International Journal of Environmental Trends (IJENT)
http://dergipark.gov.tr/ijent

International Journal of Environmental Trends (IJENT)
2024; 8 (2),100-109
ISSN: 2602-4160
Turkish JournalPark ACADEMIC

Research Article

Determination of Heavy Metal Pollution Levels in Bayramhacılı Dam Lake

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Received
2 October 2024

Accepted
18 December 2024

Keywords
Water pollution
Heavy metals
Surface water
Nevşehir

Abstract

In this study, 11 potential toxic elements (PTEs) (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, Pb) levels were determined in Bayramhacılı reservoir located within the borders of Kayseri and Nevsehir provinces and a thematic distribution map of potential toxic elements was produced with Geographical Information System (GIS). The results obtained from the analysis of the samples taken from a total of 6 measurement stations in the wet (April) and dry period (July) were evaluated according to the relevant water quality regulations. As a result of the study; PTEs were listed in the following order according to the average concentration level in surface water: Mn > Zn > Fe > As > Al > Ni > Cr > Cu > Pb > Cd > Hg. Since the Arsenic concentration level of the pond surface water is higher than the limit value reported by the World Health Organisation, it is considered that it is not suitable for use as drinking water. It is recommended that awareness raising activities should be carried out for the protection of water resources of the people of the region and water quality monitoring studies should be continued in certain periods.

BAYRAMHACILI BARAJ GÖLÜNDE AĞIR METAL KİRLİLİK SEVİYESİNİN TESPİTİ

Anahtar Kelimeler
Su kirliliği
Ağır metaller
Yüzey suyu
Nevşehir

Özet

Bu çalışmada, Kayseri ve Nevşehir il sınırları içerisinde yer alan Bayramhacılı rezervuarında 11 potansiyel toksik element (PTE) (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, Pb) seviyeleri belirlenmiş ve Coğrafi Bilgi Sistemi (CBS) ile potansiyel toksik elementlerin tematik dağılım haritası üretilmiştir. Yağışlı (Nisan) ve kuru dönemde (Temmuz) toplam 6 ölçüm istasyonundan alınan numunelerin analizinden elde edilen sonuçlar ilgili su kalitesi yönetmeliklerine göre değerlendirilmiştir. Çalışma sonucunda; PTE'ler yüzey suyundaki ortalama konsantrasyon seviyesine göre aşağıdaki şekilde sıralanmıştır: Mn > Zn > Fe > As > Al > Ni > Cr > Cu > Pb > Cd > Hg. Gölet yüzey suyunun Arsenik konsantrasyon seviyesi Dünya Sağlık Örgütü tarafından bildirilen sınır değerden yüksek olduğu için içme suyu olarak kullanımının uygun olmadığı düşünülmektedir. Bölge halkına su kaynaklarının korunması için bilinçlendirme çalışmalarının yapılması ve su kalitesi izleme çalışmalarının belirli periyotlarla devam ettirilmesi önerilmektedir.

International Journal of Environmental Trends, *8* (2), 100-109.

DOI: not now possible

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INTRODUCTION

In recent years, the increasing world population, the increase in the frequency and severity of hydro-climatic extremes caused by climate change, the increase in the demand for clean water and the amount of wastewater required with the intensity of agriculture, industrialization and urbanization have increased the deterioration of water quality, especially in developing countries [1-4]. In addition, many studies have reported that bedrock weathering, mineral oxidation, climatic conditions, soil erosion, PTEs and pesticides also have significant negative impacts on water quality [5-8]. In addition to the transport of nitrogen, phosphorus and heavy metals from land to water due to heavy metal-containing chemicals such as fertilisers, pesticides etc. used especially in agricultural lands, atmospheric accumulation of these nutrients also increases the pollution of surface waters [9-12]. In our country, it has been determined that the primary environmental problem of cities is water pollution and when the priority environmental problems are compared over the years, it has been reported that there has been an increase in the problems related to water pollution in the last five years [13]. It has been reported that PTEs released into aquatic ecosystems from geogenic and anthropogenic sources may have negative effects on both species diversity and ecosystem health due to their toxic effects and their ability to accumulate in aquatic biota [14-19]. The fact that the dam lakes, which are continuous receiving environments, are affected by environmental pollution in the first degree, not only adversely affects the organisms living in the aquatic environment, but also these negative effects reach human beings through the food chain [20]. In order to ensure the continuity of ecological balance and to benefit from water resources efficiently, rivers, lakes, dams and wetlands should be protected and controlled. For this purpose, water quality should be monitored in certain periods and it should be ensured that the important factors affecting the pollution change are identified and appropriate measures are taken by the authorized institutions [21-24]. In particular, pollutant sources around the dams utilized as drinking, irrigation and utility water should be taken under control [25]. In this study, PTEs levels were determined in samples taken from a total of 6 measurement stations in the surface water of Bayramhacılı reservoir and a thematic distribution map of PTEs along the reservoir was created using Geographic Information Systems (GIS). In addition, an important data set that can be used by relevant institutions and organizations in field applications has been created.

