ± 2.13^{bA}
	Cd	-	0.39 ± 0.06^{aA}	0.01 ± 0.01^{bA}
	Hg	-	0.07 ± 0.02^{aA}	0.04 ± 0.04^{bA}
	Pb	-	0.08 ± 0.03^{aA}	0.55 ± 0.19^{bA}
Gölcük	Cr	-	0.25 ± 0.00^{aB}	0.06 ± 0.02^{bB}
	Ni	0.80 ± 0.14^{aB}	3.06 ± 0.00^{bB}	2.98 ± 0.15^{bB}
	Cu	-	0.75 ± 0.07^{aA}	0.04 ± 0.01^{bB}
	Zn	-	0.50 ± 0.07^{aB}	0.02 ± 0.01^{bB}
	As	5.11 ± 0.10^{aB}	4.22 ± 0.38^{aB}	12.02 ± 0.91^{bB}
	Cd	-	0.2 ± 0.07^{bB}	0.31 ± 0.07^{bB}
	Hg	-	0.02 ± 0.01^{aB}	0.01 ± 0.01^{aA}
	Pb	-	0.06 ± 0.04^{aA}	0.95 ± 0.12^{bA}
Sukesen	Cr	0.36 ± 0.02^{aB}	0.64 ± 0.10^{bC}	0.76 ± 0.07^{bC}
	Ni	3.45 ± 0.04^{aC}	3.51 ± 0.66^{aB}	2.34 ± 0.30^{bAB}
	Cu	-	0.87± 0.09^{aB}	1.54 ± 0.00^{bC}
	Zn	0.21± 0.07^{aB}	0.71 ± 0.04^{bB}	0.55 ± 0.19^{bB}
	As	8.16 ± 0.63^{aC}	11.18± 1.13^{bC}	14.14 ± 0.0^{cB}
	Cd	-	0.18 ± 0.08^{aB}	0.10 ± 0.02^{bC}
	Hg	-	0.02 ± 0.01^{aB}	0.03 ± 0.02^{bA}
	Pb	-	0.08 ± 0.03^{aA}	0.87 ± 0.15^{bA}
Yavrucak	Cr	-	0.16 ± 0.03^{aB}	0.58 ± 0.06^{bC}
	Ni	0.71 ± 0.21^{aAB}	0.45 ± 0.16^{aC}	2.50 ± 0.11^{bB}
	Cu	-	0.40 ± 0.09 ^{aB}	0.05 ± 0.02 ^{bB}
	Zn	-	0.36 ± 0.11^{aB}	0.18 ± 0.04^{bAB}
	As	1.28 ± 0.31^{aD}	1.90 ± 0.29^{bB}	2.00 ± 0.17 ^{bC}
	Cd	-	0.05 ± 0.03 ^{aB}	0.02 ± 0.01^{bA}
	Hg	-	0.02 ± 0.01^{aB}	0.02 ± 0.01^{aA}
	Pb	-	0.02 ± 0.02^{aA}	0.95 ± 0.12 ^{bA}

*: The different lower-case letters in the same row show the differences between months in the same creek, while the different capital letters in the same column show the differences between the creeks at the same month ($p < 0.05$)

