

**Evaluation of Some Physico-Chemical Characteristics
of Kemeriz Dam (Zara – Sivas)****Ekrem MUTLU^{1*}, Tuğba DEMİR²**¹Faculty of Fisheries, Kastamonu University, 37150- Kastamonu, Turkey.²Kamer Örnek Vocational High School, Cumhuriyet University, Sivas, Turkey.

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Abstract

The objectives of this study were to observe the monthly and annual changes in water samples through physico-chemical methods, to determine the water quality properties, to reveal the pollution problems, to determine the suitability level in terms of aquatic life, and to classify the quality of water in accordance with the Surface Water Quality Regulation (SWQR) criteria. This study was carried out through monthly sampling during January 2011-December 2013 in 3 stations at Kemeriz Dam. The water quality in Kemeriz dam was found to be Class II according to the SWQR. In order to protect the water quality and to ensure the health of aquatic life in this dam, it is required to make regular observations and to monitor the parameters affecting the water quality and aquatic life.

Keywords: Sivas, Kemeriz, water quality, Kemeriz Dam.**Öz****Kemeriz Barajı Gölünün (Zara – Sivas) Bazı Fizikokimyasal Özelliklerinin Değerlendirilmesi**

Bu çalışmanın amacı fiziko-kimyasal metotlarla su örneklerindeki aylık ve mevsimsel değişiklikleri gözlemlemek, su kalitesi özelliklerini belirlemek, kirlilik sorunlarını ortaya koymak, sucul hayat için uygunluğu ortaya çıkarmak ve Yüzey Suları Kalitesi Düzenlemesi (YSKY) kriterleri uyarınca suyun kalitesini sınıflandırmaktır. Bu çalışma Ocak 2011 ile Aralık 2013 arasında aylık olarak Kemeriz Baraj Gölü üzerinde 3 istasyondan alınan su örnekleri ile gerçekleştirilmiştir. Kemeriz Baraj Gölünün su kalitesi YSKY kriterlerine göre 2. Sınıf olarak bulunmuştur. Su kalitesini korumak ve sucul hayatın sağlıklı devamlılığı için düzenli gözlemler yapmak ve su kalitesi ve sucul hayatı etkileyecek parametreleri takip etmek gerekmektedir.

Anahtar Kelimeler: Sivas, Kemeriz, su kalitesi, Kemeriz Baraj Gölü.**Introduction**

Water is the main source of life and is also a necessity for the organisms' survival. Total water stock of the world is 1.4 billion km³, and only 2.5% of this amount is in lakes and fresh water sources. 90% of this scarce water stock is in poles and under the ground (Anonymous, 2013). There is an increasing inclination and awareness

towards protecting the earth, and tracking the environmental effects and changes in the entire world. For this reason, the terms “sustainable development” and “environment management” nowadays became two fundamental concepts that should be considered together. The most important one of these interactions is the negative

effects of environmental or water pollution on the aquatic organisms and aquatic life (Mert et al., 2010).

In addition to the ponds containing most of the fresh water resources of the world, the reservoirs that are artificial water stocks are very limited because of their structural properties and locations (Yılmaz Öztürk and Akkoz, 2014). The number of reservoirs and barrages in our country is, except the natural lakes, 715 (Anonymous, 2015a). From the aspects of the parameters such as high flow rate, high concentration of suspended solid matters, presence of density flows, the effects of leakage water on the amount of nutrients, and short water renewal duration, the reservoirs and dams are known to be affected more from the pollution in basin due to their differences from the natural lakes and the width of the drainage basin (Alpaslan et al., 2013).

The ponds and lakes, which are constant receivers, are primarily affected from the pollution. For this reason, the water levels of the lakes and ponds gradually decrease and become unusable, so those water resources become unsuitable for the lives of fishes, aquatic creatures and organisms that live within those waters (Mutlu et al., 2014). For those reasons, it is very important to analyze the physicochemical properties of the waters of reservoirs and dams regularly and to monitor the changes. Since no study has been carried out on the water quality parameters of Kemeriz Dam, this study gains more importance.

Through the analysis of water samples taken monthly from 3 sampling stations, which are representing the whole of the dam, for 3 years between January 2011 and December 2013, the aim of this study is to reveal the water quality properties of Kemeriz Dam, one of the most important dams of Zara district, to classify

the water quality according to Surficial Water Quality Regulation (SWQR) (Anonymous, 2012, Anonymous, 2015b), and to establish a database for further studies to be carried out in this dam.