MATERIAL AND METHOD

Study area

Bayramhacılı Dam Lake, which was selected as the study area, is located on the Kızılırmak River within the borders of Kayseri Province and Avanos District of Nevşehir Province. Alternative water and nature activities are also carried out in Bayramhacılı Dam Lake, which is used for irrigation water. Bayramhacılı Dam Lake, which has a fishing surface area of 460 hectares, is one of the important inland water resources that contribute to fish production as well as its hydroelectric potential. In Bayramhacılı Dam Lake, *Cyprinus carpio*, *Capoeta pestai* and *Leuciscus cephalus* are the most commonly caught fish species [26]. The map showing the study area and sampling stations is presented in Figure 1.

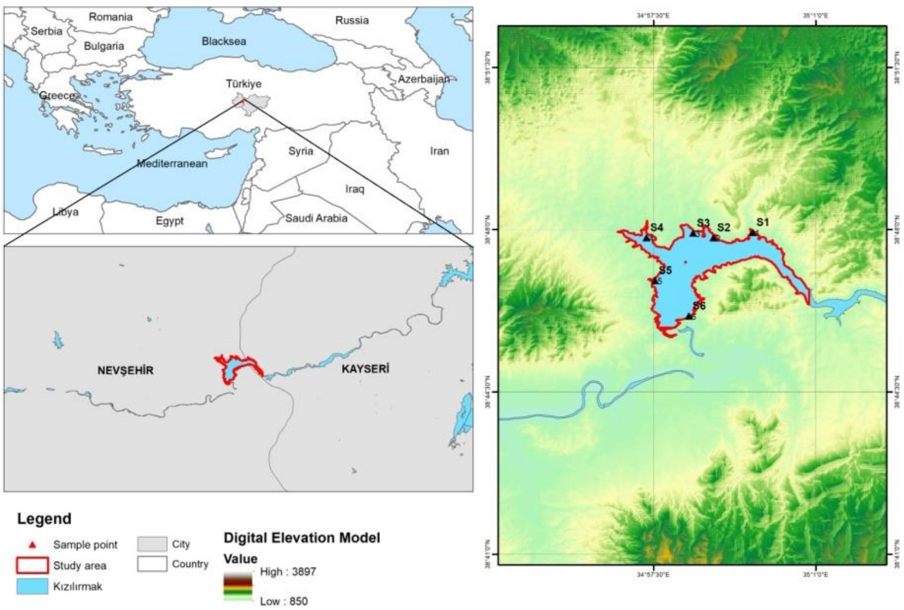

Figure 1. Research area and measuring stations.

Collection and analysis of water samples

Surface water samples were taken from six sampling stations twice (during the wet period and dry period) in April 2020 and July 2021 (Figure 1). The geographical coordinates of the sampling stations were taken by GPS (Magellan Explorist 710) and water samples were collected in 1.5 L plastic bottles as a composite from at least two points with the best mixing at each sampling station. Heavy metal concentrations in the samples brought to the laboratory and stored at +4 ˚C were determined by laboratory cuvette test kits (Hach-Lange) in accordance with standard methods (AWWA, APHA, WPCE, 1995). Analytical purity chemicals were used in all analyses and spectrophotometric measurements were performed in the laboratory using Hach Lange DR3900, thermo-reactor (Hach Lange LT-200), analytical balance (BEL brand precision) and pH meter (Metrohm laboratory version).
For the determination of toxic metal levels, surface water samples were filtered into 10 mL Teflon bottles (0.45µm Sartorius brand) and acidified with nitric acid (65 %). For calibration of the instrument, standards were created from analytically pure solutions (approximately 95% precision and accuracy) for each metal and the measurements were repeated 3 times.