- : Below detection limit

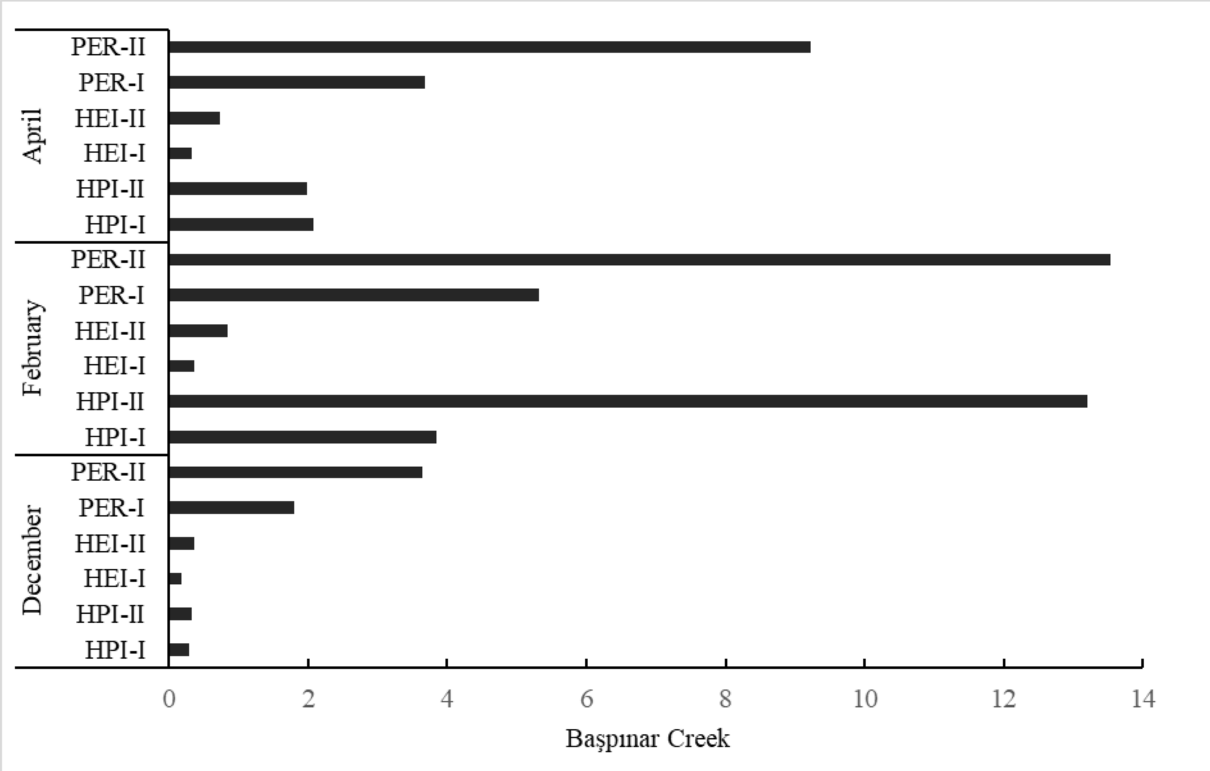

Figure 2. Variations of Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI) and Potential Ecological Risk (PER) values according to months in Başpınar Creek

