

## Metals in Two Species of Fish in Karasu River

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**Abstract** In this study, cadmium (Cd), copper (Cu), iron (Fe), nickel (Ni), lead (Pb) and zinc (Zn) levels were determined in the tissues (muscle, liver and gills) of two fish species, *Capoeta capoeta umbra* and *Chalcalburnus mosullensis*, collected from three stations of the Karasu River. The lowest metal accumulation was detected in the muscle tissues. Moreover there was some variability in the metal concentrations measured in the same tissues from samples obtained from the three different stations. A positive correlation was observed for the concentration of metal pairs Fe–Cu, Fe–Zn, Ni–Pb, Pb–Zn. These findings were also compared with national and international food standards, and Pb and Cd concentrations were determined to be above the level set by the standards. In conclusion, it was supposed that excessive consumption of these two fish species, which already occurs in this region, might pose a public health risk.

**Keywords** Metal accumulation · *Capoeta capoeta umbra* · *Chalcalburnus mosullensis* · Health risk

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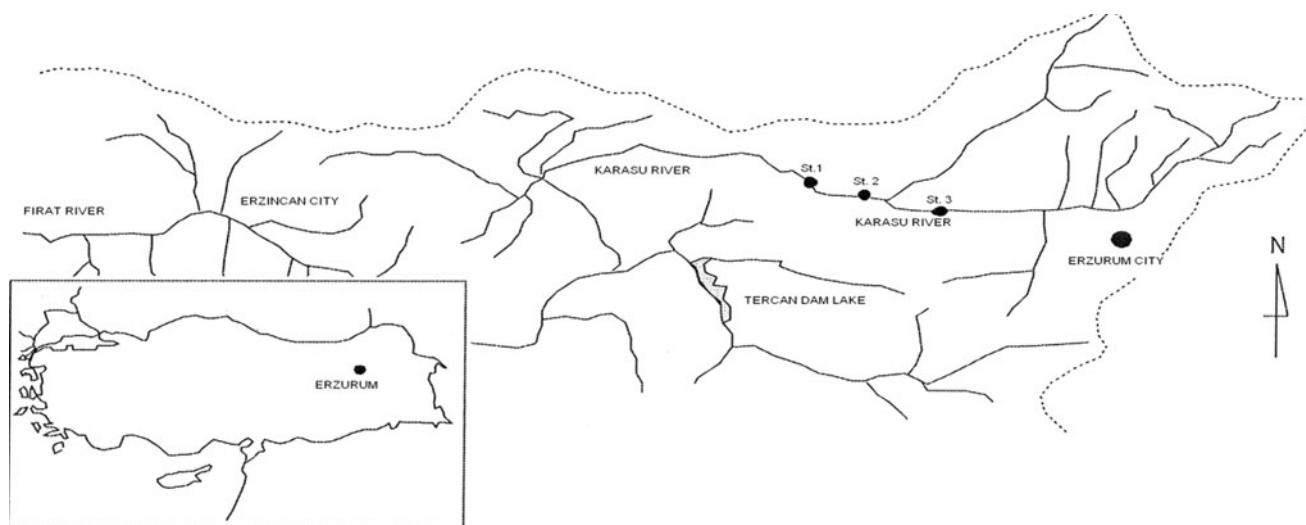
Rapid increase of industrialization, urbanization, population growth and agricultural activities causes environmental pollution, creating serious risks for the inhabitants in the adjacent lands. In Turkey, high concentrations of metals in rivers have become an increasingly debated issue for the last several years (Karadede and Unlu 2000).

Fish are among the species that are at the top of the aquatic food chain, and metals in the environment accumulate in various tissues and organs of fish (Mansour and Sidky 2002). In fish, the uptake of metals from the environment is from water passing through the gills, water taken in with food, ingestion of contaminated food and by passing through the skin. Therefore, the determination of metal concentrations in consumed fish and commercial fishery is important in terms of assessing potential risks of fish consumption (Cid et al. 2001).

*Capoeta capoeta umbra* and *Chalcalburnus mosullensis* are fish species belonging to the *Cyprinidae* family. Although the fish can be found in the upper zones of the Tigris and Euphrates Rivers, they live mainly in the upper regions of Karasu River (Geldiay and Balik 1988). Both of the fish species constitute an important nutrient source for the people living near the residential area in the research area.