Statistical analysis

Statistical analysis of the results obtained in the study was performed using SPSS Statistics 22 package programme. One-way analysis of variance (ANOVA) was applied for variables with normal distribution in intergroup comparisons. Duncan's test was used to determine the differences during significance analysis. $p < 0.05$ value was accepted as statistically significant. Pearson correlation analysis and two-way hierarchical cluster analysis were applied to reveal the relationship between heavy metals. The accumulation thematic spatial analysis map of PTEs was created using ArcGIS 10.8 software.

RESULT AND DISCUSSION

PTEs value levels detected in surface water

The results of PTEs (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, Pb) concentration analyses of Bayramhacılı reservoir surface water samples are shown in Table 1. The combined average PTE distribution of surface waters sampled during wet and dry periods according to sampling stations is shown in Figure 2. In this study, the average PTEs concentrations in the surface water of Bayramhacılı reservoir during wet and dry periods were listed in the following order: Mn > Zn > Fe > As > Al > Ni > Cr > Cu > Pb > Cd > Hg, and their levels are 69.7 > 24.17 > 23.4 > 19.12 > 14.23 > 11.02 > 3.7 > 1.14 > 0.93 > 0.60 > 0.31 ppb, respectively. The average PTEs concentrations of the surface water samples in wet and dry periods are compared with the limit values reported by WHO, USEPA and TSE and given in Table 2. Accordingly, it was measured that Arsenic level was quite high compared to WHO levels. However, in terms of PTEs (As, Cr, Cu, Fe, Mn, Ni, Pb, Zn) measured within the framework of this study, it was classified as 1st class water according to Türkiye surface water regulations.

Table 1. Distribution of potentially toxic elements according to stations (ppb).

Sample Stations	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Hg	Pb
S1 (wp)	13.75	2.12	65.1	25.5	6.39	0.51	22.13	16.50	0.58	0.27	0.39
S2 (wp)	13.65	3.32	70.65	12.22	10.0	1.79	18.82	23.09	0.58	0.39	0.78
S3 (wp)	13.55	2.1	63.04	35.52	6.40	0.45	12.20	18.25	0.58	0.21	0.34
S4 (wp)	11.85	1.06	65.4	44.72	7.17	0.10	16.40	12.17	0.48	0.27	0.68
S5 (wp)	12.09	6.32	72.00	35.77	16.67	0.51	16.11	24.2	0.53	0.22	0.97
S6 (wp)	19.85	8.43	81.24	43.76	19.30	0.96	70.25	29.98	0.87	0.74	1.35
Mean (wp)	14.12	3.89	69.6	32.9	11.00	0.72	25.99	20.69	0.60	0.35	0.75
S1 (dp)	19.60	3.07	70.48	13.2	12.05	0.48	31.27	12.81	0.65	0.18	1.77
S2 (dp)	11.60	3.52	66.06	16.88	12.00	2.63	16.97	16.06	0.57	0.23	1.00
S3 (dp)	14.46	6.1	70.24	12.90	10.08	0.60	33.09	12.38	0.36	0.21	1.49
S4 (dp)	14.43	1.24	70.88	12.57	9.01	1.93	21.3	22.73	0.48	0.45	0.93
S5 (dp)	13.26	2.43	69.02	17.33	10.04	2.68	17.08	25.58	0.87	0.33	0.68
S6 (dp)	12.77	4.67	72.10	10.86	13.10	1.07	14.43	15.81	0.76	0.26	0.85
Mean (dp)	14.35	3.51	69.80	13.9	11.05	1.57	22.35	17.56	0.61	0.28	1.12
Mean of (wp+dp)	14.23	3.7	69.7	23.4	11.02	1.14	24.17	19.12	0.60	0.31	0.93

