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Multivariate statistical evaluation of dissolved trace elements and water quality assessment in the Karaca dam, Turkey

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Abstract

This study was performed from January 2017 to December 2017 with taking samples every month from four stations to determine the water quality of Ka-raca Dam, located in Sinop. The guidelines of the World Health Organization for water quality index (WQI) and Turkey's Ministry of Forestry and Water Affairs specifications for Surface Water Quality Regulations (SWQR) were used in the determination of water quality and 28 variables were analyzed. The quality of the irrigation water was also calculated. This objective, the sodium adsorption ratio (SAR), sodium percentage, permeability index (PI), and mag-nesium index were calculated. The average WQI value of the lake was found to be 19.23. It was observed that the water quality parameters did not exceed the restrictions in any stations during the period. According to the results of the research, Karaca Dam is in a good class in terms of drinking water quality and irrigation water. The health risk evaluation, using the hazard ratio and index (HI), was carried out as suggested by USEPA, and it was found that the water of Karaca Dam is not harmful to human health in terms of Pb, Cd, and Hg.

Keywords

Karaca dam, water quality, water quality index, irrigation water quality, surface water

Introduction

Of the world's water body, 97.6% is composed of oceans, and 2.4% is fresh water. Only 1% of freshwater is suitable for human consumption. Dams and artificial dams are built to improve freshwater content. Recently, there has been concern about the shortage of water resources in the future (Ongley, 1998). The studies are aimed at meeting the water quality expectations of streams and rivers, as well as protecting the groundwater and surface water resources (Banerjee and Srivastava, 2009). The persistence of freshwater resources is important for the quality of life on earth (Manjare et al., 2010). However, water resources get affected by several contaminants in today's world. These cause changes in the physicochemical quality of water (Subramani et al., 2009). These contaminants are of industrial, agricultural, and domestic origin (Kumar and Thakur, 2017a,b; Kumar et al., 2015; Yu et al., 2015; Wu et al., 2018). Agricultural lands are easily contaminated by wastewater and soluble contaminants. Industrial wastewater, agricultural land nutrients, organic, and inorganic wastes are the main contaminants whose precise source is unknown (Ali and Khairy, 2016).

Also, nitrogen and phosphorus cause contamination by leaching to the surface water (Smith 2016). For this reason, monitoring programs are developed, which are aimed to maintain the water quality and determine water quality parameters (Mullai et al., 2013; Phung et al., 2015; Yisa and Jimoh, 2010).

High concentrations of heavy metals in water and earth directly affect human health (Mortuza and Al Misned 2017). Heavy metals are another contaminant of the aquatic system and human health (Rupakheti et al, 2017). It is known that anthropogenic activities accelerate the accumulation of heavy metals in water, which eventually deposit in the human body through the food chain. Anions and cations, such as NO_3, PO_4, SO_4, Ca, Mg, Fe, and inorganic salts, are the main contaminants in water (Zafar et al., 2017; Anwar et al., 2017; İmran et al., 2017). In drinking and irrigation waters, Na, Ca, Mg, and K are necessary for organisms to live. Although trace amounts of copper and zinc are important for life, their high concentrations cause toxic effects (Bing et al., 2013).

One of the most common methods to determine the quality of water is the water quality index (WOI), which was used by Horton (1965) (Tripathi and Singal, 2019). It is crucial for the balance of the ecosystem and public health to monitor the nutrients, metals, and physical qualities of water resources. Dams are important resources, which must be protected to increase the availability of water for human consumption, and maintain the sustainability for future generations. The quality of dam water, which is located around minerals, agriculture, and animal husbandry in the Sinop province, was evaluated using the water quality index and multivariate statistical approaches in this study, the physicochemical parameters of surface waters and water quality parameters, including nutrient and heavy metal concentrations of important irrigation dams in the Sinop region, were investigated. Using the obtained data, the surface water contamination value of Karaca Dam was determined by the WOI index. The relationship between contamination sources and their varieties were identified using Turkey's Ministry of Forestry and Water Affairs surface water quality regulations, and multivariate statistics. Accordingly, the potential usage of the water for drinking and irrigation purposes was investigated.

Materials and Methods

Karaca Dam Lake is located in part of the Kızılırmak Basin in the province of Sinop. The water source of the dam is Karacaören brook. The dam has an area of 0.144 km^2, and the capacity of the lake is 1.817 hm^3. Although the dam is located in the hunting area of Sinop province, it is within the wildlife protection area and meets the water needs of wild animals. The study was carried out every month in 4 stations for 12 months. From January 2017 to December 2017, surface water sampling was carried out monthly at four stations considered to represent the entire lake (Fig. 1). The water samples were taken in acid-cleaned 2.5L sampling bottles from 15 to 20 cm below the water surface.