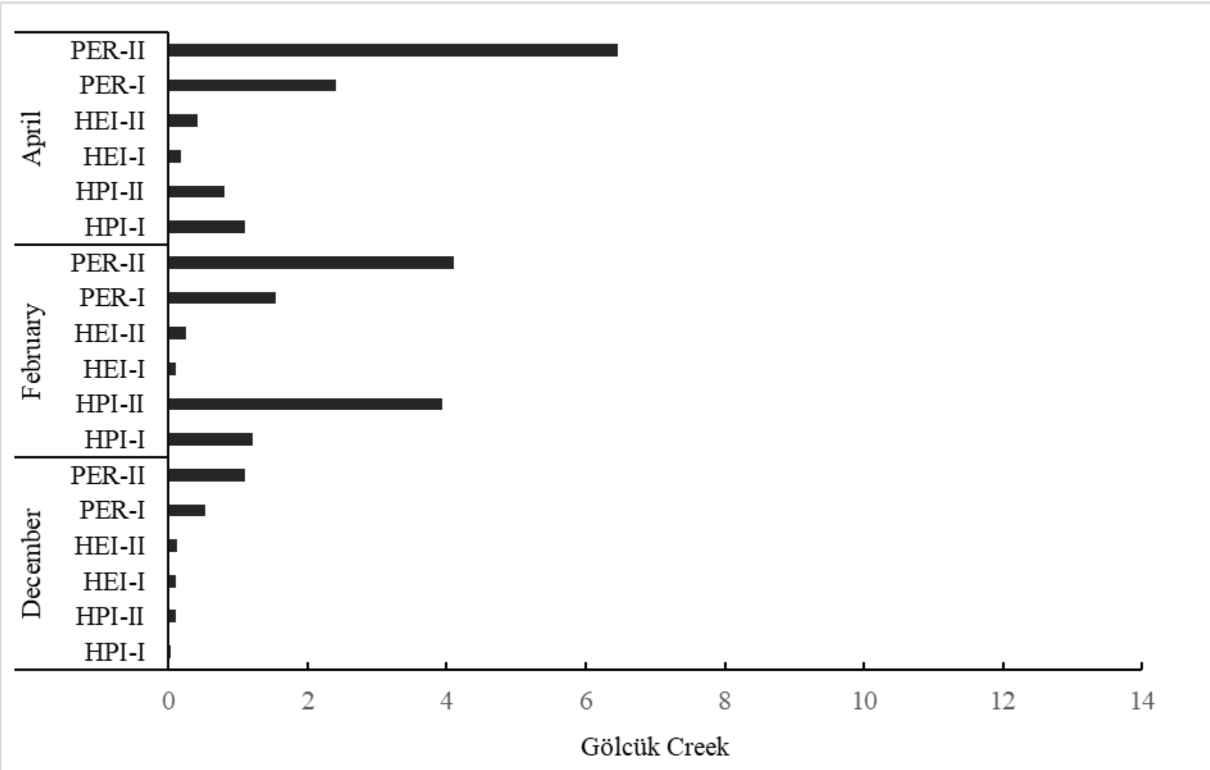

Figure 3. Variations of Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI) and Potential Ecological Risk (PER) values according to months in Gölcük Creek

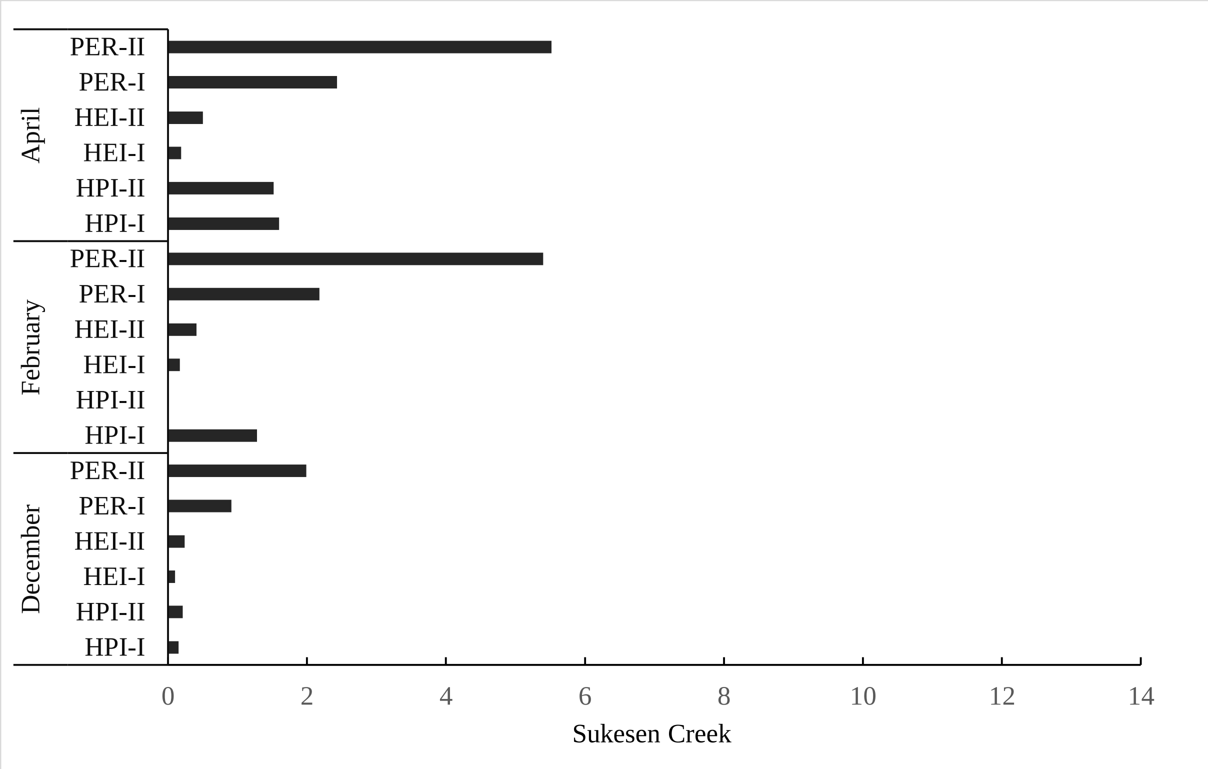

Figure 4. Variations of Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI) and Potential Ecological Risk (PER) values according to months in Sukesen Creek

