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Determination Of Trace Metal Levels In Some Fish Species In Kılıçkaya Dam Lake From Sivas Turkey

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Abstract: Heavy metal pollution in water sources can cause critical health problems for people. Therefore, analysis of heavy metal accumulation of the living organisms in waters at certain periods should be conducted. İn this study fish samples were collected from the lake Kılıçkaya in Sivas, Turkey for analysis of trace metal levels. Fish species are *Cyprinus carpio, Leuciscus cephalus, Capoeta capoeta, Silurus glanis, Barbus plebejus and Clupeonella abrau muhlisi*. Sample analyses were performed by AAS. Fish species were dried at 109 ^{0}C for 3 days. Dried whole fish bodies one by one were powdered and homogenized. Later one gram of the samples was digested microwave technique. Trace metal levels (Fe, Mn, Zn, Cu, Pb, Cr, Ni, Co) were found between 102.7-268.0; 7.6-64.5; 34.8-65.1; 3.1-9.6; 5.4-8.2; 0.3-11.8; 1.1-20.5 and 0.7-4.1 µg/g, respectively.

Keywords: Fish; Trace metal; AAS; Microwave-solving method; Dam Lake; Sivas

Türkiye Sivas'tan Kılıçkaya Baraj Gölü'ndeki Bazı Balık Türlerinde Eser Metal Seviyelerinin Belirlenmesi

Öz: Su kaynaklarındaki ağır metal kirliliği, insanlar için kritik sağlık sorunlarına neden olabilir. Bu nedenle suda yaşayan canlı organizmalardaki ağır metal birikiminin analizi belli periyotlarda yapılmalıdır. Bu çalışmada, Sivas ilindeki Kılıçkaya Baraj Gölü'nden, Eser metal düzeylerinin analizi için balık örnekleri toplanmıştır. Balık türleri *Cyprinus carpio, Leuciscus cephalus, Capoeta capoeta, Silurus glanis, Barbus plebejus ve Clupeonella abrau muhlisi*'dir. Numune analizleri Alev ve grafit fırınlı AAS ile gerçekleştirildi. Balık türleri 109 °C'de 3 gün kurutuldu. Kurutulan balık gövdeleri bütün halinde toz haline getirilip ve homojen hale getirildi. Daha sonra bir gram numune mikrodalga tekniği ile çözüldü. Eser metal seviyeleri sırasıyla (Fe, Mn, Zn, Cu, Pb, Cr, Ni, Co) 102.7-268.0; 7.6-64.5; 34.8-65.1; 3.1-9.6; 5.4-8.2; 0.3-11.8; 1.1-20.5 and 0.7-4.1 µg/g, arasında bulundu.

Anahtar Kelimeler: Balık; Eser metal; AAS; Mikrodalga çözme yöntemi; Dam Lake; Sivas

1. Introduction

Trace metal pollution continues to be an important problem all over the world. Therefore, determination of trace metal levels has become more important todays at the environment. Various toxic and helpful elements are available in the environmental. Also waters may contain high concentrations of some toxic metals. Agricultural pesticides, industrial wastes, people activities, volcanic activities are caused accumulation of toxic metals in the waters. Because it has become a very big problem, determination of the amounts of these trace elements is very important in recent years. At the result of these reasons toxic metals in the waters can pass through to fishes. Therefore accumulation of heavy metal levels in the fish and water should be checked periodically. At the result of some heavy metals which accumulated in lake waters; it is observed that they cause serious problems for lives. Some of toxic elements in environmental samples can cause risk for human health (Arain et al., 2009). Depending on the concentrations of trace elements have beneficial

and harmful effects in plants, animals and humans (Mendil and Uluozlu, 2007). These heavy metals accumulation in lake is collected by the fish species. Therefore some fish die or become sick. For these reasons, the grown fish in these waters generates risk for human health.