Materials and Methods

Study Area; Kemeriz Dam (39° 58' 48.58"N, 37° 37' 18.34"E) is located in Upper Kızılırmak basin, within the borders of Gümüşçevre village of Zara district. The dam is 17 km away from Zara district and 87 km from Sivas city center. Its altitude is 1518 m. The water sources of Kemeriz dam are Brook Karakaya and the precipitation and snow waters. Kemeriz dam has 2 hm³ of storage volume and 8.4 m of mean depth, and has been constructed for irrigation purposes. While determining the sampling stations on the dam, we consider the points that represent characteristics of dam homogeneously. The locations of the sampling stations are tagged on the map (Figure 1).

1st station is located at the entrance point of Brook Karakaya into the dam, 2nd station is at southwestern side of the dam (near the road), and 3rd station is in the middle of dam.

Water Analysis; In this study starting from January 2011, samples used in analyses of chemical and physical parameters constituting

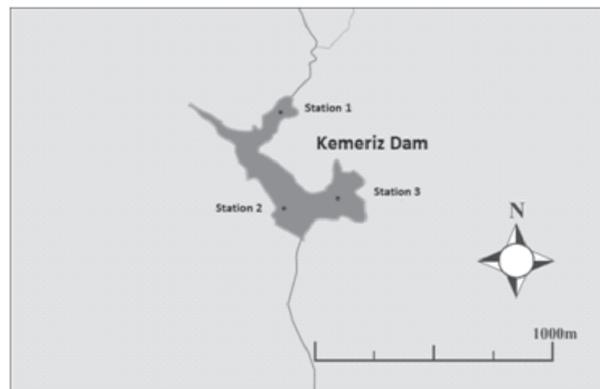


Figure 1 - Location of Kemeriz Dam.

the water quality were monthly collected from 3 stations for 36 months. The sampling ended at December 2013. The sampling tubes to be used in water sampling have been flushed and immersed into 15 cm below water surface for taking water sample. The obtained water samples have been taken to the laboratory within maximum 3 hours for analysis. Temperature, pH, dissolved oxygen, and electrical conductivity parameters have been measured in-place via land-type measurement devices.

Dissolved oxygen and temperature were measured via YSI brand S2 model oxygen-meter, pH measurement was conducted with Orion brand 420A model pH-meter, and saltiness (ppt) and the electrical conductance ($\mu\text{s}/\text{cm}$) were measured by using YSI brand 30/50 FT model conductance-meter.

Among other parameters determining water quality; total alkalinity, total hardness, ammonium nitrogen, nitrite, nitrate, phosphate, sulfite, sulfate chloride, sodium, potassium, suspended solid matter (SSM), chemical oxygen demand (COD), biological oxygen demand (BOD), calcium, magnesium, ferrous, lead, copper, zinc, nickel, mercury and cadmium analyses of water samples were conducted in Cumhuriyet University Hafik Kamer Örnek Vocational High School Laboratory in the same day.

Titration with sulfuric acid (for total alkalinity) and titration with EDTA (for total hardness) were executed. The results were presented in mg/L CaCO_3 unit. Chemical oxygen level was calculated through titration with ferrous ammonium sulfate based on determination of amount of oxygen being used while lysing the natural and organic pollutant load by using powerful chemical oxidants. The level of biological oxygen demand was

calculated via WTW brand Oxi Top BSB BOD DBO biological oxygen demand measurement device. The analyses of ammonia, nitrite, nitrate, ammonium nitrogen (NH_4^+), phosphate, sulfate, sulfite, chloride, sodium, potassium, calcium, and magnesium were conducted with CECIL CE4003 spectrophotometer by using Merck photometric test kits according to standard methods for the Examination of Water and Wastewater (Anonymous, 1998). The analyses of lead, copper, ferrous and cadmium, mercury, nickel, and zinc of water samples were conducted via ELMER ANALIST 800 Atomic Absorption Spectrometer from PERKIN ELMER in laboratory. The analysis of Suspended Solid Matter (SSM) was conducted by filtering the water through Whatman brand 42 Nr 0.45 μm membrane filters, and then keeping filter papers at 103°C for 24 hours and calculating the weight difference.