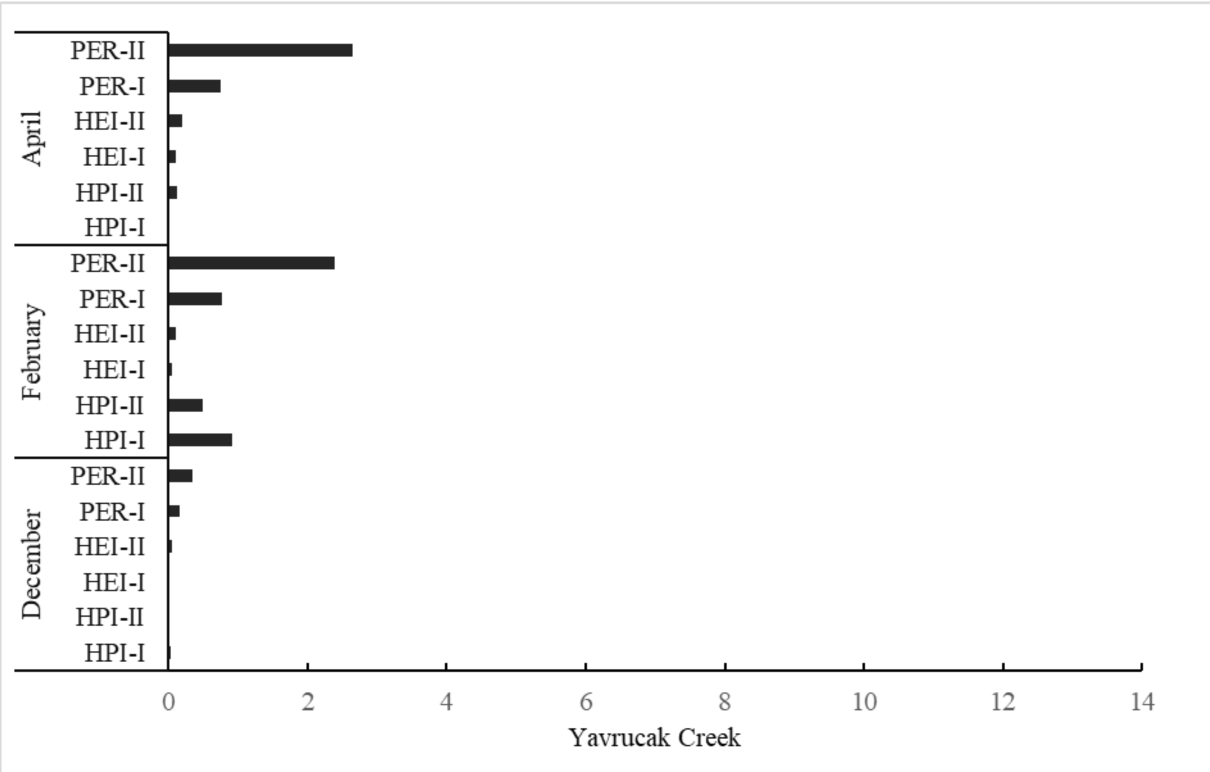

Figure 5. Variations of Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI) and Potential Ecological Risk (PER) values according to months in Yavrucak Creek

Table 4. Total variance explained and component matrixes for potentially toxic elements in Başpınar and Gölcük Creek