Karasu River, the study area, is an important distributary of the Tigris River and has been polluted substantially with the sewage water and wastes of meat, oil, sugar and cement industries. Hence, mass fish deaths have been occurred twice in the past 10 years.

This study was performed to determine the cadmium, copper, iron, nickel, lead and zinc concentrations in the tissues (gills, muscles) of the two fish species (*C. capoeta umbra* and *C. mosullensis*) found in the Karasu River. The results were compared with other study results.



**Fig. 1** Sampling area and stations

## Materials and Methods

Along a stretch of approximately 70 km, three stations were identified in the area that began from Karasu River to the point where it leaves Erzurum Plain. One of the stations selected was in a region near a spring. Another station was chosen from the point at which the river leaves the plain. In each of the three stations, individual factors that contribute to increased pollution are present (Fig. 1).

At least ten fish from each species were caught in the spring, summer and fall seasons of 2010. The *C. capoeta umbra* species ranged from 45.3 to 298.6 g in weight, and the length ranged from 13.8 to 31.5 cm. The length of *C. mosullensis* ranged between 11.2 and 18.3 cm, and these fish weighed between 5.6 and 81.4 g. The fish were transported to the laboratory on ice. Prior to the analysis, approximately 5 g of muscle (edible parts), two thorn gills and the liver were removed from each fish. The tissue samples were washed with deionized water, weighed and stored at  $-20^{\circ}\text{C}$  in polyethylene bags (Karadede et al. 2004; Papagiannis et al. 2004).

The metal content of the samples was determined with nitric acid–hydrogen peroxide (2:3) acid in three different steps [(1) at  $145^{\circ}\text{C}$ , 75% microwave power for 5 min, (2) at  $180^{\circ}\text{C}$  90% microwave power for 10 min and (3) at  $100^{\circ}\text{C}$  40% microwave power for 10 min] exposing samples to 40 bar pressure microwave wet incineration units (speedwave MWS-2 Berghof products + Instruments Harresstr.1. 72800 Enien Germany) followed by two parallel reading ICP OES spectrophotometer (Inductively Couple Plasma spectrophotometer) (Perkin-Elmer, Optima 2100 DV, ICP/OES, Shelton, CT 06484-4794, USA).

Deionized water was used, and all of the reagents were of analytical grade. Prior to use, all of the plastic and glass

materials were washed with nitric acid for 15 min and shaken with deionized water. High purity argon was used as the inert gas (Karadede et al. 2004). Standard solutions were prepared with stock solutions (Merck, multiple element standard). Two standard material DORM-3 and DOLT-4 (National Research Council Canada, Ottawa, ON, Canada) were analyzed for each of the six elements.

One way variance tests at a significance level of 5% were conducted for each metal to test the significant differences among the regions. A matrix of the Pearson correlation coefficient values was prepared to determine the correlation between the element pairs in the tissues.

## Results and Discussion

Results from the standard reference materials DORM-3 and DOLT-4 of the shark muscle and liver and recovery rates in fish are shown in Table 1.

Metal concentrations in the muscle, liver and gills of *C. capoeta umbra* and *C. mosullensis* based on wet weight ( $\mu\text{g g}^{-1}$ ) are summarized in Table 2.

As reported in Table 2, the concentration of Fe was determined to be greater than the other metals in all tissue samples from both fish species. The highest average concentration in *C. capoeta umbra* in gill tissue was determined as  $225.8 \mu\text{g g}^{-1}$ (Fe), and in *C. mosullensis* in liver tissue was determined as  $120.5 \mu\text{g g}^{-1}$ (Fe). After Fe, Pb and Zn exhibited the second highest levels in liver and gill and muscle tissue in both of the fish species.

