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ARAŞTIRMA MAKALESİ RESEARCH PAPER

Determination of Some Heavy Metal Levels in Different Tissues of Common Carp (*Cyprinus carpio*, L., 1758) and Pike Barb (*Luciobarbus esocinus*, H., 1843) From Karasu River (Erzincan)

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Abstract: Heavy metals may be harmful to human health over the short and long term. Consumption of fish, one of the most important sources of protein in human life is one of the most common ways of heavy metal exposure. In this study for determine some heavy metals (Li, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Pb and U) concentration in different tissues as muscle, liver and gill of common carp (*Cyprinus carpio*, L., 1758) and pike barb (*Luciobarbus esocinus*, H., 1843) collected from Karasu River (Erzincan, Turkey) along the upper Euphrates Basin were collected between November 2019 and October 2020 on monthly. Heavy metal analysis was performed by ICP-MS -Bruker 820-MS. The results of heavy metals in tissues were compared to acceptable international limits. The studied metals were found at a considerable level in all seasons, indicating that the Karasu River biota is particularly vulnerable to heavy metal intake. Consequently, research has shown a strong connection between various elements and in addition, the human health risk assessment (HHRA) reveals are hazardous for consumption of fish.

Keywords: Karasu river, heavy metal, fish, public health.

Karasu Nehri'nden (Erzincan) Elde Edilen Sazan (*Cyprinus carpio*, L., 1758) ve Turna Balığı (*Luciobarbus esocinus*, H., 1843) Farklı Dokularındaki Bazı Ağır Metal Düzeylerinin Belirlenmesi

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Öz: Ağır metaller kısa ve uzun vadede insan sağlığına zararlı olabilir. İnsan hayatındaki en önemli protein kaynaklarından biri olan balık tüketimi, ağır metallere maruz kalmanın en yaygın yollarından biridir. Bu çalışmada bazı ağır metallerin (Li, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Pb ve U) farklı dokulardaki konsantrasyonlarının belirlenmesi için Yukarı Fırat Havzası boyunca uzanan Karasu Nehri'nden (Erzincan, Türkiye) toplanan sazan (*Cyprinus carpio*, L., 1758) ve turna balığı (*Luciobarbus esocinus*, H., 1843) kas, karaciğer ve solungaç dokuları Kasım 2019 - Ekim 2020 tarihleri arasından aylık olarak toplanmıştır. Ağır metal analizi, ICP-MS -Bruker 820-MS ile gerçekleştirilmiştir. Dokulardaki ağır metallerin sonuçları kabul edilebilir uluslararası sınırlarla karşılaştırılmıştır. İncelenen metallerin her mevsimde önemli düzeyde bulunması, Karasu Nehri biyotasının özellikle ağır metal alımına karşı savunmasız olduğunu göstermektedir. Sonuç olarak, araştırmalar çeşitli unsurlar arasında güçlü bir bağlantı olduğunu göstermiştir ve ayrıca insan sağlığı risk değerlendirmesi (HHRA) balık tüketimi için tehlikeli olduğunu ortaya koymaktadır.

Anahtar kelimeler: Karasu nehri, ağır metal, balık, halk sağlığı.

INTRODUCTION

Fish is excellent and healthy source of protein, and its amino acid contents are richer in cysteine than other foods which has amino acid that humans consume (Attia et al., 2020; Kaushik & Seiliez, 2010; Mariotti & Gardner, 2019). Due to its acceptability, tastiness, and low cholesterol and low-fat, it is highly used for human

[*]*Bu çalışma, doktora tezinden üretilmiştir.* [*]*This study was produced from the doctora thesis.*

consumption. It is also the cheapest protein source and other vital components for urban and semi-urban poverty regions. In recent years anthropogenic pollution sources emit heavy metals into aquatic environments, constantly (Akkan et al., 2018; Cornelis et al., 2005; Mutlu et al., 2020; Sipahi et al., 2013; Yilmaz, 2006). Metallic pollutants reach the aquatic environment through air deposition, by erosion of the geological matrix, or human sources, such as industrial effluents, mining wastes, and even food processing by-products (Borah et al., 2020; Bundschuh et al., 2020). These metals may be components of both food and pollution, such as the pesticide residue found in food. Field and laboratory research have investigated the bioaccumulation of trace metals in fish, combined with the underlying processes. Industrial operations and industrial waste, often from rubber and oil palm mills, are mostly responsible for the pollution (Ke et al., 2017; Newman & Watling, 2007; Tariq et al., 1996; Zhao et al., 2021).