Especially above reasons the analysis of accumulation of trace metal in organisms is very important, before consumption. Some spectrophotometric techniques analysis is very useful and helpful for solving of this problem in recent years. Various instrumental techniques are used today but (AAS) and (ICP-MS) are very widely used for the determination of trace metal levels in some environmental samples at the worldwide. In recent years quite a lot of fish is widely consumed all over the world because the fish is high in protein and nutrition source; also it contains omega3 extremely high which is good for heart health. Fish has been often at the top of the aquatic food chain (Mansour and Sidky, 2002). In recent years due to the benefits of fish, pisciculture has increased in the worldwide widely. China is the largest fish producer in the world, and China's fishery production accounts for about one third of the world's total fishery production. China has become the world's largest exporter of aquatic products. Therefore, the control of fish products in China is very important. Because it affects people's health all over the world. (Li et al., 2014).

This present study; it was analysed of some heavy metal levels in six fish species (*Cyprinus carpio, Leuciscus cephalus, Capoeta capoeta, Silurus glanis, Barbus plebejus and Clupeonella abrau muhlisi*) by AAS after microwave digestion method. Fish samples were collected from Kılıçkaya lake in Sivas, Turkey. Fish were transferred to with containers made of polyethylene in the laboratory.

2. Material and Method

2.1. Reagents

All of the reagents used in this study had analytical purity grade. All glass and plastic materials, firstly washed with warm water and detergent, rinsed with tap water and then washed with deionized water, it was waited in 10% (w/v) nitric acid solution. And then rinsed with deionized water before use. All aqueous solutions were prepared with using De-ionized water (18.2 MΩcm). Highest quality grade (Merck) acids and oxidants were used (HNO_3 and H_2O_2). Standard solutions of the studied metals were prepared by diluting a stock solution of 1000 mg/l of the given elements.

2.2. Instrumentation

The levels of trace elements (Fe, Mn, Zn, Cu, Pb, Cr, Ni, Co) were analyzed by A Perkin Elmer Analyst 700 model AAS instrument. For lead (Pb) and Cadmium (Cd) levels were determined for graphite furnace AAS. Samples were given by Perkin Elmer AS800 auto sampler into the graphite tube. The other metal levels were determined flame AAS. Milestone Ethos D microwave solving system was used for solving the samples.

2.3. Preparation of samples

Samples were collected from Kılıçkaya Lake in Sivas, Turkey in summer months. Samples were brought to the laboratory in disinfected containers and washed with deionized water and only one of each fish species was dried in Petri dishes at 100 ^{0}C, later these dried whole fish bodies samples one by one were homogenized and powdered. Later put in polyethylene bags. This polyethylene bags were hidden for analyzed day in the desiccator.

2.4. Microwave Digestion

One gram samples were weighed into the solving system containers. And then 6 ml HNO_3 (65%) and 2 ml H_2O_2 (30%) were injected into the containers respectively and microwave digestion method were applied 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W, and vent for 8 min. And same digestion method was applied for blank sample. Also this same solving procedure was applied by analysis of certified reference materials NRCC-DORM-2 Dogfish Muscle.

3. Results and Discussion

Various trace elements levels were determined in different fish species. The recovery values of certified reference materials were nearly quantitative. The relative standard deviations were found less than 10 % for all analyses elements. This method has been successfully applied in the determination of trace metal levels in fish specimens and in some other environmental samples. Also trace metals concentrations levels are listed in (Table 1).

Table 1. The concentration of trace metals (µg/g) in fish species.
Tablo 1. *Balık örneklerinde eser metal konsantrasyonu (µg/g).*