Figure 1. *Location of sampling stations in Karaca Dam Lake.*

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The water samples for heavy metal analysis were taken in polyethylene bottles, which were previously washed with 50% HNO_3 and deionized water and acidified with 10 mL HNO_3 per liter. The samples were transported to the laboratory in iceboxes, and stored in the refrigerator at 4 °C until analysis. Water temperature, dissolved oxygen (DO), pH, salinity, and electrical conductivity (EC) values were measured in-situ with YSI 556 MPS. Chemical oxygen demand (COD), biological oxygen demand (BOD), total hardness (TH), nitrite-nitrogen (NO_2^{2-}-N), nitrate-nitrogen (NO_3^{2-}-N), ammonium-nitrogen (NH_4^+-N), total alkalinity (TA), orthophosphate (PO_4^{3-}), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), chloride (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+) analyses were performed using standard methods (APHA, 1998). Iron, lead, cadmium, zinc, nickel, copper, and mercury analyses were performed using the PerkinElmer Optima 2000 DV ICP-OES.

Water quality index (WQI)

Water quality index (WQI) is defined as a grading technique that measures the combined effect of each of the water quality parameters to evaluate the overall water quality for human consumption (Horton 1965; Kangabam et al., 2017). It has been used extensively in recent years to analyze the potential of water resources to be used for drinking and domestic purposes (Khanoranga, 2019). WQI based on the nineteen parameters (pH, EC, BOD, Cl, SO_4, Na, K, Total Hardness, Ma, Ca, NO_2, NO_3, Fe, Pb, Cu, Cd, Hg, Ni, and Zn) that are important for the analysis of water quality was determined using their seasonal and average values. An actual weight (AW) between 1 and 5 was assigned to each parameter, depending on its effect on the water quality, and its significance on human health. The relative weight (RW) value was calculated by the following formula (Eq. [1]).

$$RW = \frac{AW}{\sum_{i=1}^{n} AW} \qquad [1]$$

After calculating RW, each of the analyzed parameters is divided by drinking water values (S_i) permitted by the World Health Organization (WHO, 2011), and then multiplied by 100 to calculate the quality rating (Qi) (Eq. [2]). Whereas "Ci" is the observed concentration of each parameter and "Si"are WHO standards.

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

Later, the sub-indices (SI) were calculated (Eq. [3]) and added to determine WQI (Eq. [4]).

$$SI_i = RW \times Q_i \qquad [3]$$

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$$WQI = \sum_{i=1}^{n} SI_i \qquad [4]$$

According to WQI, it is further evaluated by

$$SAR = \frac{Na^+_{meq}}{\sqrt{\frac{Ca^{2+}_{meq} + Mg^{2+}_{meq}}{2}}} \qquad [5]$$

Sodium percentage (%). Evaluation of sodium percentage (%) is important because high sodium rates in irrigation waters cause stunted growth in plants. For this reason, the sodium rate was calculated (Ghalip, 2017).

$$\%\,Na = \frac{\left(Na^+_{meq} + K^+_{meq}\right) \times 100}{Na^+_{meq} + Ca^{2+}_{meq} + Mg^{2+}_{meq} + K^+_{meq}} \qquad [6]$$

Magnesium hazard (MH). Generally, Ca^{2+} and Mg^{2+} are present in equal amounts in water. Mg^{2+} is present in high amounts in some water sources and controls its alkalinity, which affects the growth of plants. The Mg concentration (MH) was determined using the following equation (Abdulhusseyin, 2018; Khanoranga, 2019).

$$H = \left(\frac{Mg^{2+}_{meq}}{Ca^{2+}_{meq} + Mg^{2+}_{meq}}\right) \times 100 \qquad [7]$$

Permeability index (PI). If water, which is rich in minerals, is continuously used for irrigation, the transmittance of the earth decreases. Permeability index was calculated as follows (Falowo et al., 2017).

$\mathrm{PI} = (\mathrm{Na}^{+}+\sqrt{HCO3}) * 100/(Ca2 + +Mg2 + +Na+)$ [8]

The factor, correlation, and clustering analyses were performed to determine the processes occurring in the ecosystem, identify the relationship between calculated values, and relate the sources.

Results and Discussion

The physicochemical parameters of the irrigation dam showed the natural quality of the water (Khanoranga, 2019). General qualities of the physicochemical parameters are given in Table 1.