Başpınar Creek						
Component	Initial Eigenvalues			Variables	Component	
	Total	% of Variance	Cumulative %		1	2
1	4.443	55.535	55.535	Ni	**.931**	
2	2.328	29.097	84.633	Cr	**.929**	.305
3	.694	8.671	93.303	As	**.881**	
4	.235	2.939	96.243	Pb	**.838**	-.506
5	.136	1.702	97.944	Cu	**.732**	.361
6	.095	1.181	99.125	Cd		**.945**
7	.046	.571	99.696	Zn		**.943**
8	.024	.304	100.000	Hg	.391	**.695**
Gölcük Creek						
Component	Initial Eigenvalues			Variables	Component	
	Total	% of Variance	Cumulative %		1	2
1	4.269	53.362	53.362	Cr	**.987**	
2	3.165	39.560	92.922	Cu	**.981**	
3	.382	4.772	97.694	Zn	**.957**	
4	.116	1.454	99.148	Hg	**.751**	.376
5	.043	.540	99.689	Ni	**.700**	.679
6	.017	.214	99.903	Pb		**.941**
7	.006	.076	99.979	As	-.369	**.919**
8	.002	.021	100.000	Cd	.402	**.884**

In Sukesen Creek, the first principal component, which explains 49% of the total variance, was characterized by stronger loadings for Pb (0.947), Ni (-0.904), As (0.856), Cu (0.837), and Cr (0.773) compared to other metals. In the second factor, Zn, Cd, Cu, Hg, and As were grouped together, explaining 39% of the variance (Table 5). For Yavrucak Creek, there were also two factors with eigenvalues greater than 1. In the first factor, where Pb, Ni, and Cr metals were grouped, the variance accounted for by these metals was 49%. In the second factor, Zn, Cd, Cu, Hg, and As were grouped, explaining 39% of the variance (Table 5). The lead concentration in the creek receiving agricultural wastewater in April showed similarities with that in Gölcük Creek, which was also affected by agricultural wastewater, and the lead concentrations were found to be higher compared to Başpınar and Sukesen Creek waters.

Correlation analysis

The Spearman correlation coefficient was used to determine whether there was a significant relationship between the concentration values of heavy metals (Table 6). The correlation between heavy metals provides some information about their sources and transport pathways. The identified positive values suggested that the he heavy metals examined had a common source, co-occured during transport, and exhibited similar behaviors. On the other hand, the identified negative values are indicated that these elements originated from different sources (Binici et al., 2021). According to the results of the Spearman correlation analysis ($p<0.05$), strong positive relationships were observed between Cd-Hg, Cu-Cd, and Cu-Hg (Table 6). The significant variations of these metals among the creeks (Table 3) indicated that there were similar and significant pollution sources for these heavy metals in the vicinity of the creeks.

Table 5. Total variance explaind and component matrixes for potentially toxic elements in Sukesen and Yavrucak Creek

Sukesen Creek						
Component	Initial Eigenvalues			Variables	Component	
	Total	% of Variance	Cumulative %		1	2
1	5.236	65.444	65.444	Pb	**.947**	
2	1.595	19.937	85.382	Ni	**-.904**	
3	.609	7.610	92.992	As	**.856**	.430
4	.278	3.472	96.463	Cu	**.837**	.522
5	.162	2.030	98.494	Cr	**.773**	.540
6	.091	1.140	99.633	Hg	.546	**.535**
7	.029	.359	99.992	Cd		**.929**
8	.001	.008	100.000	Zn		**.924**
Yavrucak Creek						
Component	Initial Eigenvalues			Variables	Component	
	Total	% of Variance	Cumulative %		1	2
1	3.922	49.027	49.027	Pb	**.992**	
2	3.133	39.168	88.195	Ni	**.971**	
3	.579	7.233	95.428	Cr	**.968**	
4	.193	2.407	97.835	Zn		**.980**
5	.129	1.608	99.443	Cd		**.875**
6	.036	.453	99.896	Cu	-.354	**.833**
7	.007	.084	99.980	Hg	.515	**.724**
8	.002	.020	100.000	As	.550	**.693**

Assessment of Creek Water Quality within the Scope of EQS

Under the currently effective "Turkish Surface Water Quality Regulation," priority substances and environmental quality standards have been established for surface water resources (Table 2). In Başpınar Creek, the average value (Mean-EQS) of Cr in February (2.18 µg/L) and April (2.41 µg/L) exceeded the threshold of 1.6 and the level of Cd (0.39 µg/L) in February also exceeded the average value of 0.08. In Gölcük Creek, it was found that only Cd exceeded the average value of 0.08 in February (0.20 µg/L) and April (0.31 µg/L). Similarly, in Sukesen Creek, it was observed that Cd exceeded the average value of 0.08 in February (0.18 µg/L) and April (0.10 µg/L). Based on the Max-EQS values reported in TSWQR (2016), the potentially toxic element concentrations observed in all four creeks did not exceed the limit values set for Max-EQS. However, in Başpınar Creek, the Hg concentration value in February (0.07 µg/L) was found to be equal to the Max-EQS reported for Hg.