Fish species	Seasons	Fe	Mn	Zn	Cu	Pb	Cr	Ni	Co
Cyprinus carpio	Summer	237.2±21.2	18.2±1.2	58.8±5.4	6.7±0.5	6.8±0.6	0.3±0.02	2.2±0.1	1.3±0.1
Leuciscus cephalus	Summer	102.7±8.7	7.6±0.6	53.2±5.1	3.1±0.2	5.4±0.4	BDL	1.4±0.1	0.7±0.04
Capoeta capoeta	Summer	268.0±25.2	64.5±5.4	47.6±4.2	9.6±0.8	7.8±0.5	11.8±0.9	20.5±1.8	4.1±0.3
Silurus glanis	Summer	212.8±20.1	22.3±2.1	34.8±3.1	3.8±0.3	5.6±0.4	BDL	2.9±0.2	1.6±0.1
Barbus plebejus	Summer	196.0±18.2	18.9±1.6	48.3±4.2	4.2±0.3	8.2±0.6	2.7±0.2	1.9±0.1	1.4±0.1
Clupeonella abrau muhlisi	Summer	177.6±13.4	11.3±1.0	65.1±4.8	4.8±0.4	6.5±0.6	BDL	1.1±0.1	1.0±0.1

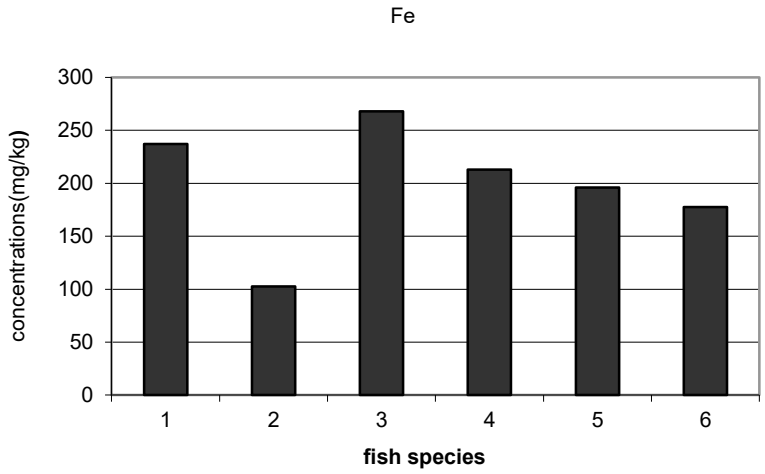
Also standard reference material analyses results were given in (Table 2). In our method, 95% to 98% of the trace metal contained in the standard reference material was detected with 95% confidence levels. According to these data the highest level of iron metal was found in samples, followed by zinc, manganese, nickel, chromium, copper, lead and cobalt respectively. At the result of according to these data the high metal accumulation in the *Capoeta capoeta* fish species were found for Fe, Mn, Ni, Cr, Cu, and Co, *Clupeonella abrau muhlisi* for Zn, *Barbus plebejus* for Pb.

Table 2. Trace element concentrations in standard reference material (NRCC-DORM-2 Dogfish Muscle), N=4
Tablo 2. *Standart Referans Maddedeki eser element konsantrasyonları (NRCC-DORM-2 Dogfish Muscle), N=4*

Element	Our value (µg/g)	Certified value (µg/g)	Recovery (%)
Fe	136.0±9.8	142	96
Mn	3.59±0.13	3.66	98
Zn	25.0±1.1	25.6	98
Cu	2.28±0.13	2.34	97
Pb	0.062±0.004	0.065	95
Cr	33.9±2.6	34.7	98
Ni	18.4±1.5	19.4	95
Co	0.176±0.011	0.182	97

3.1. Iron

Iron plays a very important role for biolgical sistem of human. Iron is formed complex with molecular of oxygen in hemoglobin and transport of protein to organisms. Also iron deficiency causes to anemia. In the present study the minimum and maximum levels of iron concentration values were found to be 102.7 µg/g in *Leuciscus cephalus* and 268.0 µg/g in *Capoeta capoeta* respectively. Fe minimum value has been reported as 102.0 µg/g (Mendil et al., 2005) and our Fe values were higher than other values (Karadede et al., 2004; Astorge-Espana et al.,1999). Iron levels in the fishes were shown in (Figure 1).



