

# A preliminary study of heavy metals in transcaucasian barb (*Capoeta capoeta capoeta* Guldenstaedt, 1772) from the Kars Creek, Turkey

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## SUMMARY

In this study, the levels of some heavy metals (Fe, Cu, Zn, Cr, Co and Cd) in the edible muscle tissues of transcaucasian barb (*Capoeta capoeta capoeta*) from the Kars Creek were investigated. Samples, collected from the river in February, May and August 2003, were analysed by Atomic Absorption Spectrophotometry (AAS). The mean concentrations of the metals accumulated in *C. capoeta capoeta* varied as follows: iron (Fe) 8.22-16.33  $\mu\text{g g}^{-1}$ , zinc (Zn) 0.610-0.757  $\mu\text{g g}^{-1}$ , cobalt (Co) 0.0038-0.0373  $\mu\text{g g}^{-1}$ , Chromium (Cr) 0.0053-0.0140  $\mu\text{g g}^{-1}$ , copper (Cu) 0.0030-0.0093  $\mu\text{g g}^{-1}$  and cadmium (Cd) 0.0018-0.0029  $\mu\text{g g}^{-1}$  (wet weight). The order of concentration of the heavy metals in the muscle samples was Fe>Zn>Cr>Co>Cu>Cd. The results were compared with the tolerance levels recommended by FAO/WHO Maximum Permissible Limits, and it was determined that the consumption of this fish species did not pose any risk to human health. However, periodic monitoring of these metals in the fish consumed by local people is recommended.

**Keywords:** heavy metals, residues, fish, risk assessment.

## RÉSUMÉ

**Analyse des concentrations en certains métaux lourds (fer, cuivre, zinc, chrome, cobalt, cadmium) dans la chair du poisson jaune du Caucase (*Capoeta capoeta capoeta* Guldenstaedt, 1772) pêché dans la rivière de Kars en Turquie.**

Dans cette étude, nous avons entrepris la caractérisation des niveaux de contamination des muscles des poissons Siraz (*Capoeta capoeta capoeta*) par des métaux comme le fer, le cuivre, le zinc, le chrome, le cobalt et le cadmium. Les échantillons ont été prélevés dans la rivière Kars pendant les mois de Février, de Mai et d'Août de l'année 2003. Ils ont été analysés par spectrophotométrie à absorption atomique.

Les teneurs en métaux observées dans les muscles des *Capoeta capoeta capoeta* sont les suivantes: le fer (Fe) 8.22 – 16.33  $\mu\text{g g}^{-1}$ , le cuivre (Cu) 0.0030 – 0.0093  $\mu\text{g g}^{-1}$ , le zinc (Zn) 0.610 – 0.757  $\mu\text{g g}^{-1}$ , le chrome (Cr) 0.0053 – 0.0140  $\mu\text{g g}^{-1}$ , le cobalt (Co) 0.0038 – 0.0373  $\mu\text{g g}^{-1}$ , le cadmium (Cd) 0.0018 – 0.0029  $\mu\text{g g}^{-1}$ . Ces résultats ont été comparés avec les valeurs limites acceptées par les autres pays, avec les normes de l'organisation d'agriculture et de nourriture et l'organisation mondiale de la santé (FAO/WHO). Ceci a permis de montrer que les niveaux de concentration de ces métaux étaient faibles dans les tissus musculaires et que, par conséquent, la consommation de ce type de poissons n'est pas dangereux pour la santé humaine. Toutefois, il convient de continuer à faire des analyses périodiques de ces métaux dans les poissons consommés par la population locale.

**Mots-clés :** poisson, métaux lourds, accumulation, rivière de Kars, Turquie.

## Introduction

Rivers and lakes are important components of freshwater ecosystems. The availability of these natural water systems has been a factor in the development of various civilisations in their vicinity [5], but in developing countries, increasing population and industrial and agricultural production has resulted in contamination of these systems [11]. For these reasons, concern about the effects of anthropogenic pollution on freshwater ecosystems is gradually increasing [4]. To meet the needs of an increasing population, heavy industries have been developed which utilize large quantities of water before discharging it back into rivers as effluent loaded with chemicals [28]. River systems may be excessively contaminated with man made heavy metal pollutants. Under certain environmental conditions, the heavy metals may accumulate to toxic concentrations, and cause ecological damage [36]. In ecological terms, fish are irreplaceable bio-indicators of the

degree of damage to the aquatic environment. However, it is also important to monitor the contamination of fish by heavy metals because frequent consumption of the contaminated fish presents a very serious health risk [34].