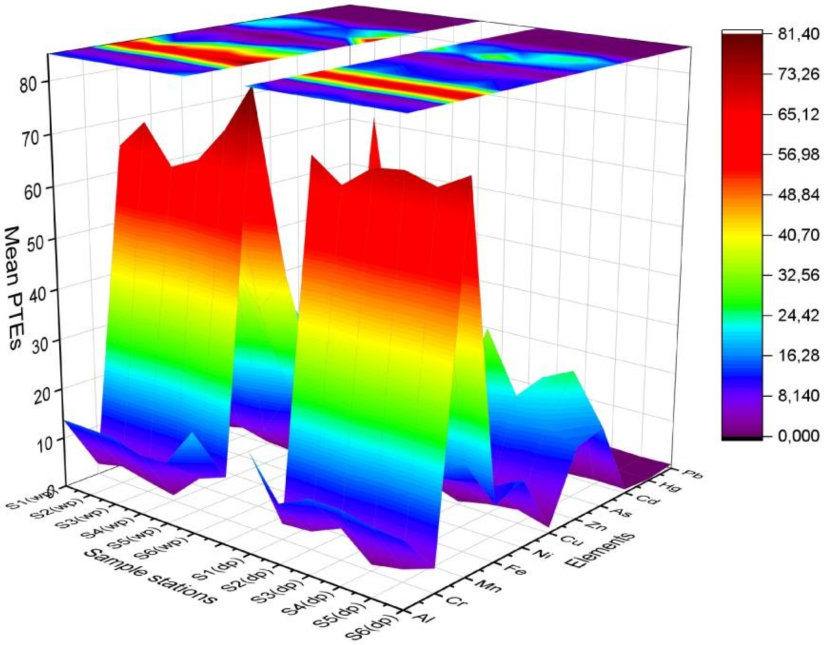

Figure 2. The distribution of combined average PTEs (ppb) according to sampling stations during wet (wp) and dry (dp) periods.

Table 2. Permissible limits for surface waters (WHO, USEPA and Türkiye standards) (Adapted from [27]).

PTEs	**This Study**	**WHO**	**USEPA**	**Türkiye surface water regulations (2015)**			
				I	**II**	**III**	**IV**
As (µg/L)	**19.12**	10	50	≤20	50	100	>100
Cr (µg/L)	3.70	50	100	≤20	50	200	>200
Cu (µg/L)	1.14	2000	1300	≤20	50	200	>200
Fe (µg/L)	23.4	300	300	≤300	1000	5000	>5000
Mn (µg/L)	69.7	100	50	≤100	500	3000	>3000
Ni (µg/L)	11.02	70	–	≤20	50	200	>200
Pb (µg/L)	0.93	10	15	≤10	20	50	>50
Zn (µg/L)	24.17	3000/1000	5000	≤200	500	2000	>2000

Table 3. Comparison of surface water PTEs concentrations (ppb) (Adapted from [6]).

Wetlands	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Bayramhacılı Dam, Türkiye	19.12	0.60	3.7	1.14	23.4	69.7	11.02	0.93	24.17	This study
Damsa Dam, Türkiye				0.6	18.3				0.4	[22]
Kızılırmak River, Türkiye	28.15	1.22	8.71	0.74	33.2	84.9	15.27	0.05	12.51	[6]
Upper Han river, China	14.20	2.31	8.14	13.35	30.6	30.7	1.71	9.26		[28-29]
Changjiang River, China	7.04	0.28	8.90	8.40	1660		3.69	6.40	18.75	[30]
Tarim River, China	3.07	0.02	0.43	1.22	61.9	16.51	1.79	0.450	7.11	[31]
To Lich River, Vietnam	39.10		2.90	4.50		216	7.60	8.100	51.1	[32]
Haraz River, Iran	55.35	2.65		13.25		116	22.4	4.4	52.75	[33]
Subarnarekha River, India	5.40		0.89	16.60	134	12.0	25.20			[34]
Rivers in CLP	5.75	0.031	5.13	5.07	45.4	71.2	5.37	0.251	6.63	[35]
Tigris River, Turkey	2.35	0.103	<5	32.00	388		45.00	0.342	<1.6	[36]
Catalan River, Spain	2.90	1.20	2.40	1.30			2.70	2.200	1.90	[37]
Seine River, France	0.75	0.031		2.23		6.26		0.354		[38]
Trinity River, USA		0.008		1.15	5.8	4.15	2.07	0.026		[39]
World average	0.62	0.080	0.70	1.48	66	34.0	0.80	0.079	0.60	[40]