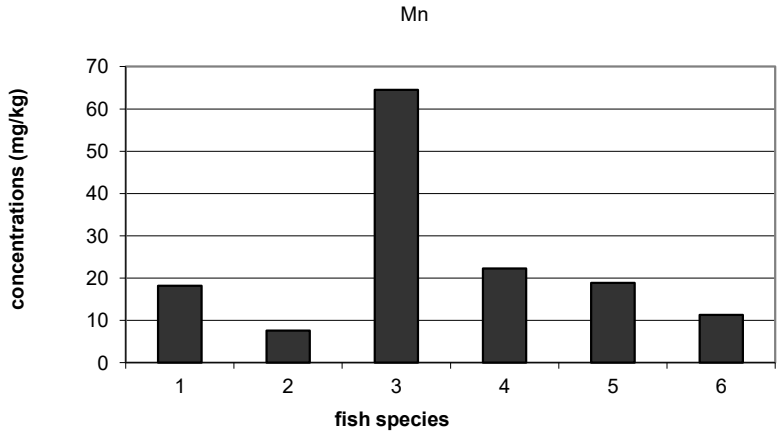
(1. Cyprinus carpio; 2. Leuciscus cephalus; 3. Capoeta capoeta; 4. Silurus glanis, 5. Barbus plebejus; 6. Clupeonella abrau muhlisi)

Figure 1. Fe results in fish species

Şekil 1. *Balık örneklerindeki Fe sonuçları*

3.2. Manganese

Manganese is one of the trace elements that play an important role in biological systems and is a structural component of some enzymes. The manganese concentrations were found from 64.5 µg/g to 7.6 µg/g in this study. These values were reported as 72.9 µg/g and 5.70 µg/g, respectively (Mendil et al., 2005; Karadede et al., 2004) Our manganese values were higher than other study values (Chale, 2002). The manganese amounts were displayed in (Figure 2).



(1. Cyprinus carpio; 2. Leuciscus cephalus; 3. Capoeta capoeta; 4. Silurus glanis, 5. Barbus plebejus; 6. Clupeonella abrau muhlisi)

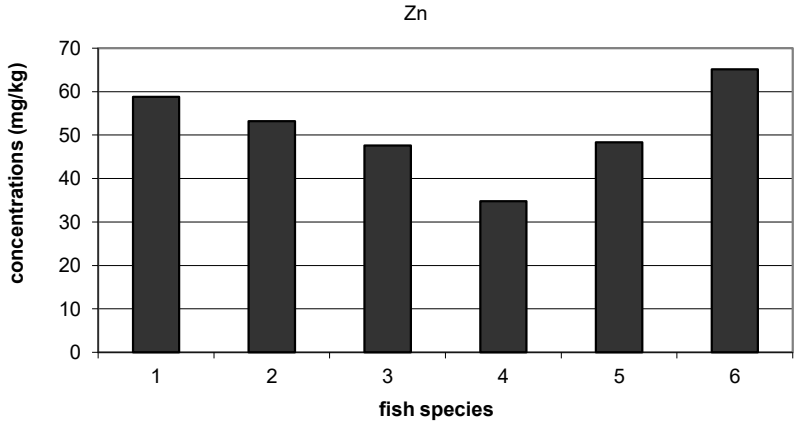
Figure 2. Mn results in fish species

Şekil 2. *Balık örneklerindeki Mn sonuçları*

3.3 Zinc

Essential Zinc element has a very important role in human health. also Zinc is a component of various enzymes involved in the synthesis and degradation of carbohydrates, lipids, proteins and nucleic acids. (WHO, 2002). Our zinc

concentrations were found from 65.1 µg/g to 34.8 µg/g. The lowest zinc concentration has been reported as 30.7 µg/g and 36.92 µg/g respectively (Karadede et al., 2004; Szefer et al., 2003). The highest zinc concentration has been reported as 73.8 µg/g (Atta et al., 1995). Our zinc concentrations lower than other literature values (Papagiannis et al., 2004) and higher than (Celik and Oehlenschlager 2004; Cid et al., 2001). Zinc concentrations in the fish samples were demonstrated in (Figure 3).