The amount of heavy metal each individual fish has varies based on several factors such as how fast it grows, how much it consumes, and how it feeds (Al-Weher, 2008; Yılmaz, 2006; Yavuzcan Yildiz et al., 2017). An issue to consider is the variation in life cycle patterns across species and how it is related to their tropic and geographic distribution of life stages (Hunnam, 2021; Palomera, 2007; Petitgas et al., 2013). When a person exceeds the prescribed limit for trace metals, that person may become toxic (acute, chronic, or subchronic), which may cause neurotoxicity, carcinogenicity, mitogenicity, or teratogenicity (Abro & Gomez-Aguilar, 2019; Dżugan, 2010; Silbergeld, 2003; Tchounwou et al., 2019). According to a recently published studies, among of the most common symptoms reported for humans who have been exposed to the toxic metals include vomiting, convulsions, paralysis, ataxia, gastrointestinal disorders, diarrhea, stomatitis, depression, and pneumonia (Ayenimo et al., 2010; Ayua et al., 2020; Bashir, 2018; Flora, 2014; Guérin et al., 2011; Onakpa et al., 2018; Rweyemamu & Nkansah, 2021; Singh et al., 2017; Shelar et al., 2021).

In this study, it is aimed to determine the concentrations of some heavy metals in different tissues of Cyprinus carpio and Luciobarbus esocinus which are preferred as a nutrient by local people and affects to human health from different locations of Karasu River (Upper-Euphrates). It is expected that the results of this research will assist in acquiring information about the level of toxic metals in this area.

MATERIALS AND METHODS

The Euphrates, a river in Western Asia, is one of the longest in the region, on the eastern side of Anatolia (Kalender & Uçar, 2013). It joins the junction of the Karasu River and the Western Euphrates at 340 km point (211 miles) and the Murat River, which is an expansion of the Eastern Euphrates 650 km (400 miles of river). The Karasu River is located on Upper-Euphrates which is in Upper Euphrates Basin at Erzincan city in the North-East part of Anatolia (Bilen, 1994; Kalender & Uçar, 2013). It feeds Karakaya Dam Lake (KDL) which is the third largest reservoir in Turkey, located in the borders of Diyarbakır city in the east Anatolia region (Kalkan, 2008; Varol et al., 2017). For the study fish samples consisted of 30 individuals common carp (*Cyprinus carpio*, L., 1758) and 21 individuals pike barb (*Luciobarbus esocinus*, H., 1843) specimens collected from different parts of Karasu River between November 2019 and October 2020 on monthly basis (Özgür, 2016). The specimens were caught using cast nets and stored on ice until arrival at the laboratory.

All tissue samples (muscle, gill, and liver) were prepared with a preliminary digesting process (samples 0.5 g, 8 mL of HNO3 (65%) via a CEM MARS-5 model microwave instrument. The Heavy metal analysis was performed by ICP-MS-Bruker 820-MS. The reference materials were used to check the accuracy and reliability of the method. Metals concentrations are expressed in µg g-1. The estimated daily and weekly intakes (EDI-EWI) were calculated by Yilmaz et al. (2016), also The target hazard quotient (THQ) was finally calculated using formula: THQ: EDI/Reference Dose (mg/kg/day). One-way ANOVA and Tukey test were performed to test the differences of the metal levels among the specimens (significance level $p<0.05$). All statistical calculations were performed with SPSS 16.0 for Windows.

RESULTS AND DISCUSSION

The present study is about common carp and pike barb in Karasu River and supplies valuable information about metal contents in different tissues. The accumulation values of the respective metals in various tissues of common carp were as follows Li, gill > muscle > liver; Na, gill > liver > muscle; Mg, gill > muscle > liver; Al, muscle > gill > liver; K, muscle > liver > gill; Ca, gill >muscle > liver; Cr, gill > liver > muscle; Mn, gill > muscle > liver; Fe, gill > liver > muscle; Co, gill > liver > muscle; Ni, gill > muscle = liver; Cu, gill > liver > muscle; Zn, gill > liver > muscle; As, gill > muscle > liver; Se, gill > liver > muscle; Ag, muscle > liver > gill; Cd, muscle > gill > liver; Pb, muscle > liver > gill; U, liver > gill > muscle. The accumulation values of the respective metals in various tissues of pike barb were as follows Li, gill > liver > muscle; Na, gill > liver > muscle; Mg, gill > muscle > liver; Al, gill > muscle > liver; K, muscle > liver > gill; Ca, gill > muscle > liver; Cr, muscle > liver > gill; Mn, gill > liver

> muscle; Fe, gill > liver > muscle; Co, gill > liver > muscle; Ni, gill > muscle = liver; Cu, gill > liver > muscle; Zn, gill > liver > muscle; As, gill > muscle > liver; Se, gill > liver > muscle; Ag, gill > muscle = liver; Cd , liver > muscle = gill; Pb, liver > gill > muscle; U, liver > gill > muscle.