The province of Kars is located in the region of North Eastern Anatolia in Turkey, and is on the Historic Silk Road. It is a famous city with its historical and archeological ruins, natural beauties and rich folklore culture.

The Kars Creek runs from the Allah-akhbar Mountains to the Arpacay Dam Lake, and is approximately 93 km in length. It is a typical freshwater ecosystem of great importance in regard to biodiversity and to aesthetic value. Due to its morphological characteristics, the Kars Creek is a suitable habitat for a variety of species, especially fish for both recreational and intensive amateur fishing. The fish species found most commonly in the creek are *Leuciscus cephalus orientalis*, *Barbus capito capito*, *Carasius carasius*, *C. capoeta*

*capoeta* and *Silurus glanis*. Amongst these species, *C. capoeta capoeta* predominates in the creek.

The province of Kars manufactures rugs, woollens, leather and milk products. The Kars Creek drains through Kars and receives many domestic, industrial and agricultural effluents, and sewage water from the surrounding areas. Moreover, effluents containing fertilizers and pesticides from animal farms reach the creek, increasing its metal burden. Along the creek, there are also a few soil washing facilities. In these facilities, soils contaminated with inorganic and organic contaminants such as heavy metals, radionuclides and pesticides are washed.

The aim of the present study was to determine the concentration of heavy metals in the edible muscle tissues of transcaucasian barb (*Capoeta capoeta capoeta*) from the Kars Creek.

## Materials and methods

The study area is located in the province of Kars. *Capoeta capoeta capoeta* (Family: Cyprinidae) was selected for the present study and caught in May, August and November, 2003 from twelve sampling sites situated along the Kars Creek and its tributaries (Fig. 1), where this species is widely distributed in the aquatic environment. The sites were selected according to the localization of principal sources of pollution (upstream and downstream from the main urban sewage discharge points and soil washing areas). The sampling sites were selected as representative regions of the creek and its tributaries, and are shown in Figure 1: site 1: Parsadan side; site 2: behind Selim Health Center; site 3: Akyar Village; site 4: below Red Bridge; site 5: Old Mill district; site 6: in front of the Faculty of Arts and Science; site 7: below the bridge on the outskirts of Mirror Village; site 8: below the bridge in Bogaz Village; site 9: below the bridge in Akcakale Village; site 10: meadow district on the Susuz Creek; site 11: below Akcakale Village (at the confluence of the Kars Creek and the Susuz Creek); site 12: below the bridge in Kucuk Catma Village (at the confluence with the Arpacay Dam Lake). These sites receive many domestic and agricultural effluents, and sewage water from areas surrounding the creek.

A total of 72 barb were caught from the creek by net and electrofishing. The mean length and weight of the collected fish were immediately measured, and were estimated as 21.64 (11,6-35,1) cm and 102.04 (20,3-419,7) g., respectively.

The fish samples were caught and transported daily to the laboratory in an ice-box, and were kept in deep freeze at -21 °C until analysis. For metal determination, muscle samples were taken (approximately 4.7-5.3 g.) from the dorso-lateral surface of each fish and weighed [12, 44]. After being individually transferred to previously weighed 100 ml glass vials and dried in an oven for 24 h. at 105 °C, they were digested on a hot plate by adding nitric acid and hydrogen peroxide (2:1) v/v according to FAO Fisheries Technical Paper No. 158 [6, 12, 44]. The digested samples were diluted to 50 ml

