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Assessment of Cd, Hg, Pb, Cu and Zn Amounts in Muscles of *Cyprinus carpio* from Karasu Stream, Sinop

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Abstract

Heavy metal contaminations in aquatic habitats effect negatively on the organisms that depend on the water. In this work heavy metal levels in edible tissues of *Cyprinus carpio* from Karasu Stream in Sinop in summer, autumn and winter were determined by Inductively Coupled Plasma Mass Spectrometer. The accumulation pattern in the work is in the order of Zn>Cu>Pb>Cd> Hg. The amounts of Hg, Cd, Pb, Cu and Zn in carps were 0.022-0.036, 0.031-0.045, 0.22-0.29, 1.32-1.61 and 8.4-12.3 mg kg^{-1} wet wt., respectively. Concentrations of heavy metals in *C. carpio* were all below the TFC and EC guidelines. Total target hazard quotient (TTHQ) was 0.10722 and below 1 which showed that consumption of carp from the Karasu Stream has no health threats by now as the heavy metals investigated was concerned.

Article History

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Keywords:

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Karasu Stream;
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Target Hazard Quotient.

Introduction

Sources of contaminants for freshwater include direct and via runoff, direct discharges into water or watersheds, atmospheric deposition as well as wastes from settlements. Accumulation of heavy metals in aquatic environments can cause accumulation in living organisms which may pose risks to human health via food.[1] Concentration of a contaminant in aquatic organisms is a good indicator of the contaminant's bioavailability.[2] Fish are incessantly exposed to contaminants released into water bodies. In general fish species as the top of the aquatic food chains may accumulate huge amounts of contaminants especially heavy metals from the water bodies and have accordingly been found to be a good bio-indicator of heavy metal contamination in aquatic systems.[1,2]

Carp species are generally herbivores that have the potential to alter aquatic plant populations

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and ecosystems. Contaminants especially heavy metals are persistent in the aquatic environment causing serious illness in organisms including fish and human. The results of many investigations of metal accumulation in fish tissues in contaminated waters pointed out that considerable level of toxic metals may be accumulated in fish including edible tissues without causing mortality.[3] Heavy metals are persistent type of contaminants and cannot be removed by heat treatment, thus their availability affect human being via consumption. Cd, Hg and Pb are non-essential metals and are known to be harmful to the organisms in any amount. In spite of Cu and Zn are essential metals, the occurrence of Cu and Zn in high amounts is toxic to living organisms. Heavy metal accumulations in fish are always at the forefront in terms of public health and such studies are required.[4]

Although there is the high capacity of common carp (*Cyprinus carpio*) in Karasu Stream as a source of protein, there is no available data on the amounts of heavy metals in the Stream. This study shows the first time carps are being used to determine of metal contamination in Karasu Stream. In this study, the amounts of Cd, Hg, Pb, Cu and Zn were determined in the muscles of common carp to appraisal the level of heavy metal pollution in Karasu Stream. The chance of health threats to people through consumption of *C. carpio* from Karasu Stream was calculated the target hazard quotient.

Materials and Methods

The location of the Karasu Stream in the province of Sinop is 42° 1' 59'' N 35° 3' 59' E. Its length is 80 km. Karasu Stream falls from 8 km west of Sinop into the Black Sea near Akliman (Figure 1).

Carp samples were caught from Karasu Stream in summer (July and August), autumn (September and October) and winter (November and December) of the year 2016. The samples were washed in bi-distilled water to remove any debris. The muscles were dissected according to Bernhard.[5] These edible parts were measured for metal analysis by ICP-MS.