Table 1. *Descriptive statistics of the variables*

Parameter	Winter (n = 12)	Spring (n = 12)	Summer (n = 12)	Autumn (n = 12)	Mean ±SD (n = 48)	Min	Max
DO (mg/L)	12.13^{a}	12.87^{b}	11.06^{c}	11.04^{c}	11.77 ±0.89	10.22	13.20
Salinity (‰)	0.10^{a}	0.27^{b}	0.42^{c}	0.28^{b}	0.27 ±0.13	0.10	0.50
pH	8.31^{a}	8.46^{b}	8.66^{c}	8.50^{b}	8.48 ±0.16	8.25	8.78
T (°C)	5.15^{a}	10.34^{b}	19.58^{c}	17.28^{c}	13.09 ±6.54	3.30	23.70
EC (μS/s)	237.11^{a}	241.88^{a}	291.77^{b}	299.34^{b}	267.52	203.50	317.66
TSS (mg/L)	0.60^{a}	0.92^{a}	2.19^{b}	1.81^{b}	1.38 ±0.76	0.35	2.76
COD (mg/L)	0.99^{a}	1.20^{a}	2.14^{b}	2.06^{b}	1.60 ±0.57	0.83	2.54
BOD (mg/L)	0.46^{a}	0.31^{a}	0.98^{b}	1.04^{b}	0.70 ±0.38	0.12	1.34
CI (mg/L)	2.84^{a}	2.79^{a}	3.01^{a}	3.79^{b}	3.11 ±0.59	2.15	4.70
PO_4 (mg/L)	0.21	0.12	0.09	0.18	0.15 ±0.18	0.00	0.98
SO_4 (mg/L)	16.57^{a}	29.16^{b}	53.70^{c}	41.99^{d}	35.36 ±14.95	14.77	59.26
SO_3 (mg/L)	0.36^{a}	0.69^{b}	1.17^{c}	0.81^{b}	0.76 ±0.32	0.29	1.30
Na (mg/L)	34.03^{a}	49.12^{b}	42.65^{c}	29^{d}	38.70 ±8.85	26.52	53.42
K (mg/L)	5.40^{ab}	5.10^{a}	6.13^{b}	4.61^{a}	5.31 ±0.99	4.02	7.10
TH ($CaCO_3$ mg/L)	185.77^{a}	239.47^{b}	218.44^{c}	180.82^{a}	206.13	161.64	244.02
TA ($CaCO_3$ mg/L)	187.40^{a}	241.13^{b}	219.18^{c}	182.72^{a}	207.61	161.94	245.66
Mg (mg/L)	23.71^{a}	30.94^{b}	36.90^{c}	26.71^{a}	29.56 ±5.99	19.52	39.68
Ca (mg/L)	27.16^{a}	50.03^{b}	57.69^{c}	44.23^{d}	44.78 ±12.38	23.40	59.02
NO_2 (mg/L)	0.00003^{a}	0.00007^{b}	0.00006^{b}	0.00005^{a}	0.00005	0.00001	0.00013
NO_3 (mg/L)	0.47a	0.70^{b}	0.74b	0.66^{b}	0.64 ±.13	0.38	0.85
NH_4 (mg/L)	0.00003^{a}	0.00003^{a}	0.00011^{b}	0.00013^{b}	0.00007	0.00001	0.00024
Fe (μg/L)	1^{a}	1.58^{ab}	2^{bc}	2.93^{c}	1.88 ±1.08	1.00	6.00
Pb (μg/L)	0.44^{a}	0.96^{b}	0.43^{a}	0.19^{a}	0.50 ±0.38	0.10	1.50
Cu (μg/L)	1.59^{a}	8.83^{b}	4.25^{c}	4.50^{c}	4.79 ±3.30	1.00	14.00
Cd (μg/L)	0.23	0.20	0.23	0.25	0.23 ±.08	0.10	0.40
Hg (μg/L)	0.001^{a}	0.007^{b}	0.006^{b}	0.006	0.005 ±.003	0.001	0.013
Ni (μg/L)	2.75^{a}	4.17^{b}	4.58^{b}	6.50^{c}	4.50 ±1.61	2.00	8.00
Zn (μg/L)	3.83^{a}	16.17^{b}	10.75^{c}	10.92^{c}	10.42 ±6.41	2.00	25.00

The mean difference is significant at the 0.05 level.

The pH value of Karaca Dam is within the restrictive limits specified by WHO (2011), and SWQR, which are 6.8, and 8.5, respectively. According to SWOR (2016), the dam water is of good quality (Rasool et al., 2017; Ali et al., 2017, Arshad and Imran, 2017), and has sustainable pH (Tables 2 and 3).

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Table 2. *Assignment of relative weight to the studied groundwater quality parameters.*

Parameters	WHO 2011	Assigned weight (AW)	Weight Relative (RW)
pH	6.5–8.5 (7.5)	4	0.056
EC (µS/cm)	1500	4	0.056
BOD (mg/L)	5	5	0.070
Cl (mg/L)	250	4	0.056
SO_4 (mg/L)	250	5	0.070
Na (mg/L)	200	3	0.042
K (mg/L)	12	2	0.028
TH (mg/L $CaCO_3$)	100	1	0.014
Mg (mg/L)	50	2	0.028
Ca (mg/L)	75	2	0.028
NO_2 (mg/L)	3	5	0.070
NO_3 (mg/L)	50	5	0.070
Fe (µg/L)	300	4	0.056
Pb (µg/L)	10	5	0.070
Cu (µg/L)	2000	2	0.028
Cd (µg/L)	3	5	0.070
Hg (µg/L)	6	5	0.070
Ni (µg/L)	70	5	0.070
Zn (µg/L)	3000	3	0.042