The average metal concentrations in muscle, gill and liver of *C. capoeta umbra* decreased in the following order: Fe > Zn > Pb > Cu > Ni > Cd, whereas the average metal concentrations in muscle, gill and liver of

**Table 1** Certificate and observed values and recovery rates for reference material DORM-3 and DOLT-4

Elements	Reference material					
	DORM-3			DOLT-4		
	Certificate value <sup>a</sup>	Observed value	Recovery (%)	Certificate value	Observed value	Recovery (%)
Cd	0.290 ± 0.020	0.31 ± 0.006	107	24.3 ± 0.80	22.873 ± 0.930	94
Ni	1.28 ± 0.24	1.19 ± 0.12	93	0.97 ± 0.11	1.026 ± 0.030	106
Fe	347 ± 20	329 ± 3.05	95	1,833 ± 75	1,707 ± 39.95	93
Cu	15.5 ± 0.63	16.05 ± 0.19	104	31.2 ± 1.1	29.46 ± 0.930	94
Pb	0.395 ± 0.050	0.361 ± 0.057	91	0.16 ± 0.04	0.17 ± 0.010	106
Zn	51.3 ± 3.1	49.82 ± 2.04	97	116 ± 6	116.14 ± 0.907	100

<sup>a</sup> All values are mg kg<sup>-1</sup> wet wt

**Table 2** Metal concentrations on the various tissues of fish *C. capoeta* and *C. mosullensis* Karasu River

Metals	Stations	<i>C. capoeta umbra</i>			<i>C. mosullensis</i>		
		Muscle	Liver	Gill	Muscle	Liver	Gill
Fe	1.St.	170.6 ± 9.6 (156.8–185.3)	199.8 ± 16.5 (173.1–229.5)	225.8 ± 12.9 (204.9–243.4)	78.1 ± 6.7 (68.1–88.6)	93.2 ± 3.8 (88.1–98.3)	85.3 ± 4.0 (79.1–89.9)
	2.St.	81.9 ± 7.4 (73.2–90.0)	121.3 ± 9.0 (109.6–134.5)	98.5 ± 9.0 (86.7–112.3)	96.0 ± 7.5 (87.6–103.2)	120.5 ± 9.9 (109.2–134.2)	102.1 ± 7.4 (93.4–113.8)
	3.St.	70.4 ± 8.0 (57.3–82.1)	77.1 ± 11.0 (58.1–100.4)	76.0 ± 8.9 (61.2–88.3)	43.4 ± 4.6 (39.1–48.9)	113.1 ± 6.4 (104.4–118.2)	60.2 ± 7.2 (53.8–74.2)
	1.St.	0.30 ± 0.02 (0.27–0.33)	0.35 ± 0.03 (0.31–0.38)	0.32 ± 0.02 (0.28–0.34)	0.32 ± 0.01 (0.31–0.34)	0.38 ± 0.04 (0.33–0.44)	0.36 ± 0.02 (0.35–0.39)
	2.St.	0.31 ± 0.02 (0.28–0.34)	0.30 ± 0.08 (0.21–0.39)	0.34 ± 0.06 (0.24–0.40)	0.28 ± 0.04 (0.24–0.32)	0.28 ± 0.05 (0.22–0.34)	0.32 ± 0.05 (0.23–0.37)
	3.St.	0.19 ± 0.02 (0.17–0.34)	0.20 ± 0.04 (0.18–0.27)	0.20 ± 0.00 (0.19–0.21)	0.24 ± 0.04 (0.19–0.29)	0.45 ± 0.10 (0.38–0.60)	0.32 ± 0.01 (0.31–0.34)
	1.St.	9.8 ± 0.8 (9.0–11.2)	37.4 ± 1.0 (36.4–38.5)	38.3 ± 1.9 (35.0–41.9)	8.6 ± 0.6 (7.9–9.3)	14.4 ± 0.3 (14.1–14.8)	14.4 ± 1.2 (13.0–16.2)
	2.St.	14.1 ± 1.3 (12.4–15.8)	16.1 ± 1.1 (14.1–17.1)	13.4 ± 0.9 (12.1–14.6)	12.8 ± 0.68 (12.2–13.8)	18.5 ± 2.7 (15.1–22.2)	16.0 ± 2.2 (13.6–18.9)
	3.St.	12.3 ± 0.7 (11.5–13.6)	12.1 ± 0.5 (11.7–13.0)	14.2 ± 2.4 (11.8–17.7)	13.3 ± 0.8 (12.3–14.2)	12.8 ± 0.8 (11.9–13.7)	13.1 ± 0.5 (12.6–13.8)
Ni	1.St.	0.60 ± 0.08 (0.49–0.69)	0.80 ± 0.10 (0.63–0.99)	1.00 ± 0.08 (0.87–1.10)	0.66 ± 0.08 (0.56–0.78)	0.68 ± 0.02 (0.66–0.71)	0.83 ± 0.06 (0.76–0.91)
	2.St.	0.97 ± 0.09 (0.86–1.11)	1.02 ± 0.15 (0.86–1.26)	0.77 ± 0.15 (0.57–0.97)	0.73 ± 0.10 (0.61–0.86)	0.44 ± 0.10 (0.31–0.56)	0.50 ± 0.13 (0.34–0.69)
	3.St.	0.59 ± 0.09 (0.47–0.68)	0.64 ± 0.17 (0.34–0.83)	0.80 ± 0.25 (0.27–1.01)	0.84 ± 0.07 (0.78–0.93)	1.05 ± 0.18 (0.89–1.26)	1.33 ± 0.16 (1.21–1.57)
	1.St.	11.7 ± 1.3 (10.0–13.4)	46.1 ± 1.8 (43.3–48.3)	50.6 ± 3.6 (47.6–58.8)	9.4 ± 0.9 (8.3–10.8)	82.7 ± 0.5 (82.0–83.2)	77.8 ± 6.4 (68.1–83.2)
	2.St.	16.4 ± 1.5 (14.6–19.2)	65.7 ± 3.5 (60.1–69.3)	72.6 ± 9.5 (60.1–86.3)	15.0 ± 1.0 (14.2–16.5)	29.4 ± 6.4 (19.2–36.4)	41.6 ± 10.2 (26.8–54.7)
	3.St.	10.4 ± 1.2 (9.3–12.4)	56.0 ± 8.0 (46.2–69.5)	66.4 ± 13.2 (49.5–87.9)	11.9 ± 1.0 (11.0–13.3)	60.2 ± 6.1 (54.3–67.9)	74.8 ± 7.1 (65.5–81.2)
	1.St.	38.7 ± 1.4 (37.0–41.4)	80.9 ± 3.7 (76.2–87.0)	90.1 ± 1.4 (87.2–91.4)	30.8 ± 4.8 (23.0–37.3)	67.3 ± 10.0 (56.4–83.5)	67.0 ± 8.4 (57.0–79.0)
	2.St.	42.9 ± 6.1 (35.0–49.9)	69.4 ± 9.4 (59.7–85.4)	66.2 ± 7.6 (51.8–74.6)	30.1 ± 3.3 (26.3–33.2)	63.1 ± 5.1 (56.6–69.8)	74.3 ± 9.0 (65.4–87.3)
	3.St.	41.6 ± 2.5 (38.8–45.6)	48.0 ± 4.1 (43.3–55.5)	47.5 ± 4.5 (44.0–56.7)	33.4 ± 2.8 (29.9–36.5)	42.2 ± 3.3 (39.0–46.4)	35.9 ± 3.6 (31.0–39.1)