Monthly mean values, and standard deviations of each of the parameters were calculated by using Office Excel 2007, which is a part of Microsoft Office Professional Edition 2007.

Results

The temperature and dissolved oxygen values are also inversely proportional to each other. The overall maximum, minimum and mean values of the parameters are presented in Table 1.

As it can be seen there, the minimum temperature measured throughout the study period is 2.6°C in year 2011, while the maximum value is 23.82°C that was measured in year 2013. The mean temperature values of the stations were 13.10°C for 1st station, 13.30°C for 2nd station and 12.99°C for 3rd

Table 1. Mean, maximum and minimum values of the water quality parameters of the stations

Year	2011			2012			2013		
	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.
Dissolved Oxygen (mg/L)	12.59	11.54	13.60	11.99	11.19	13.34	10.96	9.68	12.68
Salinity	0.03	0.00	0.07	0.04	0.00	0.08	0.06	0.00	0.10
pH	8.00	7.78	8.19	8.03	7.80	8.21	8.07	7.83	8.26
Temperature (°C)	12.50	2.60	22.52	13.15	3.30	22.59	13.75	3.90	23.82
Electrical Conductivity	147.09	130.10	165.90	151.40	133.76	169.56	158.17	136.21	177.38
Suspended Solid Matter (mg/L)	0.55	0.17	0.95	0.72	0.09	1.06	1.28	0.35	1.73
Chemical Oxygen Demand (mg/L)	0.83	0.27	1.33	1.04	0.43	1.47	1.69	0.24	2.28
Biological Oxygen Demand (mg/L)	0.40	0.07	0.71	0.44	0.12	0.75	0.48	0.11	0.80
Chloride (mg/L)	8.70	6.47	9.57	8.36	6.11	9.21	7.98	5.55	9.79
Phosphate (mg/L)	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01
Sulfate (mg/L)	43.37	22.76	67.24	46.01	25.10	69.58	49.01	25.24	73.18
Sulfide (mg/L)	1.03	0.60	1.52	1.45	0.84	3.56	1.58	0.82	2.10
Sodium (mg/L)	64.01	52.80	81.00	63.08	9.87	82.08	65.09	53.94	82.14
Potassium (mg/L)	4.97	3.51	7.04	5.44	3.97	7.50	5.54	4.09	7.62
Total Hardness (mg/L)	292.95	269.90	324.54	294.12	270.98	325.62	295.12	272.20	326.84
Total Alkalinity (mg/L)	293.37	272.02	325.00	294.55	273.10	326.08	295.54	274.32	327.30
Magnesium (mg/L)	40.88	36.56	49.52	41.40	36.98	49.94	42.27	38.04	51.00
Calcium (mg/L)	41.46	37.08	50.44	42.02	37.13	51.01	42.46	38.06	51.80
Nitrite (mg/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nitrate (mg/L)	0.76	0.48	1.18	0.90	0.60	1.30	1.03	0.61	1.46
Ammonium Nitrogen (mg/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ferrous (mg/L)	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01
Lead (µg/L)	0.42	0.00	1.58	0.53	0.00	1.62	0.70	0.00	2.48
Copper (µg/L)	2.08	0.00	8.00	6.56	0.00	15.00	7.83	0.00	17.00
Cadmium (µg/L)	0.38	0.00	1.30	0.51	0.00	1.50	0.57	0.00	1.60
Mercury (µg/L)	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.01
Nickel (µg/L)	4.36	0.00	17.00	6.28	0.00	20.00	6.95	0.00	19.00
Zinc (µg/L)	22.50	2.00	54.00	26.56	6.00	58.00	27.42	7.00	59.00

station. While the minimum dissolved oxygen level measured was 9.72 mg/L in 1st station, the maximum dissolved oxygen concentration was 13.60 mg/L in 3rd station. As it can be seen, there is an inverse proportion between temperature and dissolved oxygen parameters. The minimum suspended solid matter (SSM) level was found to be 0.09 mg/L in 2nd station, while the maximum SSM level was determined to be

1.73 mg/L in 2nd station. The minimum chloride concentration was determined to be 5.55 mg/L in 3rd station, while the maximum chloride concentration was found to be 9.79 mg/L in 2nd station. While the maximum pH value was 8.26 in 2nd station, the minimum level of pH measured in this study was 7.78 in 3rd station. On the other hand, the minimum magnesium concentration was 36.56 mg/L in 3rd station,

while the maximum concentration that was measured in this study was 51.00 mg/L in 2nd station. In addition to the magnesium concentrations, the minimum level of the calcium determined in this study was 7.08 mg/L in 3rd station, while the maximum level was found to be 51.80 in 3rd station. As it can be seen, there is a parallelism between the pH values and magnesium/calcium concentrations.