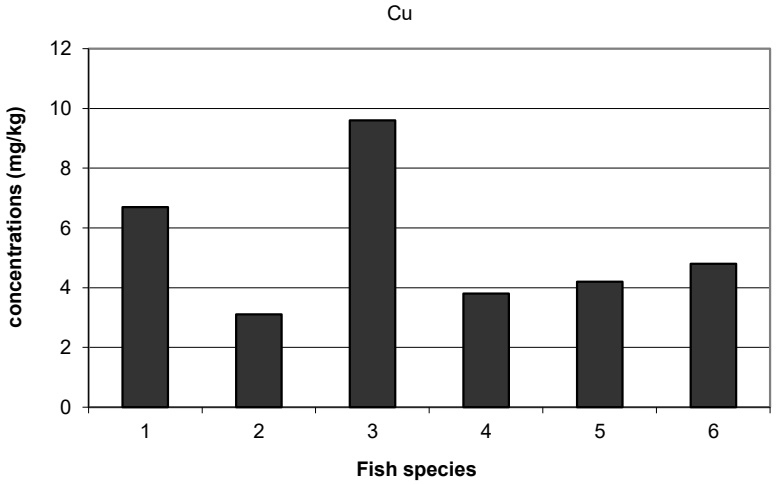
(1. Cyprinus carpio; 2. Leuciscus cephalus; 3. Capoeta capoeta; 4. Silurus glanis, 5. Barbus plebejus; 6. Clupeonella abrau muhlisi)

Figure 3. Zn results in fish species

Şekil 3. *Balık örneklerindeki Zn sonuçları*

3.4 Copper

Copper is considered necessary for good health, but very high purchases can cause adverse health effects such as liver and kidney damage. (Ikem and Egiebor 2005). The concentration of copper was found from 9.6 µg/g to 3.1 µg/g. The minimum copper level was found in *Leuciscus cephalus* fish species and maximum copper level was found in *Capoeta capoeta* fish species. These results have been reported as 9.46 µg/g and 3.1 µg/g respectively (Szefer et al., 2003; Cid et al., 2001). Our copper values were lower than (Atta et al., 1995) and higher than other studies (Mendil et al., 2005). Copper levels were given in (Figure 4).



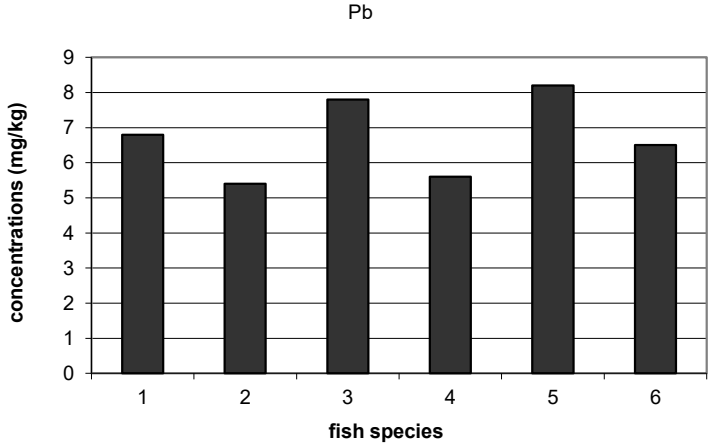
(1. Cyprinus carpio; 2. Leuciscus cephalus; 3. Capoeta capoeta; 4. Silurus glanis, 5. Barbus plebejus; 6. Clupeonella abrau muhlisi)

Figure 4 Cu results in fish species

Şekil 4. *Balık örneklerindeki Cu sonuçları*

3.5 Lead

When ingested or inhaled in high doses Lead is a very poisonous metal species for human organ and system. Lead concentrations were found 5.4 µg/g to 8.2 µg/g. The minimum lead level was found in *Leuciscus cephalus* fish species and maximum lead level was found in *Barbus plebejus* fish species respectively. Our lead levels were lower than the other literature values (Aucoin et al., 1999) and higher than other studies results (Mendil et al., 2005). Lead concentrations were shown in (Figure 5).