Table 6. Pearson correlation matrix analysis for all potentially toxic elements in the studied creeks

	Cr	Ni	Cu	Zn	As	Cd	Hg	Pb								
Cr	r	-.184	-.011	.395*	.007	.051	.364*	-.115	1.000							
	p	.211	.943	.005	.962	.732	.011	.438								
Ni	r	.263	.285*	.333*	.164	.173	.436*	.068	.286*	1.000						
	p	.071	.049	.021	.266	.239	.002	.646	.049							
Cu	r	-.270	.126	.033	.100	.181	.699*	.224	.601*	.321*	1.000					
	p	.063	.395	.825	.498	.219	.000	.126	.000	.026						
Zn	r	-.525*	.158	.248	.127	.249	.442*	.374*	.661*	.143	.665*	1.000				
	p	.000	.283	.090	.389	.088	.002	.009	.000	.332	.000					
As	r	-.114	-.233	.378*	.528*	.408*	.409*	-.173	.658*	.089	.303*	.538*	1.000			
	p	.439	.111	.008	.000	.004	.004	.240	.000	.549	.036	.000				
Cd	r	-.053	-.077	-.126	.272	.492*	.913*	.364*	.365*	.387*	.750*	.539*	.308*	1.000		
	p	.719	.604	.392	.062	.000	.000	.011	.011	.007	.000	.000	.033			
Hg	r	-.060	-.162	-.149	.044	.263	.718*	.246	.594*	.219	.746*	.570*	.319*	.784*	1.000	
	p	.683	.273	.314	.769	.071	.000	.092	.000	.135	.000	.000	.027	.000		
Pb	r	.306*	-.095	.061	.176	.129	.653*	-.250	.488*	.383*	.626*	.205	.251	.645*	.623*	1.000
	p	.035	.519	.682	.231	.383	.000	.087	.000	.007	.000	.162	.085	.000	.000	

*p<0.05

Discussion

The tributaries of Mogan Lake receive domestic, agricultural, and industrial waste.. Studies have revealed that most of the heavy metals, which constitute a significant component of pollutants, originate from various anthropogenic sources. In this study, it is known that the heavy metals (Hg, Zn, Pb, Cd, Cr, Pb, Cu, As) considered are primarily accumulated in agricultural soils, and the contamination with heavy metals is also associated with anthropogenic sources such as mining, industrial activities, agricultural practices and traffic emissions (Pulatsü et al. 2014; Xiao et al., 2019).

It was stated that mining activities from anthropogenic sources caused significant pollution in heavy metal levels in wastewater and it was indicated by examining the Heavy Metal Pollution Index (HPI) and Heavy Metal Evaluation Index (HEI) values that surface and groundwater were highly contaminated with heavy metals (Custodio et al., 2020; Moldovan et al., 2022; Pan et al., 2022). It was reported that in the Mogan Lake Basin, there were factories and facilities processing andesite stone and in earlier inspections, it was found that many facilities were discharging their wastewater directly into Sukesen Creek, without any treatment. It was also reported that high levels of heavy metals were detected in samples taken from the sludge of these facilities (Anonymous, 2013). It is believed that this activity particularly triggered the higher concentrations of Ni and As detected in Sukesen Creek compared to other creeks. The contamination of heavy metals in surface waters can have a detrimental impact on aquatic life and fishing activities, in addition to being unsuitable for drinking water and non-potable domestic and agricultural uses (Goher et al., 2014; Mollo et al., 2022; Varol and Tokatlı, 2023). For this purpose, potentially toxic element pollution indices (HPI and HEI) were calculated based on international and national standards and it was found that the index results based on national values (TSWQR, 2015) were higher compared to the international standards. However, in both cases, the index values indicated a low level of heavy metal pollution. Similar findings have been reported by Varol et al. (2021) for the Karasu River and by Kutlu and Sarıgül (2023) for the Munzur Stream. Yüksel et al. (2021), in a study investigating the effects of the garbage disposal facility built near Çavuşlu Stream (Giresun, Turkey, reported that the 1st station closest to the facility had moderate pollution, while the other stations and tap waters indicated low pollution. Based on the potential ecological risk values (PER) identified in this study, it is currently unlikely to mention a risk. Furthermore, our findings are consistent with other studies, indicating that As has thehighest contribution to low HPI and HEI values observed in our research (Tokatlı and Varol 2021; Zhang et al. 2021).