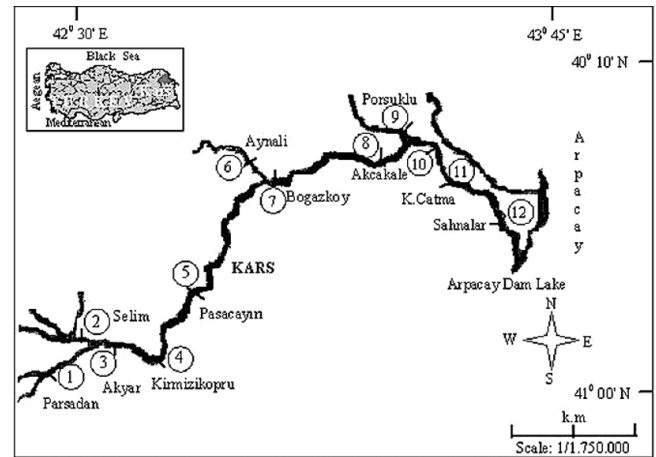


FIGURE 1. Map of the Kars Creek, Turkey, showing locations of study area.

with deionized water. Analysis of the heavy metals in the fish samples was carried out using a flame atomic absorption spectrophotometer (Perkin Elmer model 603) to determine the levels of iron, zinc, copper, cobalt, chromium and cadmium. The heavy metal concentration in the edible muscle tissues of the barb is presented in  $\mu\text{g g}^{-1}$  of the wet weight.

Statistical analysis of the results was carried out by One-way ANOVA analysis of variance. A  $P < 0.05$  value was accepted as statistically significant [33].

## Results and discussion

Table 1 presents the mean concentration of heavy metals (Fe, Cu, Zn, Co, Cr and Cd) in the muscle tissues of the barb from twelve sites in the Kars Creek. Figure 1 shows the sampling sites in the Kars Creek.

Iron concentrations were found in the range 8.22-16.33  $\mu\text{g g}^{-1}$  on a wet weight (w. wt.) basis (Table 1). Iron concentrations in the muscle tissues of the barb varied significantly ( $P < 0.05$ ) from site to site. The highest concentration of iron (16.33  $\mu\text{g g}^{-1}$ ) was observed at locality 9 (downstream). Significant variations were observed between sites 6, 9 and 11 ( $P < 0.05$ ). Although the concentration of iron was higher in November than in May (Table 2), no trend was observed in the monthly variations ( $P > 0.05$ ).

A high level of iron in comparison to other metals is typical of fish muscle [13, 20, 31, 43]. The iron values found in this study were higher than those reported by EKBO and IBOK, [13] in fish from the River Calabar, S.E Nigeria; by KARADEDE et al. [24, 25] in fish from the Atatürk Dam Lake; by GULFRAZ et al. [21] in fish from the Rawal and Mangla Lakes; and by GOKSU et al. [20] in fish from the Seyhan Dam Lake. However, the mean iron levels in the muscle tissues of the barb were found to be much lower than those reported by AJMAL et al. [2] in fish from the River Kali Nadi U.P. India; by WINGER et al. [43] in fish from the Lower Savannah River, Georgia and South Carolina; by CANPOLAT and CALTA [11] in fish from Lake Hazar, Turkey, and by MENDIL et al. [31] in fish from lakes in Tokat, Turkey.