*C. mosullensis* occurred in the following descending orders, respectively:  $\text{Fe} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Cd}$ ;  $\text{Fe} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Cd}$ ;  $\text{Fe} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Cd}$ . As average values were considered, *C. capoeta umbla* demonstrated higher average values of each metal than *C. mosullensis* in all tissues. The differences of metal levels among the species were due to dietary habits (Romeoa et al. 1999), ecological needs, metabolism status and habitat (Canli and Atli 2003), age, size and length of the fish (Linde et al. 1998). In general, metal accumulation levels in liver and gills were higher than the accumulation level in muscles for both of the fish species. It has been shown that the muscle tissue of the fish is not active in binding metals, and hence, accumulation in the other tissue and organs remained low (De Conto Cinier et al. 1999).

In terms of Fe, for *C. capoeta umbla* the lowest and highest concentrations were identified as  $57.3\text{--}185.3 \mu\text{g g}^{-1}$  in muscles,  $58.1\text{--}2,229.5 \mu\text{g g}^{-1}$  in liver and  $61.2\text{--}243.4 \mu\text{g g}^{-1}$  in gills. For *C. mosullensis*, these values were determined as  $39.1\text{--}103.2 \mu\text{g g}^{-1}$  in muscles,  $88.1\text{--}134.2 \mu\text{g g}^{-1}$  in liver and  $53.8\text{--}113.8 \mu\text{g g}^{-1}$  in gills.