According to WHO (2011), the EC values of Karaca Dam are within acceptable limits. The presence of contaminants might cause an increase in the EC value of surface waters (Şener et al., 2017). An increase in the EC hampers ionic absorption by the plants resulting in physiological drought (Naseem et al., 2010). A high value of EC could be due to animal farms, agricultural wastes, sewage, and discharge wastes (Kanhabam et al., 2017). Additionally, our study found that the EC values increase with the rise in temperature. Upon evaporation, the salinity increases, resulting in a rise in EC (Jiang et al., 2015; Zhang et al., 2016). According to the SWQR classification, the dam is first class in terms of EC value and included in the clean water class

The chemical oxygen demand (COD) is one of the important parameters used to measure the contamination of domestic and industrial wastewater. The fact that the quality increased during the autumn season suggests that it may be caused by the chemical contaminants in agricultural lands (Imneisi and Aydın, 2016). The biological oxygen demand (BOD), on the other hand, increased in December, whereas it decreased in March. This is due to the anthropogenic activities along with domestic waste and fish activities (Sallam and Elsayed 2018). The COD and BOD values are inversely related to DO (Table 4). In Karaca Dam, the concentration of sodium (Na) was within limits prescribed by the WHO (2011). The cationic exchange is associated with the geological characteristics of the solution of lithogenic sodium (Guo et al., 2007; Rafigue et al., 2008). The results show parallelism with our study. High cation rates might be the result of the change in the concentration of calcium and sodium on earth. The calcium concentration is generally low in natural water but is sufficiently high in drinking water, industrial, and irrigation waters (Kutlu et al 2017; Tepe and Kutlu, 2019). Calcium concentrations are within limits suggested by the WHO (2011). Similar results were obtained by Rapan et al., (2017) and Alam et al., (2017).The magnesium concentration is within the WHO (2011) terms. It is most commonly found in mineral rocks and seeps into the water through natural or anthropogenic ways. Its high rate negatively affects human health (Daud et al., 2017; Rasol et al., 2017). Potassium concentration is within limits specified by the WHO (2011). It is supposed to have come from potassium-containing rocks and agricultural fertilizers (Mumtaz et al., 2017). In the study of the Karaca Dam, sulfate was found to be the highest in September and lowest in March, although it did not exceed the WHO (2011) values. The primary source of sulfate is the degradation of sulfide compounds by bacteria and the use of sulfated fertilizers (Yamamura, 2008,Varol and Davraz, 2015).

According to SWOR (2016), it was observed that the phosphate values did not exceed the limits (Class II). The agricultural fertilizers might be the cause of the presence of phosphate. The domestic and organic wastes increase the phosphate levels and cause eutrophication, which results in excessive levels of toxic algae (Boyd and Tucker, 1998). The nitrite concentration was lowest during other seasons compared to winter and autumn, and reached the maximum in spring. Nitrate concentration also shows increase and decrease in the same manner. Nitrite is a by-product of the reaction between ammonium and nitrate. Compared to others, it has a toxic effect on animals (Belal et al., 2016). The concentration of nitrate present in the water in our area is much lower than those in other places (Soomro et al., 2017). It is within the limits of the WHO (2016) and does not pose a threat to human health (Debels et al., 2005). Ammonium ions are produced during the biological degradation of organic matter and directly used by plants. Ammonium sulfate is commonly used by farmers as both organic and inorganic fertilizers (Vega et al., 1998). Fertilizers leach into the lakes and dams via the overflow of irrigation water.

In this study, the heavy metal concentrations, apart from Fe, were found to be over the limit suggested by the WHO (2011) (Table 2). It is thought that the reason for the high rates of these metals might be due to agricultural activities, mineral deposits, and anthropogenic wastes along with rocks (Kumari et al., 2017). The results show parallelism to other studies (Fatmi et al., 2009; Podgorski et al., 2016). Heavy metals accumulate in the liver, kidneys, and muscle tissues of aquatic organisms. Secondary sources of heavy metals are atmosphere and underground water (Ali et al., 2017). It is thought that the high concentration of heavy metals identified in the dam is a result of natural or anthropogenic activities.

Sodium absorption ratio (SAR). The values of sodium absorption ratio (SAR) are used to determine the water quality of irrigation water. The SAR value of Karaca Dam is 1.11 mEq/L (Table 4). If the SAR value is >9, the sodium level is hazardous and water cannot be used for irrigation (Awais et al., 2017). High SAR values might cause a decrease in salinity values and result in a decrease in the calcium and magnesium levels, which are essential elements for the growth of plants (Vasantvigar et al., 2010; Rasool et al., 2016). The result of the study shows that Karaca Dam water is suitable for irrigation.

Table 4. *Water quality classification based on Na%, SAR, MH and WOI.*

Na %	Water quality	SAR (meq/L)	Water quality	MH (meq/L)	Water quality	WOI Range	
< 20	Excellent	0–6	Good	< 50	Suitable	< 50	Excellent
20–40	Good	6–9	Doubtful	> 50	Unsuitable	50–100	Good
40–60	Permissible	> 9	Unsuitable			100–200	Poor
60–80	Doubtful					200–300	Very Poor
> 80	Unsuitable					> 300	Water unsuitable for drinking purpose

Sodium percentage (%). In the study, the average percentage of sodium was found to be 36.18% (Table 4). Water has been classified based on the sodium percentage by several researchers (Srinivas et al., 2017; El Aziz, 2017; Islam et al., 2017). According to Table 4, the dam water belongs to the good quality category of water. Its high rate in water might be due to the use of fertilizers in agriculture. The high level of sodium (9%) in the land negatively affects the tightness, ventilation, and texture of the soil (Singara et al., 2014). The plants treated with water with high sodium showed a low fertility rate because sodium affects the osmotic pressure between the soil and plant. Thus, it blocks the mineral uptake by the plant from soil (Nasseem et al., 2010).