It is known that the alkalinity values are correlated with the total hardness values. While the minimum total hardness value measured in this study was 269.10 mg/L in 3rd station, the maximum level was found to be 326.84 mg/L in 2nd station. Moreover, the minimum total alkalinity level was 272.02 mg/L that was measured in 3rd station, while the maximum total alkalinity level was measured to be 327.30 mg/L in 2nd station. It can be concluded here that there is a parallelism between the total alkalinity and the total hardness parameters.

Within the scope of this study, the sodium concentrations were also examined. While the minimum sodium level throughout the study was 49.87 mg/L in 3rd station, the maximum sodium concentration was found to be 82.14 mg/L in 2nd station. On the other hand, the sodium concentrations are related with the potassium levels. While the minimum potassium level was 3.51 mg/L, which was measured in 3rd station, the maximum potassium level was measured to be 7.62 mg/L in 2nd station.

The concentrations of sulfate and phosphate are correlated with the use of agricultural fertilizers. The minimum sulfate level was 22.76 mg/L in 3rd station, while the maximum sulfate concentration was found to be 73.18 mg/L in 2nd station.

In addition to that, the minimum phosphate level was measured to be under the measurable limits in all of 3 stations, while the maximum phosphate concentration was found

to be 0.01 mg/L in all of the stations.

The nitrite levels were also measured to be lower than measurable limits. But, the minimum nitrate level was 0.48 mg/L in 3rd station, while the maximum level was found to be 1.46 in 1st station.

In addition to other parameters, the heavy metal levels were also examined within the scope of this study.

While the maximum lead concentration was 2.48 µg/L that was measured in 3rd station, the minimum level was found to be lower than the measurable limits in all of the stations. In addition to lead level, the minimum level of copper determined in this study was lower than the measurable limits in all 3 stations, while the maximum level was determined to be 17.00 µg/L in 2nd station.

While the minimum concentration was lower than the measurable limit in all stations for calcium, the maximum cadmium level was found to be 1.60 µg/L in 2nd station. On the other hand, the minimum zinc level was 2.00 µg/L that was measured in 3rd station, while the maximum zinc concentration was measured to be 59.00 µg/L in 2nd station.

The minimum nickel level in this study was lower than the measurable limits in all 3 stations, while the maximum concentration was found to be 20.00 µg/L in 2nd station. On the other hand, while the minimum mercury levels were lower than the measurable limits in all 3 stations, the maximum concentration was measured to be 0.01 µg/L in all the stations.

Discussion

One of the most important factors influencing the biological activity of the aquatic organisms and fish is the water temperature. The changes in this parameter result from seasonal temperature changes (Mutlu *et al.*, 2013 b). The

temperature differences measured in 3 stations during the study were not at the level that can affect the aquatic life negatively.

pH is a parameter indicating the chemical and biological properties and used for classifying the weak acid and alkalinity. This classification determines the toxicity level of many compounds (Atay and Pulatsü, 2000). For a water sources that is suitable for aquaculture, the pH value vary between 6.5 and 8.5 (Kara and Gömlekçioğlu, 2004). The mean value of water samples taken during this study was 8.03, while the maximum value was 8.26. According to these results, it can be concluded that the dam has mildly basic character and is in first class according to SWQR in terms of pH value and suitable for aquaculture.

Dissolved oxygen (DO) concentration is another parameter that affects the development of a balanced fauna. Besides being important for aquatic life, DO is also required for biochemical oxidations. In fresh waters, the minimum level of dissolved oxygen should be at least 5 mg/L for the aquatic life (Atay and Pulatsü, 2000). The lowest DO value measured in this study was 9.72 mg/L; this level indicates that the water of Kemeriz Dam is suitable for aquaculture from the aspect of DO concentration, and it is in Class I in accordance with SWQR.