Site	n	Fe	Cu x 10 <sup>3</sup>	Zn x 10	Co x 10 <sup>3</sup>	Cr x 10 <sup>3</sup>	Cd x 10 <sup>3</sup>
1	6	9.14±0.98 <sup>ab</sup>	6.0±3.0	6.10±0.4	3.8±1.0 <sup>b</sup>	12.7±6.0	2.3±0.05
2	6	9.31±0.91 <sup>ab</sup>	3.0±1.0	6.53±1.2	37.3±17.0 <sup>a</sup>	13.0±7.0	1.9±0.05
3	6	8.97±2.30 <sup>ab</sup>	5.0±2.0	6.53±0.3	17.2±13.0 <sup>ab</sup>	12.7±7.0	1.8±0.05
4	6	11.01±1.53 <sup>ab</sup>	5.0±2.0	6.13±0.4	3.8±0.0 <sup>b</sup>	5.3±1.0	1.9±0.06
5	6	9.10±1.01 <sup>ab</sup>	7.7±4.0	7.00±0.3	3.8±2.0 <sup>b</sup>	12.7±7.0	2.9±0.12
6	6	8.22±0.06 <sup>b</sup>	3.3±1.0	6.30±0.3	5.0±3.0 <sup>b</sup>	8.0±0.0	2.3±0.05
7	6	13.92±2.71 <sup>ab</sup>	6.7±3.0	6.70±0.7	5.1±1.0 <sup>b</sup>	12.7±7.0	2.9±0.05
8	6	10.24±1.82 <sup>ab</sup>	9.3±4.0	7.57±1.0	5.1±1.0 <sup>b</sup>	14.0±6.0	2.9±0.00
9	6	16.33±2.31 <sup>a</sup>	6.3±3.0	6.33±0.7	6.3±1.0 <sup>b</sup>	12.7±7.0	1.9±0.05
10	6	12.69±0.82 <sup>ab</sup>	7.7±5.0	7.30±0.2	5.0±1.0 <sup>b</sup>	13.3±5.0	1.9±0.05
11	6	8.39±0.07 <sup>b</sup>	4.0±2.0	6.53±0.5	5.1±1.0 <sup>b</sup>	5.3±1.0	1.9±0.05
12	6	9.35±1.11 <sup>ab</sup>	3.7±2.0	6.67±0.7	5.2±1.0 <sup>b</sup>	5.3±1.0	1.8±0.05
Mean		<b>10.56±2.51</b>	<b>5.6± 0.7</b>	<b>6.64 ±0.2</b>	<b>86.0±2.2</b>	<b>10.6±1.0</b>	<b>22.0±0.5</b>
Range		(8.22-16.33)	(3.0-9.3)	(6.10-7.57)	(3.8-37.3)	(5.3-14.0)	(1.8-2.9)
P.Value		<0.05	N.S	N.S	<0.05	N.S	N.S
FAO / WHO & EVM <sup>14</sup> Max. Limits		<b>800 [38]</b>	<b>500 [39]</b>	<b>1000 [40]</b>	<b>N/A [3]</b>	<b>150 [14]</b>	<b>7 [41]</b>

All values in  $\mu\text{g g}^{-1}$  (Mean±S.D.)

All max. permissible limits in  $\mu\text{g kg}^{-1}$  bw/day.

NS: Non-significant.

a, b: Indicates statistical differences among the mean within the same row ( $P<0.05$ ).

N/A : Not available

TABLE I.-The mean concentrations of heavy metals determined in the muscle tissues of the barb from the monitoring sites along the Kars Creek.

Months	Fe	Cu x 10 <sup>3</sup>	Zn x 10	Co x 10 <sup>3</sup>	Cr x 10 <sup>3</sup>	Cd x 10 <sup>3</sup>
May	9.48±0.61	5.7±0.8 <sup>ab</sup>	6.40±0.17	13.04±18.0	15.2±3.0	2.2±0.3 <sup>ab</sup>
August	10.96±1.20	2.6±0.4 <sup>b</sup>	6.92±0.32	6.0±0.7	8.6±2.0	1.6±0.1 <sup>b</sup>
November	11.24±0.94	8.5±1.6 <sup>a</sup>	6.59±0.35	8.7±4.7	8.0±0.0	2.5±0.1 <sup>a</sup>
P.Value	N.S	<0.05	N.S	N.S	N.S	<0.05

All values in  $\mu\text{g g}^{-1}$  (Mean±S.D.).

NS: Non-significant.

a, b: Indicates statistical differences among the mean within the same row ( $P<0.05$ ).

TABLE II.- Monthly variations of average heavy metal concentrations detected in the muscle tissues of the barb from the Kars Creek.

Concentrations of copper in the muscle tissues of barb at all sites were in the range

0.0030 - 0.0093  $\mu\text{g g}^{-1}$  w.wt (Table 1). Copper concentrations did not vary significantly ( $P>0.05$ ) from site to site in the muscle tissue samples. The highest copper concentrations were found in samples from site 8. Copper levels were higher in November than in August (Table 2). Similar results have also been reported earlier by NAMMINGA, [32], BRUNNER et al., [8] and

IQBAL et al., [22]. In contrast, MATHIS and CUMMINGS [30] reported greater concentrations of copper in August than in February. The monthly trend in the distribution of Cu and Cd showed significant changes ( $P<0.05$ ). Our copper results are much lower than those reported in the literature [12, 21, 26, 36] and probably represent background levels for this system.