The thematic spatial analysis map showing the accumulation of PTEs (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Hg, Pb) in the surface water of Bayramhacılı pond is given in Figure 3. In the present study, ArcGIS 10.7 software was used for thematic spatial distribution analysis and a continuous surface was created for the study area with the inverse distance weighted (IDW) approach, one of the interpolation techniques. The method used in this study is based on the assumption that the spatially distributed surface water sampling points in the study area are connected to each other [41-42]. As seen in Figure 3, Cd and Ni concentrations in the southwestern part of Bayramhacılı Pond are relatively high in both wet and dry periods. It was observed that the As concentration, which increased in the southern part of the lake in the wet period, spread towards the southwestern parts together with Cu in the dry period. It can also be observed from the thematic maps that Al, Cr, Pb, Mn, Hg, Fe concentrations measured in April, when precipitation is intense in the region, increased especially at the sampling points in the area towards the Hydroelectric Power Plants dam mouth (Fig.3). As can be seen in Table 3, the concentration levels of As, Cd, Cr, Fe, Mn, Mn and Ni in Bayramhacılı pond on the Kızılırmak River were found to be lower than the values in the study of Cüce et al. [6] in the Kızılırmak River, while Cu, Zn and Pb levels were found to be higher (Table 3). Cu, Fe and Zn concentration levels in this study were higher than the levels reported in the study of Kalipci et al. [22].