In order to measure of heavy metal amounts in carp muscles, digested with Suprapur® HNO_3 using Milestone Systems, Start D 260 microwave for metal assay. All chemicals used in the study were of reagent grade. The metal solutions from Merck were made use of the calibrations by diluting stock solutions of 1000 mg l^{-1}. After digestion, the heavy metal levels were operated by ICP-MS (Agilent Technologies, 7700X). Metal amounts in muscles of *C. carpio* were determined on wet wt. basis as µg

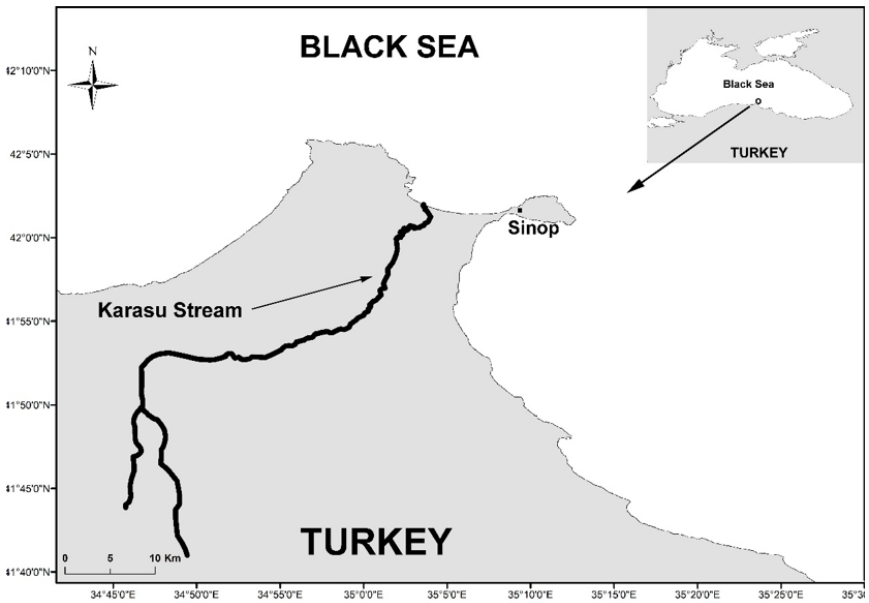

Fig. 1: Study area

g^{-1}. Standard reference material DORM 2 dogfish muscle from National Research Council of Canada for elements was used to measure the reliability of the analysis. All digested edible tissues were performed triplicate for each element.

The estimated daily intake (EDI)[6] depends on both the metal concentration and the amount of consumption of fish. The EDI of elements was calculated using the following equation:

$$EDI = \frac{E_f x E_d x F_{ir} x C_m}{W_{ab} x T_a} x10^{-3}$$

Where E_f is the exposure frequency (365 days/year); E_d is the exposure duration, equivalent to mean lifespan (70 years); Fir is the fish ingestion rate (g/person/day), which was considered to be 27.4 g/person/day in Sinop,[4] this value is equal to about 191.8 grams in week; Cm is the concentration of heavy metal in fish (mg kg^{-1} wet wt.); Wab is the average body weight (an adult body weight was noted to be 70 kg); and Ta is the mean exposure time for non-carcinogens (which is equal to $E_f \times E_d$). EWI values were computed from EDI values. Intake estimates were stated as per unit body wt. (mg kg^{-1} body wt. /weekly).

Target hazard quotient (THQ),[6] which is a proportion of the evaluated exposure (EDI) to the oral reference dose (RfD), is used to appraise the potential non-carcinogenic risk of the people of the sensed contaminated fish.

$$TQH = EDI / (R_fD)$$

Where, the R_fD values for Hg, Cd, Cu and Zn are 0.0003, 0.001, 0.04 and 0.3 mg/kg-day, respectively.[7] R_fD is not available for Pb. The U.S. Department of Health and Human Services Public Health Service[8] pointed out that it would be unsuitable to develop a R_fD for inorganic Pb and its compounds because some of the sanitary impacts related with exposure to Pb happen at blood Pb amounts as low as to be essentially without a threshold.[9] Therefore, the R_fD value for Pb in this study was 0.0035 as used by many researchers.[10,11]

Exposure to more than one contaminant may induce contribution and/or interactive impacts, and hereby, accumulative health effect from plural contaminants' exposure was counted by summing THQ value of individual contaminant and clarified as total target hazard quotient (TTHQ) as follows:

$$TTHQ = THQ_1 + THQ_2 + \ldots\ldots + THQ_n$$

Where n is number of THQ values for each metal. In this study, n, which represents for number of metal, is five.