The mean concentration Li, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Pb and U in different tissues of common carp and pike barb were given in Table 1. 30 individuals common carp and 21 individuals pike barb were analyzed in this study. The highest metal concentrations were found in the gill on common carp samples. Especially Cu, Fe and Zn were the most abundant metals in the liver with the concentrations of 52250, 12060, 7.508, 48.160, 152.023 µg g-1, respectively. The second highest metal concentrations were found in the muscle. Al, Ag and Pb were the most abundant metals in the muscles with the concentrations of 518.9, 0.679, 2.80 µg g-1, respectively. Liver values showed dramatically lowest level of concentration throughout the study on common carp samples. Except U all metal concentrations in livers were lower than others.

There were significant differences among different tissues of pike barb. For the pike barb samples, the highest rates were found on gills, too. The differences were especially on Al, Cd, Mn, Fe, Co, Ni, Zn, As and Se values with the concentration of 674.71, 126290, 42.631, 30731.9, 18.052, 123.747, 511.457, 143.645, 258.389 µg g-1 for the liver samples. The second highest metal concentrations were found in the liver. Cd and Pb were the most abundant metals in the muscles with the concentrations of 0.524 and 2.532 µg g-1, respectively. With the concentration of 18497.25 µg g-1, heavy metal values in muscle exhibited lower rates than the amounts found in pike barb gills and liver, except K.

The total concentrations of Li, Na, Mg, Al, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Ag, Cd, Pb and U in common carp were 1.293 (±0.270), 3013.621 (±507.339), 874.574 (±131.135), 102.094 (±40.903), 10580.74 (±982.242), 8117.244 (±4496.401), 21.004 (±1.795), 6.781 (±1.267), 2186.789 (±1017.546), 1.453 (±0.615), 5.666 (±4.199), 25.638 (±2.770), 124.822 (±36.402), 9.997 (±5.369), 36.677 (±11.651), 0.066 (±0.056), 0.019 (±0.013), 1.026 (±0.207), 0.055 (±0.004) µg g-1, respectively. For the pike barb the total concentrations were found as Li: 1.049 (±0.193), Na: 2901.3 (±382.0), Mg: 1458.3 (±381.3), Al: 94.1 (±53.8), K: 10892.6 (±1083.6), Ca: 25261.5 (±11556.4), Cr: 23.565 (±1.246), Mn: 10.964 (±3.363), Fe: 6426.4 (±2819.0), Co: 3.904 (±1.703), Ni: 23.449 (±12.251), Cu: 37.077 (±6.565), Zn: 143.930 (±43.760), As: 28.379 (±12.995), Se: 65.585 (±23.014), Ag: 10.541 (±10.538), Cd: 0.124 (±0.065), Pb: 1.255 (±0.205) and U: 1.049 (±0.193) µg g-1 in this study.