Çapar et al. (2016) stated that based on the salinity and alkalinity values they observed in water samples collected from wells and springs in some villages of Gölbaşı district (Ankara), a group of water samples were deemed unsuitable for irrigation under normal conditions. Within the scope of this study, Sukesen Creek, which runs through the Gölbaşı district, was determined to be the creek with the highest levels of potentially toxic element contamination following Başpınar Creek. According to Leventeli and Yalçın (2019), an increase in HPI values was observed in the locations between Alakır Dam and Alakır Bridge (Antalya, Turkey), indicating the influence of the dam in the upper region and agricultural activities in the lower region. In this study, it is believed that the increase in certain potentially toxic element concentrations (As, Ni, Cr) in the creeks, particularly in April, can be attributed to increased agricultural activities.

Wuhan by Zhang et al. (2021), reported that natural sources control Mn, Fe, Co, Ni, and Mo, while As was predominantly derived from the combined input of urban and agricultural activities. In this study, high levels of As were detected in Başpınar and Sukesen Creeks, where waste waters from the residential areas and agricultural activities were discharged. In this study, metals such as Cd, Hg, Zn, and Cu were detected at lower levels compared to other heavy metals. However, the high correlation values suggested the likelihood of similar anthropogenic sources. Furthermore, heavy metals such as chromium, nickel, and lead, which were identified as having a high contribution to the total variance in the PCA analysis, are associated with anthropogenic sources such as domestic-agricultural waste and motor-vehicle pollution (Wang et al., 2017; Saleem et al., 2019). The above-mentioned heavy metals align with the finding that they are the primary pollutants from both point and non-point sources, to which all the creeks are exposed.

In a study by Karaouzas et al. (2021) where potentially toxic element pollution indices were calculated in surface waters for a period covering 1999-2019 in Greece, potentially toxic element concentrations were found to be below the Environmental Quality Standards (EQS) and categorized as good quality according to surface water pollution indices. In the present study, it was determined that heavy metal concentrations in the majority of samples did not exceed the Environmental Quality Standards (EQS) for heavy metals, except for Cd, which exceeded the Mean-EQS in the 3 out of 4 creeks examined. Long-term studies monitoring EQS will enhance the accuracy of assessments regarding surface water quality.

Conclusion

The contamination of surface waters by heavy metals is widely recognized as a significant environmental issue. The transportation of domestic and agricultural waste through creeks and the uncontrolled discharge of waste into lakes occur in many parts of the world. In the Mogan Lake Basin, despite intensive urbanization, agricultural activities still exist. In this study, it was determined that the irrigation water qualities of the four significant tributaries (Başpınar, Gölcük, Sukesen, and Yavrucak) of Lake Mogan were moderately contaminated with heavy metals. However, according to the findings, it was revealed that the Başpınar Creek is more threatened compared to the other creeks. Furthermore, the effects of pollutants can vary through physicochemical interactions and this study provides only preliminary results. In this context, regular monitoring of potentially toxic element levels in creek waters by local authorities and taking necessary environmental interventions, if required, are of great importance. The findings are believed to provide a quantitative reference for future studies on the subject.

Conflict of Interest

The authors declare that they have no conflict of interest

Author Contributions

All authors took part in designing the research, collecting, and writing the manuscript. All authors took part in a part of the article.

Ethics Approval

There are no ethical issues with the publication of this manuscript.

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