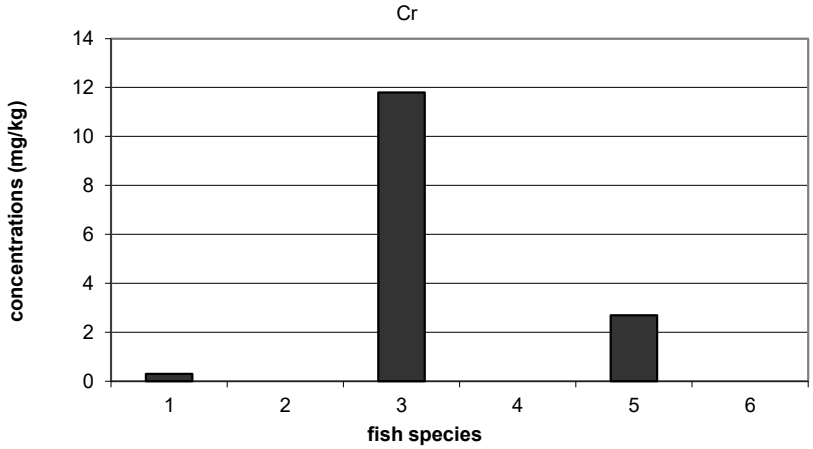
(1. Cyprinus carpio; 2. Leuciscus cephalus; 3. Capoeta capoeta; 4. Silurus glanis, 5. Barbus plebejus; 6. Clupeonella abrau muhlisi)

Figure 5. Pb results in fish species

Şekil 5. *Balık örneklerindeki Pb sonuçları*

3.6 Chromium

Concentration of chromium is very important role in the diet. it is involved in insulin function and lipid metabolism (Bratakos et al., 2002; Yılmaz et al., 2010). In this present study, the measured Chromium concentrations results were found range from 11.8 µg/g to 0.3 µg/g. Our lowest value was reported as 0.95 µg/g (Uluozlu et al., 2007) and highest value was reported as 11.8 µg/g (Aucoin et al., 1999) Our concentrations were lower than other study results (Mansour and Sidky, 2002). Chromium levels were demonstrated in (Figure 6).



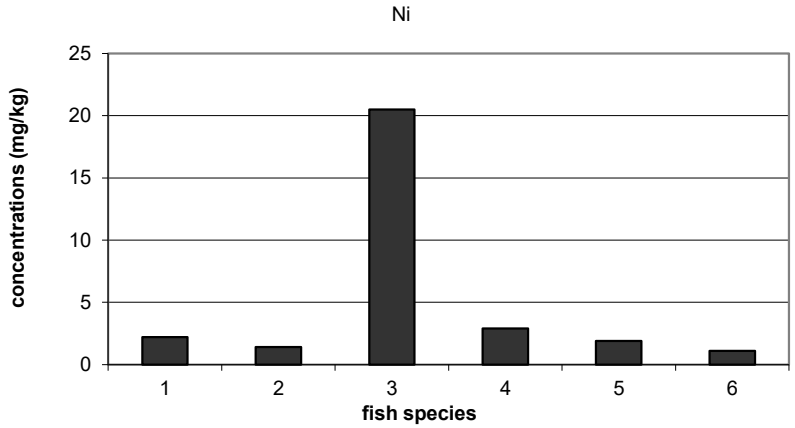
(1. Cyprinus carpio; 2. Leuciscus cephalus; 3. Capoeta capoeta; 4. Silurus glanis, 5. Barbus plebejus; 6. Clupeonella abrau muhlisi)

Figure 6. Cr results in fish species

Şekil 6. *Balık örneklerindeki Cr sonuçları*

3.7 Nickel

Nickel plays important roles in the biology of microorganisms and plants, and some enzymes contain nickel (Li et al., 2014). The concentrations of nickel were determined from 2.9 µg/g to 1.1 µg/g in the samples. These results were lower than other literature reports (Mendil et al., 2005; Cohen et al., 2001) Nickel concentrations in the fish samples were demonstrated in (Figure 7).