Zafarzadeh et al (2018) reported that the accumulation of heavy metal concentrations in common carp muscle samples as Zn: 120.90 (477), Cd: 0.02 (0.14), Pb: 5.84 (21.86) and Cu: 7.92 (39.43) µg g-1. Bat & Öztekin (2018) were found that Zn was the highest in muscles and livers of C. carpio Altınkaya Dam Lake of Samsun Province as 9.85 and 25 µg g-1, respectively. Cu showed also high concentrations on the Common carp muscle and liver samples 0.90 and 7.6 µg g-1, respectively. Metal concentrations in carp from Euphrates river were found in as: 124.8(291), Cd: 1,29(2,02), Cu: 0,78 (0,97, Pb: 17.93(38.76), and Zn: 12.33(18.04) ppm (Varol & Sünbül, 2017). Kaymak et al, (2021) were reported the higher concentrations of Cu, Fe, Zn, Pb and Cd in common carp gill samples from Sapanca Lake as 4.67, 201.18, 1414.15, 1.09 and 1.02 µg g-1, respectively. The higher concentrations of Cu, Fe, Zn and Cd values were also reported 20.76, 53.69, 31.06 and 0.32 in muscles of common carp; 100.81, 631.97, 603.75 and 1.69 µg g-1, respectively (Kaymak et al, 2021). Güldiren & Tekin-Ozan (2018) reported that the heavy metals concentration from Carp Seyhan Dam Lake (Adana) were found in muscle; Cd: 0.38, Cr: 4.06, Cu: 48.89, Fe: 875.21, Mn: 36.52, Mo: 0.38, Ni: 178.93, Pb: 1.7, Se: 5.9, and Zn: 1129.36, liver; Cd: 45.86, Cr: 30.15, Cu: 210.51, Fe: 1048.89, Mn: 14.87, Mo: 2.41, Ni: 105.83, Pb: 1.84, Se: 12.72, and Zn: 2554.08, gill; Cd: 1.46, Cr: 3.43, Cu: 12.17, Fe: 745.61, Mn: 36.77, Mo: 0.51, Ni: 127.24, Pb: 1.72 Se: 7.7, and Zn: 1872.38 µg g-1. In this study the results of heavy metal total concentrations on common carp as mean (max.); Li: 1.293 (3.486), Na: 3013.6 (6267.6), Mg: 874.6 (1859.4), Al: 102.1 (518.9), K: 10659.9 (18219.9), Ca: 8117.2 (52249.9), Cr: 21.004 (36.119), Mn: 6.782 (17.901), Fe: 2186.8 (12059.7), Co: 1.454 (7.508), Ni: 5.666 (48.160), Cu: 25.638 (47.197), Zn: 124.822 (386.821), As: 9.997 (58.204), Se: 36.677 (152.023), Ag: 0.067 (0.680), Cd: 0.019 (0.136), Pb: 1.026 (2.800), U: 0.055 (0.087) µg g-1. According the mean concentrations of heavy metals on this study, K is the highest and Cd is the lowest values in all tissues of common carp samples. The highest mean concentration showed on K and Ca in gill samples. A total heavy metals concentration was found in this study K>Ca>Na>Fe>Mg>Zn>Al>Se>Cu>Cr>As>Mn>Ni>Co>Li>Pb>Ag>U>Cd. Moreover, there is a significant positive correlations between Al and Li; Ca and Mn; Mn and Al; Fe and Mg, Ca; Co and Mg, Fe, Ca, Ni and Mg, Ca, Fe; Cu and Mg, Ca, Fe, Co, Ni, Zn and Ca; Fe, Co and Ni, As and Mg, Ca, Fe, Co, Ni, Zn; Se and Ca, Fe, Co, Ni; Cd and Al, Mn found in carp tissues ($p<0.01$).

Varol & Sünbül (2018) were reported maximum values of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in Pike barb muscle samples from Keban Dam Lake as 297.6, 2.52, 1.81, 1.58, 2.16, 17.0, 1.49, 1.55, 133.9 and 14.6 µg g-1, respectively. In comparison to the other fish species, pike barb and common carp muscle samples had the highest amount of Co values (Varol & Sünbül, 2018). Heavy metal trainings obtained from L. esocinus samples taken from the Euphrates river showed values as Cu: 0.52, Fe: 16.08 and Zn: 9.01 µg g-1 (Düşükcan et al, 2017). In this study the results of heavy metal total concentrations on common carp as mean (max.); Li: 1.049 (2.932), Na: 2901.3 (5353.0), Mg: 1458.3 (4552.8), Al: 94.1 (674.7), K: 10892.6 (18497.3), Ca: 25261.5 (126290.0), Cr: 23.565 (31.762), Mn: 10.964 (42.631), Fe: 6426.4 (30731.9), Co: 3.904 (18.053), Ni: 523.449 (123.747), Cu: 37.077 (93.714), Zn: 143.930 (511.457), As: 28.379 (143.645), Se: 65.585 (258.390), Ag: 10.541 (126.464), Cd: 0.124 (0.524), Pb: 1.255 (2.532), U:1.049 (2.932) µg g-1. Analyses of the heavy metal levels in all tissues of fish samples showed that, on average, Ca is the highest and U is the lowest. The highest mean concentrations of Fe and Ca were found in the Pike barb gill samples. A total heavy metals concentration was found in this study Ca>K>Fe>Na>Mg>Zn>Al>Se>Cu>As>Cr>Ni>Mn>Ag> Co>Pb>Li>Cd>U. In addition, the pike barb tissues also showed significant positive correlations between Mg and Na; Al and Mg; Ca and Li, Na, Mg; Mn and Mg, Al; Fe and Li, Na, Mg, Ca; Co and Li, Na, Mg, Ca, Fe; Ni and Na, Mg, Ca, Fe, Co; Cu and Li, Na, Ca, Fe, Co, Ni; Zn and Na, Mg, Ca, Fe, Co, Ni, Cu; As with Li, Na, Mg, Ca, Fe, Co, Ni, Cu and Zn; Se with Li, Na, Mg, Ca, Fe, Cu, Ni, Cu, Zn and as; Ag with Li, Ca, Fe, Co, Ni, Cu, Zn, As and Se ($p<0.01$). As a result, heavy metal accumulation levels in various tissues of fish captured in the Karasu River are an extremely high level when compared to previous researches in the literature. In addition, that; its dramatically increase according to Human health risk assessment of heavy metals in muscle showed that the estimated daily and weekly intakes (EDI-EWI) for Ni, Zn, As, Cd, and U were above the reference doses for oral exposure (Table 4). The mean concentrations of heavy metals analyzed in the muscle of common carp were higher than the maximum permitted concentrations proposed by FAO (1983). Likely, the THQ showed that for health risk through ingestion, Mn (common carp and pike barb) had the lowest THQ value and Cr (common crap), Cr, Ni, and Ag (pike barb) had the highest potential for risk with a value >1.