Permeability index (PI). The permeability of the soil is affected by the presence of excessive minerals (Ca, Mg, Na, HCO_3) in water, and greatly affects long-term agricultural productivity (Sing et al., 2008). The permeability index negatively affects the fertility of soil

(Obiefuna and Sheriff, 2011). The use of water that is rich in minerals prevents the growth of seedlings by blocking the ventilation in soil. This index was developed by Doneen (1975) to classify water. According to this index, the water that has PI > 75 is the first class water, that with PI = 25–75 is the second class water, and that with PI < 25 is the third class water (Doneen, 1975; Raju et al., 2011). In our study, the permeability index (PI) was found to be 59.95; thus the region is in the second class water category (Table 4).

Magnesium hazard (MH). In our study, the average magnesium was found to be 40.39 mEq/L (Table 4). The classification of water in terms of magnesium hazard is related to its suitability for agricultural purposes. The high concentration of magnesium in water is a factor that threatens the fertility of soil (Kharonga, 2019). This is because high magnesium and clay pieces prevent the absorption of water (Hussain et al., 2016a, 2016b). The value detected in our study was found to be lower compared to those in other countries (Patet et al., 2017; Golekar et al., 2017; Padhi et al., 2017).

Water quality index (WOI). The water quality index (WOI) was employed to determine the water quality of the Karaca Dam. To calculate the index, Cd, Cl, Cu, Pb, Hg, Ni, nitrate, Na, bitterness, pH, SO_4^{2-}, and Zn concentrations were determined. The WHO (2011) limit, as given in Table 2, was used as reference. The WOI values were analyzed for each season (rainy season–dry season) and were at the lowest level during winter (16.47) and at the highest level in summer (21.70). The suggested limit of water quality parameter did not exceed in any of the stations. According to these values, the Karaca Dam was found to have the perfect water quality.

Table 5. *Water classification grading based on the Water Quality Index (WQI).*

WOI	Season Mean
16.47	Winter
19.55	Spring
21.70	Summer
19.23	Autumn

According to the Cluster Analysis, it was detected that Chlorine (Cl), Potassium (K), Copper (Cu), and Nickel (Ni) have a close relationship with each other and mostly originate from common sources. The salinity, concentrations of Cd, PO_4, NO_2, NH_4, Fe, SO_3, NO_3, Pb, TSS, BOD, and COD are closely related. This might be the result of their origin from the same source. The DO, temperature, pH, and zinc analyses formed a group together. SO_4^{2-}, Ca, Na, and Mg formed another group. The cationic group in the water created equalization. TA, TH, and electrical conductivity constituted a separate group (Fig. 2).

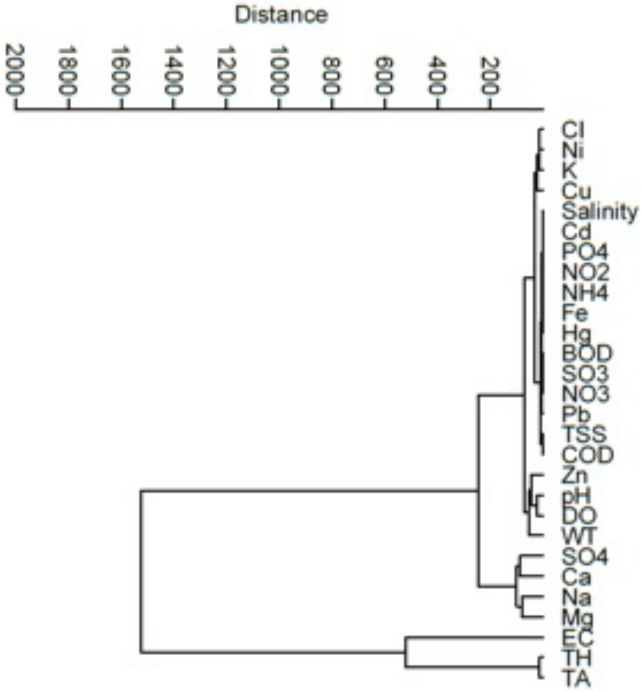

Figure 2. *Dendrogram obtained by the cluster analysis.*

The eigenvalues of the four factors were > 1. The total variables of these four factors were calculated to be 88% (Table 6). The first factor was 42%. While primarily TSS, COD, WT, SO_4, EC, BOD, SO_3, NH_4, salinity, pH, Fe, Ca, and Ni were positive, DO was negative.
The rate was calculated to be 42%. Ammonium and temperature are in the first factor; this shows that they are the two important indicators of primary concern (Kutlu et al., 2017). DO is in negative correlation with the first factor (Table 6).