Chemical Oxygen Demand (COD) is another parameter used for finding the level of pollution in waters and waste waters (Mutlu et al., 2013c). The COD level of the waters higher than 25 mg/L indicate the presence of pollution, while the values more than 50 mg/L indicate the severe pollution and possible toxicity for aquatic organisms (Güler, 1997). The maximum COD value measured in Kemeriz Dam was 2.28 mg/L. In accordance with the SWQR and the rule that the worst value determines the

class, the Kemeriz Dam is in Class I from the aspect of COD.

Biological Oxygen Demand (BOD) shows the oxygen amount that is required by the microorganisms for dissolving the organic matters in the aquatic environment under aerobic conditions. It is used for determining an environment's pollution potential and a receiver environment's assimilation capacity by calculating the amount of dissolved oxygen that they consume while being released into the receiving mediums (Anonymous, 2013). The maximum BOD value in Kemeriz Dam was 0.80 mg/L, and it is Class I according to SWQR in terms of BOD.

Electrical conductivity (EC) is another important parameter for aquatic products; the conductivity level exceeds 100 $\mu\text{s}/\text{cm}$ when the pollution increases (Verep et al., 2005). The electrical conductivity values decrease in winter months, and increase in months when the water temperature and inorganic salts in the system increased. The maximum EC value in this study was 177.38 $\mu\text{s}/\text{cm}$, and it is Class I according to SWQR in terms of electrical conductivity.

Suspended Solid Matter (SSM) amount consists of inorganic matters such as clay and loam. The maximum acceptable level of SSM in aquaculture was specified as 10 mg/L (Ntengue, 2006). The maximum SSM amount determined in Kemeriz Dam during the study was 1.73 mg/L, which means that the conditions in the dam are suitable for aquaculture.

The sources of the nitrogen penetrating into the surface waters are originated from natural domestic and agricultural resources (Mutlu et al., 2013a). The nitrite (NO_2^-) sources in waters are the organic matters, nitrogenous fertilizers, and some of minerals.

The nitrite concentration in waters higher than 1 mg/L indicates the presence of pollution (Taş, 2011). While the concentration of NO_2^- in natural waters is low, it is high in waters where the organic pollution is high (İmamoğlu, 2000). Nitrogen derivatives of nitrite (NO_2^-), nitrate (NO_3^-) and ammonium nitrogen (NH_4^+) play important role in the process of water pollution, while they also significantly affect the level of dissolved oxygen and eutrophication. According to the SWQR, the dam has Class I water characteristic from the aspect of nitrite (NO_2^-) and ammonium nitrogen.

Nitrate (NO_3^-) is the final product of nitrogenous organic matters. High concentration of nitrate in surface waters indicates that the water has been polluted before by the industrial and domestic wastewaters containing ammonium and organic nitrogen and the fertilizers used in agricultural lands and containing nitrate (Topal and Arslan Topal, 2012). Even though the low doses of nitrate are not toxic for fish, it has been reported that fish mortality starts at the doses of 4 mg/L and higher (Acu, 2000). Its concentration within surface waters is an indicator of the pollution of those waters caused by domestic and industrial waste waters containing ammonium and organic nitrogen and the nitrogenous fertilizers used in agricultural lands (Topal and Arslan Topal, 2012). According to the SWQR, Kemeriz Dam is Class I water in terms of nitrate (NO_3^-).

The total alkalinity and total hardness values in lime soils are similar with each other (Boyd and Tucker, 1998). The alkalinity levels of the natural waters vary between 5 and 500 mg/L, and are closely related with the structure.

The carbonate and bicarbonate give the alkalinity to the water (Tepe et al., 2006). According to the results obtained from our analyses, it can be concluded that the Kemeriz Dam has mildly-hard water characteristics.

Among natural anions of the water, the presence of the sulfate (SO_4^{2-}) in natural resources is important for the improved biological productivity (Taş et al., 2010). The maximum limit for sulfate in water from the aspect of aquatic products has been determined as 90 mg/L (Küçük, 2007). The maximum sulfate level was measured to be 73.18 mg/L in this study. Besides the sulfate, also the chloride level is an important indicator of healthy water. The maximum chloride amount measured during this study was 9.79 mg/L. These values can be considered as suitable for aquaculture.