Table 1. The heavy metal concentrations in different tissues of Common Carp (µg g^{-1}).

	Mean.±SE (Max.-Min.)			
	Common Carp			Total
	Muscle	Liver	Gill	
Li	1.435±0.732 (0.204-3.486)	1.262±0.380 (0.620-2.338)	1.181±0.330 (0.559-2.101)	1.293±0.270 (0.204-3.486)
Na	1380.2±122.4^{a} (1089-1680)	2697.7±252.6^{a} (2209-3402)	4962.9±750.5^{b} (3620.4-6267.6)	3013.6±507.3 (1089.0-6267.6)
Mg	841.6±76.9^{ab} (678.7-1020)	496.5±55.788^{a} (339.6-582.2)	1285.7±275.3^{b} (700.4-1859.4)	874.6±131.1 (339.6-1859.4)
Al	153.7±122.3 (9.505-518.9)	49.0±12.808 (24.7-83.7)	103.6±38.2 (51.8-216.8)	102.1±40.9 (9.505-518.9)
K	14395.7±1351.3^{b} (11917-18220)	9253.5±714.4^{a} (7576-11043)	8330.5±1075.3^{a} (6087.1-10581)	10659.9±982.2 (6087.1-18219.9)
Ca	1237±272.4^{a} (516.9-1808)	794.4±167.2^{a} (553.7-1264.7)	22320.2±11018.1^{b} (2377.2-52250)	8117.2±4496.4 (516.9-52249.9)
Cr	18.687±2.355 (13.857-24.306)	20.137±2.361 (15.717-26.793)	24.188±4.350 (17.187-36.119)	21.004±1.796 (13.858-36.119)
Mn	6.642±3.77 (1.937-17.9)	5.958±1.133 (2.845-8.270)	7.746±1.281 (4.729-10.116)	6.782±1.268 (1.937-17.901)
Fe	486.2±135.9^{a} (190-842.9)	618.2±116^{a} (408.8-896.1)	5456.0±2451.7^{b} (891.3-12059.7)	2186.8±1017.5 (190.0-12059.7)
Co	0.371±0.143^{a} (0.035-0.653)	0.496±0.066^{a} (0.310-0.606)	3.493±1.433^{b} (1.305-7.508)	1.454±0.615 (0.035-7.508)
Ni	0.000±0.000 (0.000-0.000)	0.000±0.000 (0.000-0.000)	16.999±11.391 (0.000-48.160)	5.666±4.199 (0.000-48.160)
Cu	21.658±2.930 (14.777-28.273)	26.182±2.57 (22.46-33.46)	29.074±7.742 (10.639-47.197)	25.638±2.771 (10.639-47.197)
Zn	25.675±0.558^{a} (24.34-27.068)	113±37.477^{ab} (68.78-225.18)	235.772±75.795^{b} (84.560-386.821)	124.822±36.402 (24.340-386.821)
As	1.589±1.274^{a} (0.000-5.343)	0.768±0.43^{a} (0.000-1.953)	27.635±12.636^{b} (2.776-58.204)	9.997±5.369 (0.000-58.204)
Se	18.401±1.847 (14.09-21.667)	23.023±13.574 (3.859-62.522)	68.607±28.145 (31.772-152.023)	36.677±11.651 (3.859-152.023)
Ag	0.17±0.170 (0.000-0.680)	0.029±0.029 (0.000-0.114)	0.002±0.002 (0.000-0.007)	0.067±0.056 (0.000-0.680)
Cd	0.034±0.034 (0.000-0.136)	0.000±0.000 (0.000-0.000)	0.024±0.024 (0.000-0.095)	0.019±0.013 (0.000-0.136)
Pb	1.357±0.618 (0.242-2.8)	0.898±0.106(0.689-1.191)	0.824±0.143 (0.567-1.116)	1.026±0.207 (0.242-2.800)
U	0.048±0.004 (0.037-0.057)	0.067±0.008(0.051-0.087)	0.049±0.006 (0.035-0.059)	0.055±0.004 (0.035-0.087)