Table 6. *Factor loading matrix after varimax rotation.*

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
TSS	**.985**	.035	.057	-.030
COD	**.976**	.126	-.073	-.001
WT	**.954**	.222	.090	-.045
SO_4	**.938**	.225	.047	.217
EC	**.926**	.021	-.248	-.115
BOD	**.911**	-.109	-.337	-.080
SO_3	**.907**	.254	.238	.194
NH_4	**.899**	-.115	-.058	-.357
Salinity	**.852**	.285	.339	.124
pH	**.850**	.133	.455	.024
DO	**-.837**	.434	.236	.107
Fe	**.714**	.253	.027	-.477
Ca	**.675**	.460	.490	.184
Ni	**.634**	.502	-.333	-.352
Zn	.115	**.946**	.226	-.007
Cu	-.017	**.940**	.298	-.079
NO_2	.071	**.925**	.070	.205
Hg	.316	**.910**	.165	.051
NO_3	.485	**.808**	.088	.179
Pb	-.384	**.632**	.561	.075
TA	.030	.374	**.884**	.064
TH	.034	.376	**.884**	.088
Cl	.283	.122	**-.816**	.042
Na	-.180	.464	**.765**	.352
Mg	.624	.192	**.671**	.274
PO_4	-.157	-.037	**-.566**	.015
K	.120	.119	.347	**.633**
Cd	.421	-.344	.299	**-.532**
Eigen values	12.703	7.874	3.046	1.273
Variability (%)	42,034	22,213	18.838	5.831
Cumulative%	42,034	64,247	83.084	88.915

As EC increased, especially in summer, the level of oxygen decreased. It was observed that in the primary production, among the nitrate forms, ammonium was preferred by phytoplankton. According to, Tepe and Kutlu (2019), while temperature, pH, and EC increase during summer, DO decreases. Such levels of BOD and COD in the lake water are due to excessive input of organic materials. Organic materials in lakes result from domestic wastes and the use of chemicals and fertilizers. Ammonium sulfate fertilizers are commonly used in agriculture (Vega et al., 1998), which have probably leached into the lake along with agricultural discharge and organic wastes. The second factor was 2.22% of the total change and contained NO_3, NO_2, Zn, Cu, and Pb.

Factor 3 (F3) showed a cumulative positive effect at the rate of 18.83%, which includes the total bitterness, TH, and concentrations of Cl, Na, Mg, and PO_4 (Table 6). These are the result of the discharge of agricultural wastes into the Karaca Dam, and excessive use of

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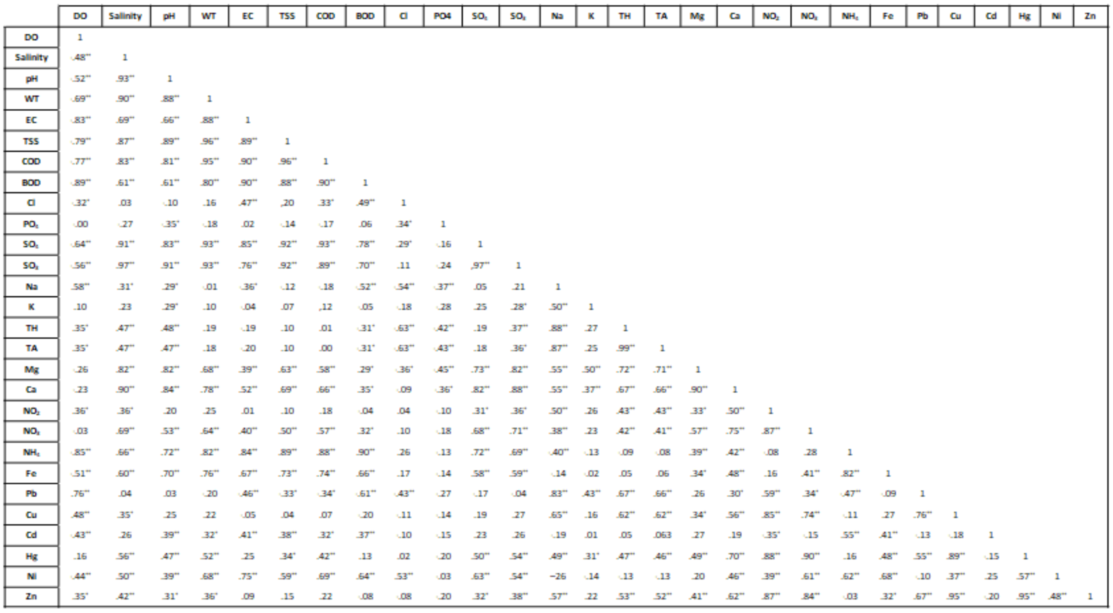
fertilizers (Kıymaz, 2010; Kıymaz and Karardavut, 2014). In the third factor, the presence of phosphate shows the effect of fertilizers and organic wastes. It was understood from the non-opposite directions that the sources of K and Cd are unnatural rocks. Pesticides contain nitrogen and phosphorus, which contribute to agricultural fertilization. Sugar beets, grains, barley, and corn are generally produced in the lake basins. Besides, the flow of phosphorus from agricultural lands to lake basins causes contamination of the lake. Pearson's correlation test showed a negative correlation for pH, WT, EC, TSS, and COD. Also, the values of pH, WT, EC, SSD, BOD, NO, Mg, Ca, NH_4, Fe, and Ni showed a positive correlation with each other. There was a positive correlation between NO_3 and NH_4, as well. Na, Ca, and HCO_3 are the dominant ions in natural water. Similarly, there was a positive correlation between heavy metals and trace elements. Major sources of these heavy metals were the phosphate and inorganic nitrate fertilizers used in agricultural lands (Table7).