Zinc concentrations in the muscle ranged from 0.610 to 0.757  $\mu\text{g g}^{-1}$  w. wt. (Table 1). The highest zinc concentration

( $0.757 \mu\text{g g}^{-1}$ ) was detected at site 8. No significant differences were observed in the mean monthly and spatial changes. The zinc concentrations in the muscle tissue of *C. capoeta capoeta* were found to be lower than values reported in the literature [13, 20, 21].

Cobalt concentrations varied from  $0.0038$  to  $0.0373 \mu\text{g g}^{-1}$  w. wt (Table 1). The maximum values of cobalt ( $0.0373 \mu\text{g g}^{-1}$ ) were found at site 2. Cobalt concentrations varied significantly among sites in the muscle tissue samples (Table 1), ( $P < 0.05$ ).

With the exceptions of cobalt and iron, it was determined that the average concentrations of the analysed metals (Cu, Zn, Cr and Cd) did not vary significantly ( $P > 0.05$ ) among sites. Cobalt levels were higher in May than in August (Table 2). However, the overall monthly variations showed no significant changes. These concentrations were found to be much lower than those reported (approximately  $0.1 \mu\text{g g}^{-1}$ ) for bivalves in unpolluted water [21, 42].

Chromium concentrations in the muscle tissue of *C. Capoeta capoeta* ranged from  $0.0053$  to  $0.0140 \mu\text{g g}^{-1}$  w. wt (Table 1). These values are much lower than those reported earlier [13, 31, 36, 44]. The highest chromium concentrations were found in the muscle tissues from site 8. No significant differences were observed in the mean monthly and spatial changes.

Cadmium concentrations ranged from  $0.0018$  to  $0.0029 \mu\text{g g}^{-1}$  w. wt (Table 1). The highest cadmium concentrations were found between sites 5, 7 and 8. Cadmium concentration was higher in November than in August (Table 2). The monthly trends in the distribution of Cd showed significant changes ( $P < 0.05$ ). Cadmium concentrations in the muscle samples were found to be much lower than other literature values reported earlier [20, 21, 34, 43].

While significant differences were found in the levels of copper and cadmium in the muscle between seasons ( $P < 0.05$ ), there were no statistical differences between seasons in the concentrations of the other metals (Fe, Zn, Co and Cr) in the muscle tissues.

As a concentration tendency was not found along the river, the mean values for the fish samples were used to evaluate the extent of contamination and to compare the levels found with those reported for freshwater ecosystems and similar fish species where possible [7]. The concentrations found in *C. capoeta capoeta* in this study are generally much lower than values reported from fish in other contaminated sites such as the River Yıldız in Turkey (values ranging from  $7.2$  to  $17.00 \mu\text{g g}^{-1}$  w wt for Fe; from  $4.1$  to  $18.3 \mu\text{g g}^{-1}$  w wt

for Zn and from  $1.0$  to  $3.7 \mu\text{g g}^{-1}$  w wt for Cu in *Leuciscus cephalus* [1]; the River Tigris in Turkey (Zn levels from  $11.1$  to  $61.4 \mu\text{g g}^{-1}$  w wt., Cu levels from  $23.8$  to  $55.6 \mu\text{g g}^{-1}$  w wt, Cr levels from  $18.9$  to  $25.9 \mu\text{g g}^{-1}$  w wt in *Liza abu*) [36]; and the River Seyhan in Turkey (Cu levels from  $6$  to  $11 \mu\text{g g}^{-1}$  dry weight, Cd levels from  $3$  to  $6 \mu\text{g g}^{-1}$  dry weight in *Capoeta barroisi*) [26]. They are of the same order as values found for fish living in unpolluted waters such as the River Plate in Argentina (Zn levels ranging from  $70.0$  to  $92.0 \mu\text{g g}^{-1}$  dry weight and Cu levels ranging from  $2.0$  to  $10.0 \mu\text{g g}^{-1}$  dry

weight for different species such as *Cyprinus carpio* and *Mugil cephalus*), and the Jacarepaguá Lagoons in Brazil ( $0.26 \mu\text{g g}^{-1}$  w wt for Cu and  $7.9 \mu\text{g g}^{-1}$  w wt for Zn content in *Centropomus sp.*) [7]. Among the metals, iron was found to be present in the highest concentration in the muscle, and cadmium in the lowest. Similar results have been reported from a number of fish species that the muscle is not an active tissue in accumulating heavy metals [23, 24].