Previously obtained data showed similar results for liver and gill tissue of the fish in the studies in Sariçay (Yilmaz et al. 2007), the Nil River (Alaa Osman and Kloas 2010), the Tanganyika Lake (Chale 2002), the Tuzla Lagoon (Dural et al. 2007), the Atatürk Dam Lake (Karadede and Ünlü 2000), the Tokat Lakes (Mendil et al. 2005), and the Kasumigaura Lake (Alam et al. 2002). Metal levels in the liver and gills were lower, and muscle concentrations were higher than in the studies performed in the Mediterranean (Canli and Atli 2003), compared to those determined in the current study. The values were also determined to be higher than those in the studies conducted in the Seyhan Dam Lake (Göksu et al. 2003) and North Anatolian Mediterranean Coast (Turkmen et al. 2005).

For *C. capoeta umbla*, the lowest and the highest concentrations of Cd were  $0.17$  and  $0.40 \mu\text{g g}^{-1}$ , respectively. For *C. mosullensis*, the lowest and highest values were  $0.19$  and  $0.60 \mu\text{g g}^{-1}$ , respectively. The levels of Cd were similar to the study that investigated metal levels in different fish species in the Tanganyika Lake (Chale 2002). Again, studies on different fish species in the Köyceğiz Lake (Yilmaz 2009), the Tokat Lake (Mendil et al. 2005) and the Seyhan Dam Lake (Göksu et al. 2003) gave similar results. In the study performed for the Yangtze River (Yi et al. 2011), similar results were obtained for some fish species, whereas higher results were obtained for some fish species. The levels were higher than those measured in the Sariçay (Yilmaz et al. 2007), the Atatürk Dam Lake Karadede and Ünlü (2000), the Taihu Lake (Qiao-qiao et al. 2007) and the Kasumigaura Lake (Alam et al. 2002). However, Cd data were lower than the study data obtained in six fish species in the Mediterranean (Canli and Atli

2003) and for the African cat fish in the Nile River (Alaa Osman and Kloas 2010).

Lead levels varied between  $9.3$  and  $87.9 \mu\text{g g}^{-1}$  in *C. capoeta umbla*. The Pb levels ranged between  $8.3$  and  $83.2 \mu\text{g g}^{-1}$  in *C. mosullensis*. Pb levels from this study were higher than the levels (Karadede and Unlu 2000; Chale 2002; Alam et al. 2002; Mendil et al. 2005; Turkmen et al. 2005; Qiao-qiao et al. 2007; Yilmaz et al. 2007; Dural et al. 2007; Yilmaz 2009; Alaa Osman and Kloas 2010). Our results showed similarities with some of the data from the study performed on 6 fish species in the Mediterranean by Canli and Atli (2003).

Cadmium and lead data were above the maximum limits defined in the Turkish Food Codex (TFC 2002). Industrial operations are the most important sources of these two metals. They are known to accumulate in human tissue and have toxic effects. Human beings are exposed to Pb mostly through ingestion of contaminated food. Therefore, Pb levels were above the allowed limits and could pose a health risk to humans.

Copper levels varied in the *C. capoeta umbla* between  $9.0$  and  $41.9 \mu\text{g g}^{-1}$ , and in the *C. mosullensis*, the levels varied between  $7.9$  and  $22.2 \mu\text{g g}^{-1}$ . Findings from this study showed similar results to the studies conducted in the Nil River, the Atatürk Dam Lake, the Tokat Lake and the Mediterranean (Karadede and Unlu 2000; Canli and Atli 2003; Mendil et al. 2005; Turkmen et al. 2005; Alaa Osman and Kloas 2010). They were higher than values of the studies conducted in Yangtze River, Sariçay ve Kasumigaura Lakes (Alam et al. 2002; Yilmaz et al. 2007; Yi et al. 2011), and lower than the values of the study conducted at Köyceğiz on *Mugil cephalus*, *Angiulla anguilla* and *Oreochromis niloticus* fish (Yilmaz 2009).

Zinc levels were as low as  $23.0 \mu\text{g g}^{-1}$  in *C. mosullensis* and as high as  $91.4 \mu\text{g g}^{-1}$  in *C. capoeta umbla*. Alaa Osman and Kloas (2010) found similar results in *Claris gariepinus* tissues in the study conducted in the Nil River. Again, the studies conducted in the Mediterranean, Tuzla Lagoon and Tanganyika Lake showed similarities with our work (Chale 2002; Canli and Atli 2003; Dural et al. 2007). However, Zn levels in Sariçay were higher than the study values on *Leuciscus cephalus* and *Lepomis gibbosus* (Yilmaz et al. 2007) and lower than the levels measured at Köyceğiz Lake on three fish species (Yilmaz 2009).