Table 7. Results of correlation analysis of the physiochemical parameters of the dam lake of study



	DO	Salinity	pH	WT	EC	TSS	COD	BOD	Cl	PO4	SO_4	SO_4	Na	K	TH	TA	Mg	Ca	NO_2	NO_3	NH_4	Fe	Pb	Cu	Cd	Hg	Ni	Zn
DO	1																											
Salinity	-.48**	1																										
pH	-.52**	.93**	1																									
WT	-.69**	.90**	.88**	1																								
EC	-.83**	.69**	.66**	.88**	1																							
TSS	-.79**	.87**	.89**	.96**	.89**	1																						
COD	-.77**	.83**	.81**	.95**	.90**	.96**	1																					
BOD	-.89**	.61**	.61**	.80**	.90**	.88**	.90**	1																				
Cl	-.32*	.03	-.10	.16	.47**	,20	.33*	.49**	1																			
PO_4	-.00	-.27	-.35*	-.18	.02	-.14	-.17	.06	.34*	1																		
SO_4	-.64**	.91**	.83**	.93**	.85**	.92**	.93**	-.78**	.29*	-.16	1																	
SO_4	-.56**	.97**	.91**	.93**	-.76**	.92**	.89**	-.70**	.11	-.24	,97**	1																
Na	.58**	.31*	.29*	-.01	-.36*	-.12	-.18	-.52**	-.54**	-.37**	.05	.21	1															
K	.10	.23	.29*	.10	-.04	.07	,12	-.05	-.18	-.28	.25	.28*	.50**	1														
TH	.35*	.47**	.48**	.19	-.19	.10	.01	-.31*	-.63**	-.42**	.19	.37**	.88**	.27	1													
TA	.35*	.47**	.47**	.18	-.20	.10	.00	-.31*	-.63**	-.43**	.18	.36*	.87**	.25	.99**	1												
Mg	-.26	.82**	.82**	.68**	.39**	.63**	.58**	.29*	-.36*	-.45**	.73**	.82**	.55**	-.50**	.72**	.71**	1											
Ca	-.23	.90**	.84**	.78**	.52**	.69**	.66**	.35*	-.09	-.36*	.82**	.88**	.55**	-.37**	.67**	.66**	.90**	1										
NO_2	.36*	.36*	.20	.25	.01	.10	.18	-.04	.04	-.10	.31*	.36*	.50**	.26	.43**	.43**	.33*	.50**	1									
NO_3	-.03	.69**	.53**	.64**	.40**	.50**	.57**	.32*	.10	-.18	.68**	.71**	.38**	.23	.42**	.41**	.57**	.75**	.87**	1								
NH_4	-.85**	.66**	.72**	.82**	.84**	.89**	.88**	.90**	.26	-.13	.72**	.69**	-.40**	-.13	-.09	-.08	.39**	.42**	-.08	.28	1							
Fe	-.51**	.60**	.70**	.76**	.67**	.73**	.74**	.66**	.17	-.14	.58**	.59**	-.14	-.02	.05	.06	.34*	.48**	.16	.41**	.82**	1						
Pb	.76**	.04	.03	-.20	-.46**	-.33*	-.34*	-.61**	-.43**	-.27	-.17	-.04	.83**	-.43**	.67**	.66**	.26	.30*	.59**	.34*	-.47**	-.09	1					
Cu	.48**	.35*	.25	.22	-.05	.04	.07	-.20	-.11	-.14	.19	.27	.65**	.16	.62**	.62**	.34*	.56**	.85**	.74**	-.11	.27	.76**	1				
Cd	-.43**	.26	.39**	.32*	.41**	.38**	.32*	.37**	-.10	-.15	.23	.26	-.19	.01	.05	.063	.27	.19	-.35*	-.15	.55**	.41**	-.13	-.18	1			
Hg	.16	.56**	.47**	.52**	.25	.34*	.42**	.13	.02	-.20	.50**	.54**	.49**	.31*	.47**	.46**	.49**	.70**	.88**	.90**	.16	.48**	.55**	.89**	-.15	1		
Ni	-.44**	.50**	.39**	.68**	.75**	.59**	.69**	.64**	.53**	.03	.63**	.54**	−26	-.14	-.13	-.13	.20	.46**	.39**	.61**	.62**	.68**	-.10	.37**	.25	.57**	1	
Zn	.35*	.42**	.31*	.36*	.09	.15	.22	-.08	.08	-.20	.32*	.38**	.57**	.22	.53**	.52**	.41**	.62**	.87**	.84**	-.03	.32*	.67**	.95**	-.20	.95**	.48**	1