TTHQ value >1 displays the possibility of reverse health effects and commits the necessity for bearing a further appraisal and likely remedial action. However, TTHQ <1 displays no feasible health consequence from exposure of examined contaminants at existing consumption rate.

Results

Recovered values of all metals range between 98% and 105% of the certified value. In this study, *C. carpio* is used as a bioassay organism for sensitivity to heavy metals effects. Concentrations of heavy metals in fish samples from Karasu Stream are shown in Figures 2-6. The order of accumulation in carps is Zn>Cu>Pb>Cd>Hg. The amounts of Hg, Cd, Pb, Cu and Zn in carps were 0.022-0.036, 0.031-0,045, 0.22-0.29, 1.32-1.61 and 8.4-12.3 mg kg^{-1} wet wt., respectively.

EDIs of these metals were calculated taking into account the means of metals in edible tissues of fish samples and the mean consumption of carps per day for adults and given in Table 1. THQ and TTHQ values of this study were shown in Table 2.

Discussion

Hg and Cd are toxic to biota, the existing of these elements in fish may cause harm on human health at any trace levels. Similarly, Pb is also harmful to human health at even low concentrations. However, in this study (Figures 2-4), concentrations of these metals in *C. carpio* were lower than the safe limits (0.3 mg/kg wet wt. for Pb, 0.5 mg/kg wet wt. for Hg and 0.05 mg/kg wet wt. for Cd) proposed by EC[12] and TFC.[13] Cu and Zn are essential elements to biota but they make health threat when took in big amount exceeded the allowable limits by the Ministry of Agriculture, Forestry and Fisheries14, 30 mg/kg wet wt. for Cu and 50 mg/kg wet wt. for Zn. In this

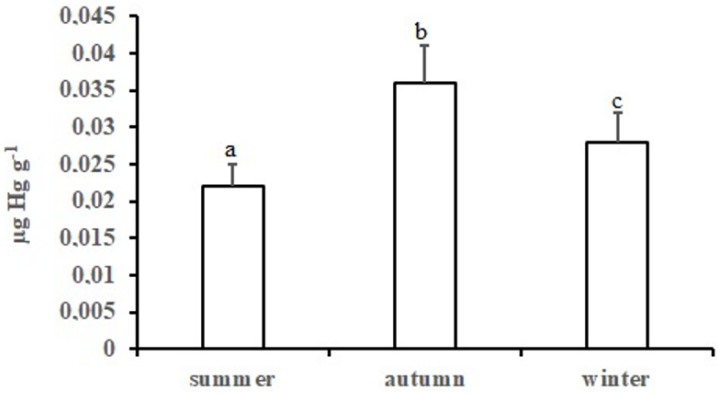

Fig. 2: The concentrations of Hg (wet wt.) in carps from Karasu Stream. a, b, c= The same letters beside the vertical bars in each graph indicate the values are not significantly different (p > 0.05)

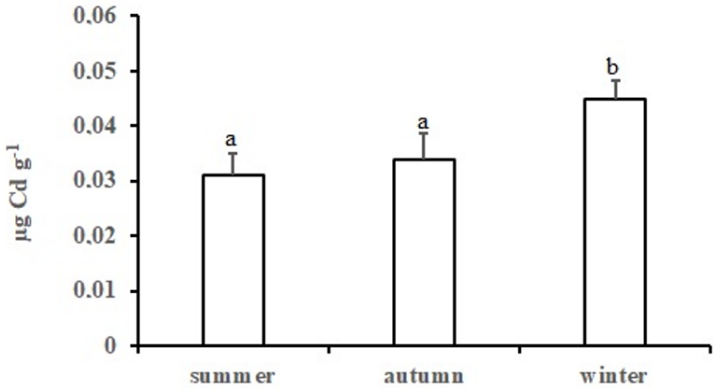

Fig. 3: The concentrations of Cd (wet wt.) in carps from Karasu Stream. a, b= The same letters beside the vertical bars in each graph indicate the values are not significantly different (p > 0.05)