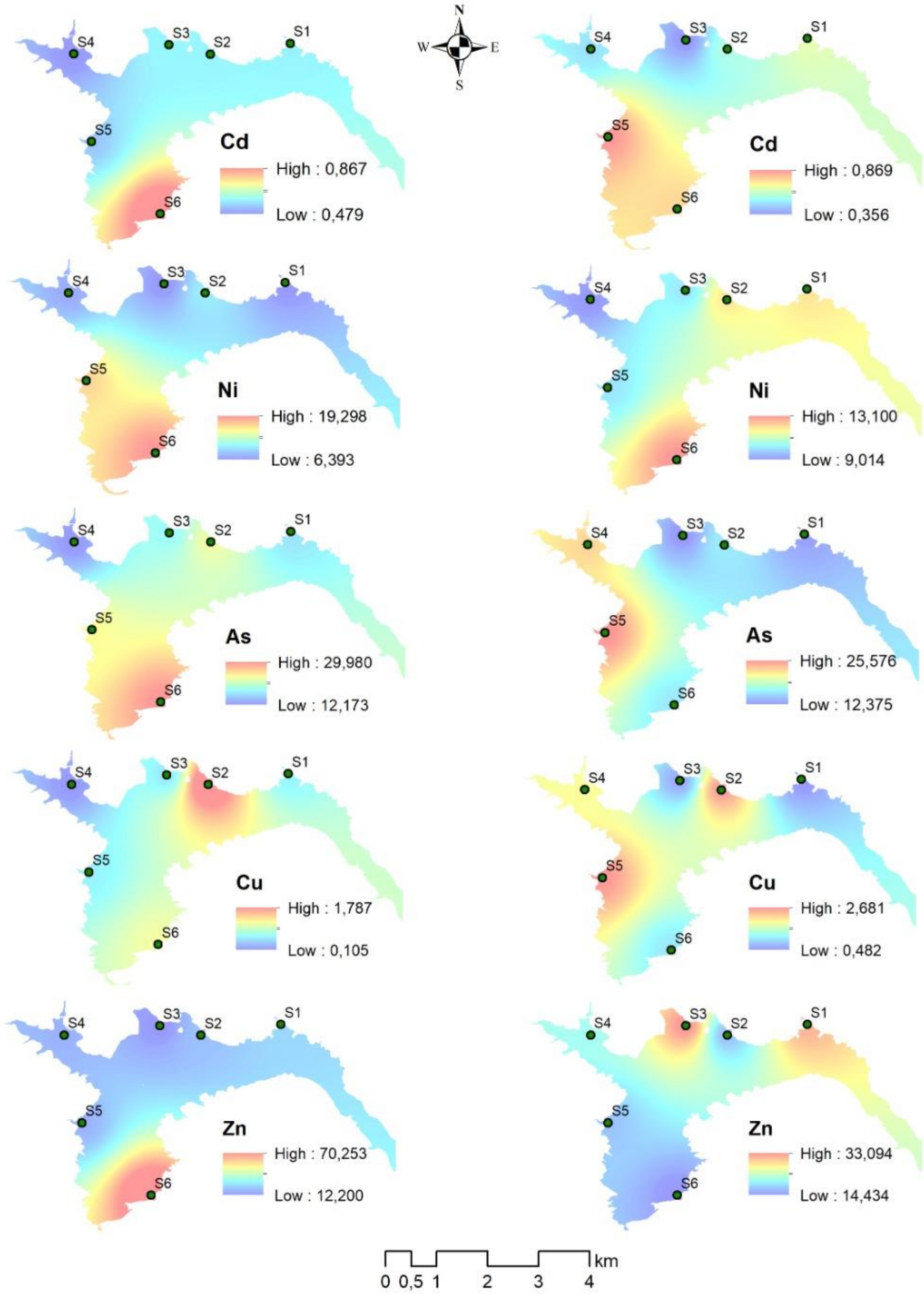

Figure 3. PTEs thematic distribution map (wet and dry period).