Hazard index (HI index). The health risks of surface water in the Karaca Pond were calculated using the US EPA risk evaluation models. With the help of Hazard Quotients (HQ), the intake of seven heavy metals to the body and its absorption through the skin were calculated (Tables 8 and 9). These values should not be more than 1. The hazard index (HI) values for children are higher than that of adults. However, the observed values for both children and adults were lower than 1. The total hazard index metal contamination is as follows: Pb >Cu >Cd >Ni> Hg >Fe.

Table 8. *Hazard quotient (HQ) and hazard index (HI) for the trace levels in the Karaca Dam*

	Adult		Child		Adult		Child		Adult	Child
Pb	1.67×10^{-3}	7.40×10^{-6}	1.87×10^{-3}	1.65×10^{-5}	1.19×10^{-3}	1.75×10^{-5}	1.33×10^{-3}	3.92×10^{-5}	1.12×10^{-3}	1.37×10^{-3}
Cd	3.29×10^{-4}	3.43×10^{-5}	3.68×10^{-4}	7.59×10^{-5}	6.57×10^{-4}	1.37×10^{-3}	7.36×10^{-4}	3.03×10^{-3}	2.02×10^{-3}	3.77×10^{-3}
Fe	7.52×10^{-4}	2.80×10^{-4}	8.42×10^{-4}	6.20×10^{-4}	$1{,}07 \times 10^{-6}$	2.00×10^{-6}	1.20×10^{-6}	4.43×10^{-6}	3.08×10^{-6}	5.63×10^{-6}
Cu	7.80×10^{-2}	7.14×10^{-4}	8.73×10^{-2}	1.58×10^{-3}	1.95×10^{-3}	8.93×10^{-5}	2.18×10^{-3}	1.97×10^{-4}	2.04×10^{-3}	2.38×10^{-3}
Zn	5.95×10^{-2}	9.32×10^{-4}	6.66×10^{-2}	2.06×10^{-3}	1.98×10^{-4}	1.55×10^{-5}	2.22×10^{-4}	3.43×10^{-5}	2.14×10^{-4}	2.57×10^{-4}
Ni	5.14×10^{-3}	1.34×10^{-4}	5.76×10^{-3}	2.97×10^{-4}	2.57×10^{-4}	1.68×10^{-4}	2.88×10^{-4}	3.71×10^{-5}	4.25×10^{-4}	3.25×10^{-4}

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Table 9. *Reference done (RfD) in the Karaca dam.*

	Kp^a	$RFD^a_{ingestion}$	$RFD^a{}_{dermal}$	ABS$_g$ $(\%)^b$
		µg/kg/day	µg/kg/day	%
Pb	$1x10^{-4}$	1.4	0.42	11.7
Cd	$1x10^{-3}$	0.5	0.025	5
Fe	$1x10^{-3}$	700	140	1,4
Cu	$1x10^{-3}$	40	8	57
Zn	$6x10^{-4}$	300	60	20
Ni	$2x10^{-4}$	20	0.8	4
Hg	$1x10^{-3}$	0.3	0.021	7

[a] = [b] =

The values obtained by Tesi et al., (2019) in the river delta showed similarity with our study. Pb, Cd, Fe, Cu, Zn, Ni, and Hg concentrations are quite low. Pb, which causes hematopoietic toxicity, was reported to be within limits. Kidney failure and immune deficiencies, along with bone injuries, are caused by Cd. Co is related to allergic dermatitis and rhinitis.

Conclusions

To determine the water quality of Karaca Dam Lake,which is used to provide drinking water, irrigation water to the sur-rounding area, samples were taken for 12 months from four stations representing the entire dam lake and waterquality analyses were carried out. To determine water quality, WQI was calculated by taking into account WHO (2011) standards. WQI values in the lake were found to be between 16.47 and 21.70. According to these results, Karaca Dam Lake surface water is in the 'Excellent class'. In the calculations made to determine irrigation water quality, the surface waters were found suitable in terms of SAR and sodium percent age content, whereas different properties were determined in terms of RSC throughout the year. According to SWQR, the water quality was found to be 'very good' in terms of DO, COD, BOD, nitrate and ammonium, but in terms of phosphate, it varied in range between the 'very good' and 'medium' classes . This suggests that there are no nutrient inputs from the surrounding domestic and agricultural areas that could damage the health of the eco-system. The limit values for heavy metals Cu, Zn and Fe were exceeded. The results of the present study showed that water quality parameters are within limits permitted by the WHO. Besides, this study is a pioneering effort for further investigation and risk assessment of trace metals present in water bodies located in regions with limited information in the Sinop province.

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