Copper and zinc can be dangerous to aquatic animals and to human health at elevated levels. Therefore, in spite of that they accumulate at least in muscle tissues (Sanpera et al. 1983), their concentration in fish should be evaluated for ecological management and to ensure safe fish consumption by humans.

The maximum allowable levels of Cu and Zn, according to the Turkish Food Codex (2002), are  $20$  and  $50 \mu\text{g g}^{-1}$ , respectively. On the basis of these standards, the findings

from this study were within the allowable limits, particularly for muscle tissues. The study findings complied with Canadian, Hungarian and international standards (Papagiannis et al. 2004).

The lowest nickel concentration was  $0.27 \mu\text{g g}^{-1}$ , whereas the highest concentration was  $1.57 \mu\text{g g}^{-1}$ . Our data showed similar levels with *Silurus triostegus* from the study conducted in the Atatürk Dam Lake (Karadede et al. 2004). Ni levels were lower than measurements obtained from the Tokat Lake by Mendil et al. (2005) and higher than the measurements from the Kasumigaura Lake by Alam et al. (2002).

According to our study results, metals accumulated in muscle tissues, with the highest level of accumulation in the liver and gill tissues. Many studies demonstrated that metals accumulated in metabolic organs, such as the liver (Karadede et al. 2004; Yilmaz et al. 2007). Our results confirmed that different levels of accumulation of metals occur in different tissues. Measurements taken in the liver revealed the tendency of metal accumulation, while levels measured in the gills reflected the metal concentration of the aquatic environment from which the fish were taken. Therefore, liver and gills are better indicators of environmental metal contamination than other organs in fish (Karadede et al. 2004). The comparison of metal concentrations in the same tissues from two different fish species was quite difficult because of the feeding habits, dissimilarities in the aquatic environment and growth rates of the species (Papagiannis et al. 2004; Yilmaz et al. 2007).

On the basis of the variance analysis, in muscle tissue form the two fish species, there was an important difference with regard to Fe, Cd, Cu, Ni versus Pb levels ( $p < 0.05$ ) whereas there was no difference for Zn ( $p > 0.05$ ). Substantial differences were identified in liver tissue of both fish species among stations in terms of the Fe, Cd, Cu, Ni, Pb levels versus Zn ( $p < 0.05$ ). Finally, Fe, Cd, Cu, Ni, Pb versus Zn levels measured in gill tissue from *C. capoeta umbra* were very different among the stations, ( $p < 0.05$ ), and Fe, Cu, Ni, Pb versus Zn levels measured in gill tissue of *C. mosullensis* were very different among the stations ( $p < 0.05$ ) as well. Conversely, no difference in the Cd value was observed among the stations ( $p > 0.05$ ). The difference that was observed in the same tissues at the stations provided some sense of the level of metal contamination at each station. The three stations were being exposed to metal pollution from different discharge sources. It also revealed that there was no water treatment facility in the regions near the stations to reduce the metal concentrations to allowable limits.

According to the correlation analysis results of the metals, a significant positive correlation between Fe and Cu ( $r = 0.788$ ), Fe and Zn ( $r = 0.560$ ) were observed. In addition, there was a significant correlation between Cu

and Zn ( $r = 0.748$ ), Ni and Pb ( $r = 0.346$ ) and Pb and Zn ( $r = 0.501$ ), respectively. Moreover, there was no significant correlation between other metal pairs. These results demonstrated that some metals had similar sources, which could be related to the geological nature of the region (Yilmaz et al. 2007).

This study was conducted to determine the metal concentration of two fish species in Karasu River, an important branch of the Tigris River. The results of this study showed similarities with some previously published studies, and our findings were partially compatible with national and international standards. Cadmium and lead were above the highest limits defined in the standards. Metal accumulations in muscles were lower than those measured in the liver and in gills. Metal accumulation varied among the stations and revealed the pollution level of the river. As a general result of the study, it was concluded that the consumption of this river's fish could cause a significant health hazard, although some data were within the maximum allowable limits defined in international standards.

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