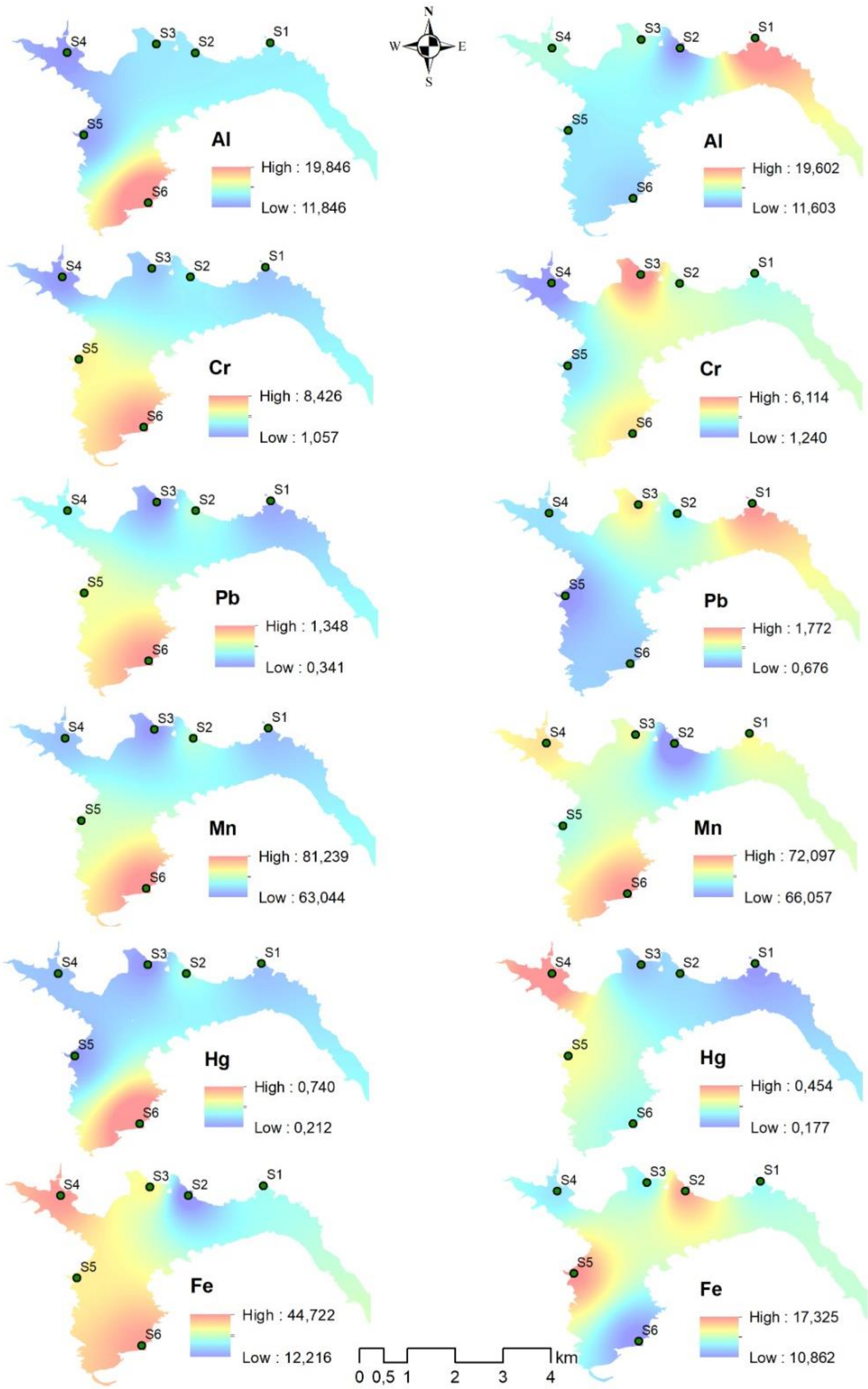

Figure 3 (continued). PTEs thematic distribution map (wet and dry period).

Correlation between heavy metals in the surface water samples

Analyzing the sources of heavy metals can help to understand their distribution [43-45], so Pearson correlation analysis was used in this study. Pearson correlation coefficients for PTEs in surface water sampled at 6 different measurement stations on the dam pond are given in Figure 4. In the surface water, a high correlation was found between Ni and Cd (r = 0.95), Pb and Al (r = 0.94), As and Ni (r = 0.85), Ni and Mn (0.93), As and Mn (0.71), Al and Zn (r = 0.82) considering the averages of the wet and dry periods. The fact that significant correlations are only positive indicates that there is a direct proportional increase between metal levels (Figure 4). Al and As are the two highest elements found due to the geogenic nature of the region. Therefore, these elements are naturally distributed from rocks to surface water. The presence of arsenic is thought to be of lithogenic and anthropogenic origin.

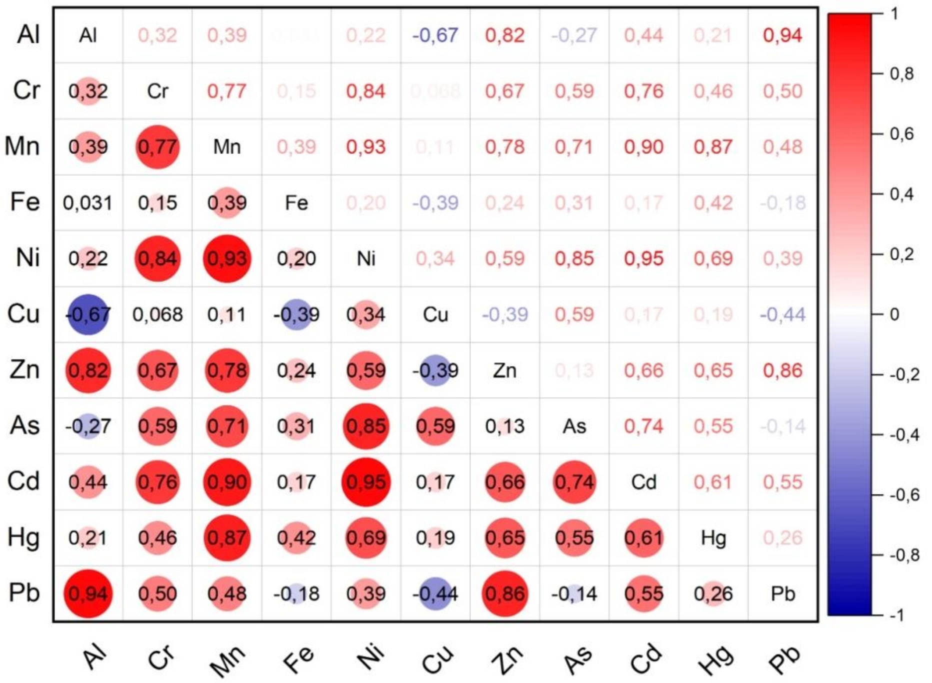

Fig.4. Correlations detected in surface water samples.