The phosphor in water resources is an element that is necessary for eutrophication (Harper, 1992). The reason for fluctuation in phosphorus level is the use of agricultural fertilizers containing phosphor. The maximum level of phosphate in the dam was 0.01 mg/L. This phosphate concentration doesn't jeopardize the aquaculture activities and the aquatic life.

Ca^{++} and Mg^{++} are the most important dissolved solid matters in water (Mutlu et al., 2013b). Mg^{++} and Ca^{++} are alkali soil minerals, and are among the ions existing in fresh waters at most. The maximum recommended Ca^{++} level is reported to be 75 mg/L (Taş, 2006). In our study, the maximum calcium (Ca^{++}) level was found to be 51.80 mg/L. This calcium concentration indicates that the amount of Ca^{++} in Kemeriz Dam is within the acceptable limits. The level of magnesium in natural waters should vary from 5 mg/L to 60 mg/L. In mildly hard waters, the values between 60 and 100 mg/L can be accepted as typical, and the recommended concentration of Mg^{++} is 50 mg/L (Taş, 2006). In our study performed in Kemeriz Dam, the maximum value found is 51.00 mg/L. The concentration of potassium (K^+) and sodium (Na^+) vary within the ranges of 1-10 mg/L and 2-100 mg/L in natural waters,

respectively (Boyd, 1998). The maximum potassium level in our study was 7.62 mg/L that can be considered to be within the normal ranges, while the maximum level of sodium concentration was found to be 82.14mg/L. Under the light of these results, it can be stated that the sodium and potassium levels of Kemeriz Dam are considered to be within the acceptable limits.

The waters having lead (Pb) concentration of 0.01 mg/L and higher are considered to be polluted. It has also been reported that the lead affects the osmotic balance and ion arrangement in fish and leads to histopathologic change in liver (Atay and Pulatsü, 2000).

Although the presence of cadmium (Cd) in waters at the concentration of 5 µg/L and higher is reported to be toxic and it directly leads to mortality in aquatic organisms at high concentrations, it leads to metabolic and physiologic disorders and changes especially in fish (Mutlu, 2013a). The maximum levels of lead (Pb) and cadmium (Cd) in Kemeriz Dam were found to be 2.48 µg/L and 1.60 µg/L, respectively. The reason for this this level of cadmium concentration in the dam can be the utilization of artificial phosphate fertilizers for the agricultural purposes around the lake. Under the lights of those values, it can be concluded that the dam has Class I water characteristic from the aspect of lead (Pb) and cadmium (Cd) elements according to SWQR.

Maximum concentration of the copper (Cu) element was 17.00 µg/L. The reason for this level is believed to be the penetration of copper, which accumulate in the soil due to common use of copper vitriol during maintenance and pruning in fruit gardens, into the dam via the rain waters. According to the SWQR,

the dam has Class I water characteristic from the aspect of copper (Cu).

The maximum concentration of ferrous (Fe) in the dam was 0.01 mg/L. Since the use of ferrous-containing agricultural pesticides for increasing the grain productivity of wheat plants increases especially between May and June, the ferrous-containing waters and particles can penetrate into the dam through the rain waters and the leakages.

The maximum concentrations of Zinc (Zn), nickel (Ni) and mercury (Hg) during the study have been found to be 59.00 µg/L, 20.00 µg/L, and 0.01 µg/L, respectively. This mercury concentration can be caused from the flows from cultivation areas into the lake, since the use of fertilizers is very common in Zara district. Under the lights of these values, it can be concluded that the dam has Class I water characteristic in terms of zinc (Zn), and mercury (Hg) and Class II in terms of nickel (Ni) according to SWQR.

It is widely known that the heavy metals constitute an important pollutant group and, besides their important toxic and carcinogenic effects, they also accumulate within the bodies of living organisms. Heavy metals having strong poisonous effects, even at very low concentrations, can disrupt the self-cleaning of natural waters, and they are also important for the usability of water sources for irrigation and aquaculture purposes.

As it can be seen in results of the analyses, the water quality in Kemeriz dam is considered to be Class II according to SWQR. In order to protect the water quality and to ensure the health of aquatic life in this dam, it is required to make regular observations and to monitor the parameters affecting the water quality and aquatic life.

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