Horizontally. letters a. b and c show statistically significant differences ($p < 0.05$). Vertically. letters x. y. z and w show statistically significant differences ($p < 0.05$). nd: not detected

Table 2. The heavy metal concentrations in different tissues of Pike barb (µg g^{-1}).

	Mean.±SE (Max.-Min.)			
	Pike barb			Total
	Muscle	Liver	Gill	
Li	0.735±0.067 (0.596-0.879)	0.900±0.169 (0.603-1.382)	1.513±0.513 (0.735-2.932)	1.049±0.193 (0.596-2.932)
Na	1589.3±96.1 (1384.7-1826.7)	2601.0±192.8 (2200.6-3121.5)	4513.7±297.3 (3978.6-5353.0)	2901.3±382.0 (1385-5353.0)
Mg	885.3±100.6 (697.7-1078.8)	453.1±47.3 (325.8-554.3)	3036.6±557.1 (2111.2-4552.8)	1458.3±381.3(325.8-4552.8)
Al	30.5±6.8 (18.5-49.7)	24.7±4.2 (16.9-36.7)	227.0±151.5 (31.0-674.7)	94.1±53.8 (16.91-674.7)
K	15442.7±1392.8 (12700.8-18497.3)	8840.6±706.0 (6777.5-9976.6)	8394.5±305.7 (7767.3-9231.6)	10892.6±1083.6 (6777-18497.3)
Ca	1881.2±428.0 (1320.3-3137.9)	858.9±165.1 (572.2-1218.7)	73044.4±18085.3 (45699.8-126290.0)	25261.5±11556.4 (572.2-126290.0)
Cr	24.033±2.859^{a} (18.004-31.762)	23.385±2.587^{ab} (16.178-27.909)	23.275±1.447^{ab} (20.262-26.193)	23.565±1.246 (16.178-31.762)
Mn	3.595±0.523 (2.460-4.887)	6.384±0.818 (5.208-8.764)	22.914±7.124 (8.629-42.631)	10.964±3.363 (2.460-42.631)
Fe	523.9±114.9 (351.1-860.1)	678.1±91.6 (488.7-927.2)	18077.1±4417.9 (10158.6-30731.9)	6426.4±2819.0 (351.1-30731.9)
Co	0.336±0.063 (0.188-0.487)	0.341±0.035 (0.258-0.420)	11.035±2.545 (5.944-18.053)	3.904±1.703 (0.188-18.053)
Ni	0.000±0.000 (0.000-0.000)	0.000±0.000 (0.000-0.000)	70.346±23.480 (21.610-123.747)	23.449±12.251 (0.000-123.747)
Cu	22.130±2.218 (19.401-28.734)	28.436±7.855 (17.343-51.229)	60.665±11.077 (47.504-93.714)	37.077±6.565 (17.343-93.714)
Zn	23.727±4.522 (13.274-34.246)	100.241±27.64 (31.580-157.411)	307.824±76.641 (148.345-511.457)	143.930±43.760 (13.274-511.457)
As	4.130±2.154 (0.000-9.220)	1.127±0.667 (0.000-2.910)	79.881±22.906 (35.015-143.645)	28.379±12.995 (0.000-143.645)
Se	9.191±2.536 (4.471-15.599)	29.113±9.652 (4.519-51.218)	158.450±36.720 (100.422-258.390)	65.585±23.014 (4.471-258.390)
Ag	0.000±0.000 (0.000-0.000)	0.000±0.000 (0.000-0.000)	31.622±31.614 (0.000-126.464)	10.541±10.538 (0.000-126.464)
Cd	0.000±0.000 (0.000-0.000)	0.373±0.125 (0.000-0.524)	0.000±0.000 (0.000-0.000)	0.124±0.065 (0.000-0.524)
Pb	0.672±0.306 (0.238-1.550)	1.513±0.411 (0.561-2.532)	1.578±0.176 (1.199-2.048)	1.255±0.205 (0238-2.532)
U	0.735±0.067 (0.596-0.879)	0.900±0.169 (0.603-1.382)	1.513±0.513 (0.735-2.932)	1.049±0.193 (0.596-2.932)