Two-way cluster analysis

In the present study, cluster heat map and dendrogram of surface water sampled gauging stations were constructed by Ward linkage approach using Euclidean distance (Figure 5). By forming a cluster of similar samplings, various samplings are placed in separate clusters, which helps to determine the pollution degree of surface waters with the same PTE concentration [46]. As seen in Figure 5, the Dendrogram presented two main clusters in the vertical section: Cluster 1 includes Al, Cu, Mn, Cd, Co, Hg, Cr, Pb, Ni, As and Zn, while Cluster 2 includes only Fe metal. This is consistent with the results of the thematic spatial analysis map of PTEs produced by GIS and shows the accumulation distribution of the selected metals in the sample stations. Among all the analyzed sample stations, S1, S3, S4, S5 and S6 were assigned to the first cluster. Cluster 2 included only S2 station (Fig. 5). It was found that the results of the two-way cluster analysis and the thematic spatial analysis map of PTEs generated by Geographical Information Systems (GIS) are compatible with each other and there is a high correlation between PTEs.

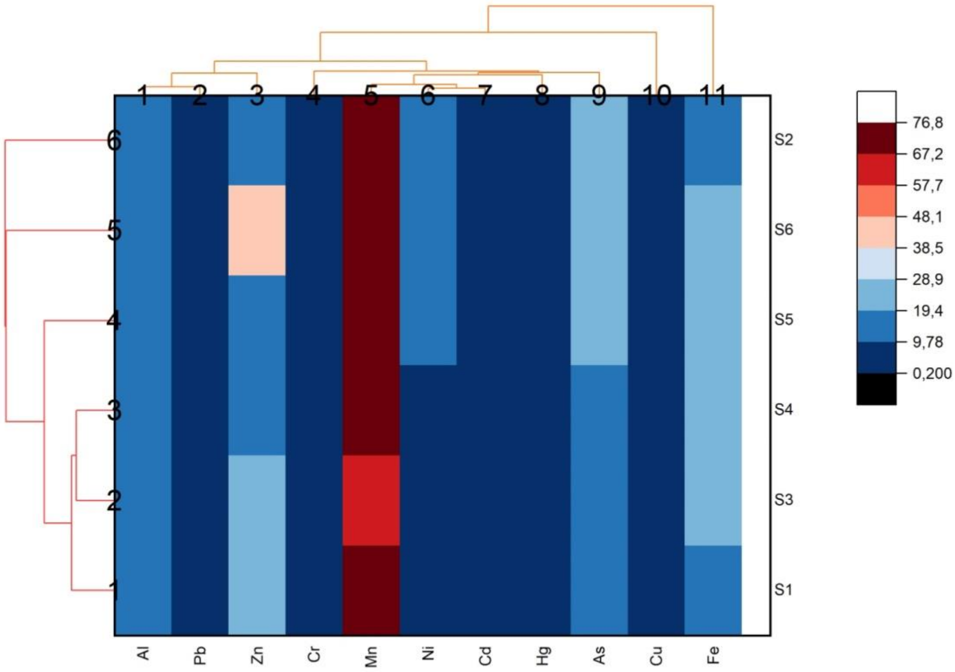

Fig. 5. Two-way hierarchical cluster heat map of the sampled stations levels of PTEs.

CONCLUSION

In this study, the heavy metal contamination status of surface water from six different measurement points in Bayramhacılı reservoir was analyzed. In addition, a thematic spatial distribution map of PTEs in the region was prepared using Geographic Information Systems (GIS).In the present study; in all surface water samples, all eleven PTEs were detected and their mean concentrations were determined in the order Mn > Zn > Fe > As > Al > Al > Ni > Cr > Cu > Pb > Cd > Hg. When PTEs concentrations were compared with the limit values determined by WHO, USEPA and TSE, it was determined that only Arsenic concentration was well above the level determined by WHO. The source of arsenic is thought to originate from the geogenic rock structure of the region. In this study, when the measured heavy metals As, Cr, Cu, Fe, Fe, Mn, Ni, Pb, Zn were evaluated, the surface water of Bayramhacılı reservoir was classified as 1st class water according to Türkiye surface water regulations. But, when the arsenic analysis results in surface water samples are compared with the limit values determined by the World Health Organization [47], it is thought that it is not suitable to be used as drinking water. This study also suggests that surface water could be ingested only after taking due precautions. It is recommended that periodical inspection and monitoring studies in wetlands should be investigated in more depth.

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