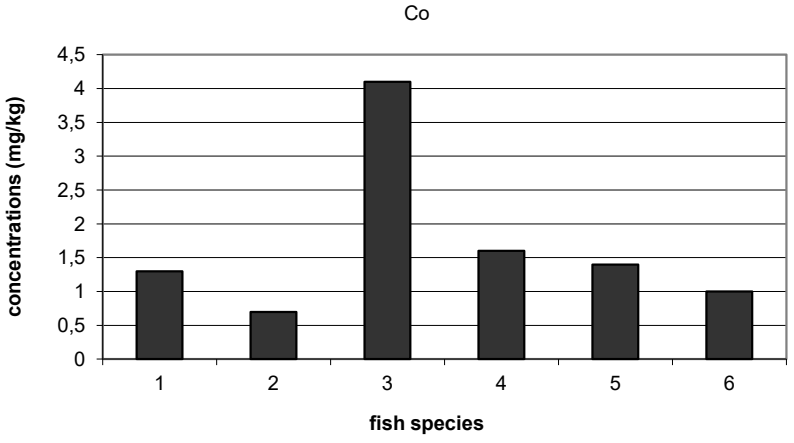
(1. Cyprinus carpio; 2. Leuciscus cephalus; 3. Capoeta capoeta; 4. Silurus glanis, 5. Barbus plebejus; 6. Clupeonella abrau muhlisi)

Figure 7 Ni results in fish species

Şekil 7. *Balık örneklerindeki Ni sonuçları*

3.8 Cobalt

The last metal, an integral part of vitamin B12, plays a role in the regulation of cobalt blood pressure and is found necessary for proper thyroid function. (Yılmaz et al., 2010). Cobalt values were found from 4.1 µg/g to 0.7 µg/g. The maximum cobalt concentration was determined in *Capoeta capoeta*, the minimum cobalt concentration was determined in *Leuciscus cephalus.* These values were lower than other literature values (Mansour and Sidky, 2002). The cobalt amounts were displayed in (Figure 8).



(1. Cyprinus carpio; 2. Leuciscus cephalus; 3. Capoeta capoeta; 4. Silurus glanis, 5. Barbus plebejus; 6. Clupeonella abrau muhlisi)

Figure 8 Co results in fish species

Şekil 8. *Balık örneklerindeki Co sonuçları*

Figure 9. Location of Kılıçkaya Dam Lake in Sivas,Turkey
Şekil 9. *Kılıçkaya Baraj Gölünün konumu*

Table 3. Correlation between metal concentrations
Tablo 3. *Metal konsantrasyonları arasındaki korelasyon*

	Fe	Mn	Zn	Cu	Pb	Cr	Ni	Co
Fe	1.000							
Mn	0.957	1.000						
Zn	0.415	0.194	1.000					
Cu	-0.268	-0.221	0.092	1.000				
Pb	0.477	0.609	0.086	0.574	1.000			
Cr	-0.199	-0.033	-0.202	0.836	0.633	1.000		
Ni	-0.381	-0.242	-0.239	0.863	0.461	0.962	1.000	
Co	-0.325	-0.170	-0.327	0.868	0.534	0.961	0.981	1.000

4. Conclusions

In this study, we performed trace element analysis in fish species living Kılıçkaya Dam Lake in Sivas, Turkey. Fish samples were collected in the summer days. Trace metal analysis in environmental samples is very important for human health. All trace metal concentrations were determined on a dry weight basis. Microwave digestion/ atomic absorption method was successfully employed to fish samples and standard reference material. The levels of trace metals concentrations in fish species (Fe, Mn, Zn, Cu, Pb, Cr, Ni, Co) were found between 102.7-268.0; 7.6-64.5; 34.8-65.1;

3.1-9.6; 5.4-8.2; 0.3-11.8; 1.1-20.5 and 0.7-4.1 μg/g, respectively. The validity of this method was tested with the standard reference material and quantitative results were obtained in accordance with the certificate values. Trace metal accumulation in the fish species was found acceptable levels for human consumption. The correlations between metal concentrations were given in Table 3. As a result, analysis of trace elements in fish species must be done at certain time intervals.

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