The levels of heavy metals in the muscle were determined to be in the order  $\text{Fe} > \text{Zn} > \text{Cr} > \text{Co} > \text{Cu} > \text{Cd}$ . A similar order has also been found in the muscles of *Heteropneustes fossilis* [2], Mirror Carp (*Cultured Cyprinus carpio*) and Pike Perch (*Stizostedion lucioperca*) [20], Wild Carp (*Cyprinus carpio*) and *Siluris glanis* [37], and *Leuciscus cephalus* [1]. There appear to be no reported baseline studies on heavy metals in fish species from the Kars Creek. Therefore, no comparison can be made with the present data from the creek. Trace metal assessment in fish muscle is one of the means for investigating the amount of trace metals entering the human by food chain enrichment [16]. The concentration of metals in muscle tissue is important in respect of the edible parts of the fish. The concentrations of heavy metals analysed in the muscle of barb were lower than the maximum permitted concentrations proposed by the FAO/WHO [15, 38, 39, 40, 41]. Heavy metal levels in different species depend on the feeding habits [10, 18, 25, 44], age, size and length of the fish [17, 27], and on their habitats [9, 18, 19].

A significant correlation was observed statistically among the elements in muscle of the *C. Capoeta capoeta* analyzed. There were both positive and negative correlations among some element pairs ( $r = 0.34$ ,  $P < 0.05$  between Cd and Cu;  $r = 0.22$ ,  $P > 0.05$  between Co and Fe), while other elements had no significant relationships in the study area. YILMAZ et al. (in press.) reported that highly positive relationships were between Cd and Cu, and Co and Fe in muscle of chub. Degrees of correlations found in our study were lower than those reported in the literature [29, 46]. In addition, these results show that the element pairs may have similar sources and these may be related to the geochemical structure of the region. There was no clear difference in the levels of the metals tested when factors such as length, age and weight were compared. These findings are similar to those in previous reports [1, 19, 35]. The results presented (Table 1) in this study indicate that the concentrations of all metals in the muscle tissue of the barb studied were much lower than those reported previously, even in unpolluted waters, and were under the thresholds prescribed as dangerous by the FAO/WHO [15, 38, 39, 40, 41].

In addition, our findings are in agreement with cited results. Therefore, the consumption of *C. capoeta capoeta* caught from the Kars Creek (Turkey) poses no risk to public health.

## Conclusion

This preliminary study was carried out to provide information on heavy metal concentrations in the muscle tissues of barb from the Kars Creek.

The lack of trend in the spatial distribution of the metals in the Kars Creek indicates random distribution from diverse sources: municipal liquid and solid wastes, agricultural inputs, atmospheric fallout, soil washing inputs and geological weathering, the direct impact of which was not quantitatively assessed in this study.

Heavy metal pollution affects not only the health of the aquatic ecosystem, but also public health as a result of bioaccumulation in the food chain. Our results showed that the concentrations of the metals detected in the edible muscle tissue of barb from the Kars Creek were well below the FAO/WHO maximum permissible limits. These results, however, serve as baseline data against which future impact assessments will be evaluated.

High concentrations of Zn, Cu, Cr, Co and Cd may have a detrimental effect on the health of the rural community in the vicinity of the river, who use the untreated creek water directly for domestic purposes. Therefore, to continue to protect both aquatic life and public health in the creek and its surrounding area, it is suggested that the practice of depositing municipal liquid and solid wastes into the creek without prior treatment should be stopped. Furthermore, since consumption of barb by the rural and urban communities in the vicinity of Kars is high, the levels of metals accumulated in the fish should be systematically monitored.

## Acknowledgements

The authors are grateful for the financial support of Unit of the Scientific Research Projects of Kafkas University.

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