Horizontally. letters a. b and c show statistically significant differences ($p < 0.05$). Vertically. letters x. y. z and w show statistically significant differences ($p < 0.05$). nd: not detected

Table 3. Pearson correlation coefficients between heavy metal concentrations.

										Pike Barb										
Common Carp	Li	Na	Mg	Al	K	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Ag	Cd	Pb	U	Mo
Li	1	0.692*	0.401	0.054	-0.401	**0.765****	0.038	-0.009	**0.741****	**0.710****	0.663*	**0.755****	0.678*	**0.736****	**0.773****	**0.888****	-0.284	0.163	0.226	
Na	-0.280	1	**0.731****	0.381	-0.655*	**0.887****	-0.085	0.579*	**0.885****	**0.884****	**0.802****	**0.844****	**0.882****	**0.850****	**0.900****	0.584*	-0.147	0.418	0.168	
Mg	0.016	0.397	1	**0.826****	-0.303	**0.808****	-0.028	**0.849****	**0.827****	**0.820****	**0.893****	0.678*	**0.782****	**0.789****	**0.847****	0.412	-0.438	0.220	-0.379	
Al	**0.738****	-0.229	0.055	1	-0.268	0.419	-0.165	**0.852****	0.463	0.448	0.668*	0.310	0.514	0.421	0.557	0.095	-0.222	0.128	-0.619*	
K	-0.293	-0.438	-0.114	-0.103	1	-0.419	0.180	-0.435	-0.428	-0.429	-0.401	-0.433	-0.506	-0.386	-0.512	-0.214	-0.221	-0.439	-0.104	
Ca	0.127	0.405	**0.893****	-0.082	-0.421	1	0.095	0.485	**0.998****	**0.995****	**0.941****	**0.903****	**0.935****	**0.991****	**0.966****	**0.795****	-0.368	0.189	-0.003	
Cr	-0.378	0.500	-0.166	-0.184	-0.012	-0.196	1	-0.113	0.091	0.099	0.059	0.068	0.016	0.100	0.042	0.192	-0.118	0.129	0.434	
Mn	0.560	0.080	0.406	**0.758****	-0.226	0.292	-0.223	1	0.518	0.529	0.607*	0.365	0.526	0.460	0.566	-0.063	-0.217	0.360	-0.415	
Fe	0.138	0.426	**0.891****	-0.056	-0.453	**0.998****	-0.195	0.330	1	**0.997****	**0.958****	**0.901****	**0.950****	**0.993****	**0.974****	**0.784****	-0.350	0.195	-0.030	
Co	0.166	0.480	**0.867****	-0.068	-0.442	**0.987****	-0.112	0.317	**0.988****	1	**0.945****	**0.884****	**0.940****	**0.993****	**0.961****	**0.755****	-0.364	0.190	-0.031	
Ni	0.163	0.348	**0.860****	-0.122	-0.363	**0.986****	-0.239	0.288	**0.981****	**0.980****	1	**0.835****	**0.943****	**0.947****	**0.968****	**0.744****	-0.332	0.152	-0.199	
Cu	0.007	0.349	**0.620***	-0.330	-0.101	**0.719****	-0.227	0.199	**0.720****	**0.750****	**0.788****	1	**0.921****	**0.878****	**0.893****	**0.784****	-0.128	0.371	0.103	
Zn	-0.056	0.677*	0.705*	-0.243	-0.489	**0.787****	0.036	0.271	**0.795****	**0.806****	**0.780****	0.650*	1	**0.938****	**0.951****	**0.764****	-0.085	0.285	0.003	
As	0.057	0.471	**0.907****	-0.120	-0.421	**0.985****	-0.196	0.286	**0.984****	**0.966****	**0.966****	0.691*	**0.832****	1	**0.955****	**0.806****	-0.366	0.139	-0.022	
Se	0.360	0.237	0.644*	-0.002	-0.547	**0.875****	-0.150	0.137	**0.867****	**0.868****	**0.864****	0.520	0.569	**0.822****	1	**0.762****	-0.333	0.286	-0.055	
Ag	0.033	-0.272	-0.112	-0.111	0.293	-0.143	-0.377	-0.328	-0.160	-0.144	-0.134	0.004	-0.262	-0.166	-0.187	1	-0.174	-0.024	0.189	
Cd	0.483	0.056	0.341	**0.725****	0.046	0.084	-0.303	**0.826****	0.108	0.089	0.080	-0.006	0.182	0.140	-0.094	-0.156	1	0.197	0.365	
Pb	0.526	-0.264	0.060	0.672*	0.298	-0.117	0.052	0.627*	-0.106	-0.079	-0.082	0.025	-0.185	-0.190	-0.078	-0.279	0.546	1	0.236	
U	-0.224	-0.025	-0.515	-0.062	-0.100	-0.419	0.281	0.029	-0.386	-0.383	-0.412	-0.068	-0.356	-0.460	-0.391	-0.279	-0.315	0.105	1	
Mo	-0.227	-0.086	-0.203	-0.112	0.035	-0.139	-0.127	-0.019	-0.131	-0.141	-0.123	0.017	-0.109	-0.169	-0.256	-0.107	-0.132	-0.149	0.358	1

**Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed).

Table 4. Summary of health risk assessment for metals in fishes from Karasu River.

Metal	THA*	THA[b]	TGA[c]	Total common carp HHA[d](HGA)[e] / THQ	Total pike barb HHA[d](HGA)[e] / THQ
Li				418 (60) / 0.5	411 (59) /0.04
Cr	–	–	–	5056 (722) / 3.4	4447 (635) / 3.03
Mn	980[g]	68.600	9800[h]	2506 (358) / 0.04	5968 (853) / 0.1
Co	–	–	–	1051 (150) / 0.1	2527 (361) / 0.3
Ni	35[g]	2450	350[f]	6742 (963) / 0.7	17325 (2475) / 1.8
Cu	3500[a]	245000	35000	6608 (944) / 0.3	13120 (1874) / 0.7
Zn	7000[a]	490000	70000	54155 (7736) / 0.4	71604 (10229) / 0.5
As				8149 (1164)	20110 (2873)
Se				21283 (3040)	36175 (5168)
Ag				95 (14) / 0.04	17705 (2529) / 7.2
Cd	7[a]	490	70	19 (3) / 0.04	73 (10) / 0.2
Pb	25[a]	1750	250	392 (56) / 0.2	355 (51) / 0.2
U				12 (2)	9 (1)

* Provisional Permissible Tolerable Weekly Intake (PTWI) in lg/week/kg body weight.
Mean weekly fish consumption in Turkey is 0.14 kg per person (FAO. 2005).
[a] (FAO/WHO. 2004).
[b] PTWI for 70 kg adult person (lg/week/70 kg body weight).
[c] PTDI. permissible tolerable daily intake (lg/day/70 kg body weight).
[d] EWI. estimated weekly intake in lg/week/70 kg body weight.
[e] EDI. estimated daily intake in lg/day/70 kg body weight.
[f] WHO recommends a TDI (tolerable daily intake) of 5 lg/day/kg body weight. i.e. 350 lg/day for a 70-kg person (WHO. 1993).
[g] Calculated for a week (lg/week/kg body weight).
[h] EPA recommends a RfD (reference dose) of 0.14 mg/day/kg body weight. i.e. 9800 lg/day for a 70-kg person (EPA. 2008).

CONCLUSIONS

In this study, the accumulation of metals detected in fish samples obtained from the Karasu River was compared with the acceptable values determined by national and international standards. It was determined that some metals in fish tissues were above acceptable values. This negative situation originated by agricultural fields, mining and iron-steel factory along the Karasu River. Especially the wastes of the mines and iron-steel factory in the region, pesticides and fertilizers used in agricultural activities contain heavy metals. These metals reach The Karasu River especially through climate patterns (rains, snow melting etc.). In addition, the sewage and household wastes of the settlements around the river are mixed into the river. Especially, the local people living around the river, as well as the authorities in the region, should be made aware of these issues; the discharge of mine and iron-steel factory wastes into the aquatic ecosystem should be avoided; and they should be informed about the contents of fertilizers and the treatment of domestic waste.

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