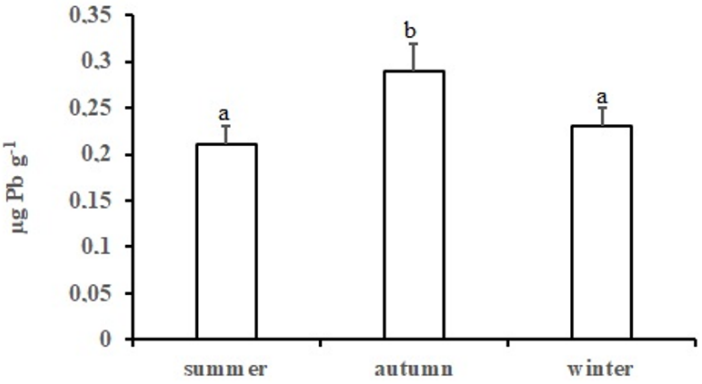

Fig. 4: The concentrations of Pb (wet wt.) in carps from Karasu Stream. a, b= The same letters beside the vertical bars in each graph indicate the values are not significantly different (p > 0.05)

study (Figures 5 and 6), the amounts of Cu and Zn in the muscles of carps were lower than the maximal allowed limits. Therefore *C. carpio* from the Karasu Stream is healthy for consumption.

EDI values are significantly lower than the recommended values of FAO/WHO.[15,16] Health risk appraisal of consumer from the consumption of carp contaminated with heavy metals was calculated by applying the THQ. If THQ < 1 express that the exposed people is unapt to experience some non-carcinogenic reverse impacts throughout the life span. If THQ > 1 express that there is a risk of non- carcinogenic effects, with a getting probability as the level rises. It can be seen from Table 2 that all metals had THQ well below 1 and overall TTHQ was 0.10722.

Consumption of *C. carpio* from Karasu Stream can consequently be said to create no health threats so far as the heavy metals analysed are concerned. This is set on the thought that the individual obtains all their fish supplies from the Karasu Stream and that food processing has no effects on the amounts of heavy metals available in the fish.

In this study Hg, Cd, Pb, Cu and Zn amounts in carps were 0.022-0.036, 0.031-0.045, 0.22-0.29, 1.32-1.61 and 8.4-12.3 mg kg-1 wet wt., respectively. In the literature, heavy metal levels in the muscles

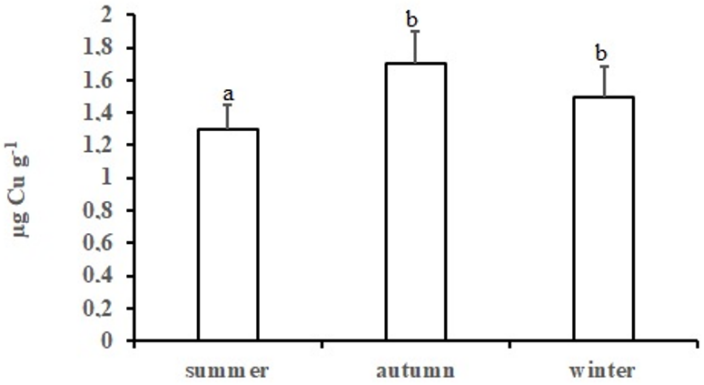

Fig. 5: The concentrations of Cu (wet wt.) in carps from Karasu Stream. a, b= The same letters beside the vertical bars in each graph indicate the values are not significantly different (p > 0.05)

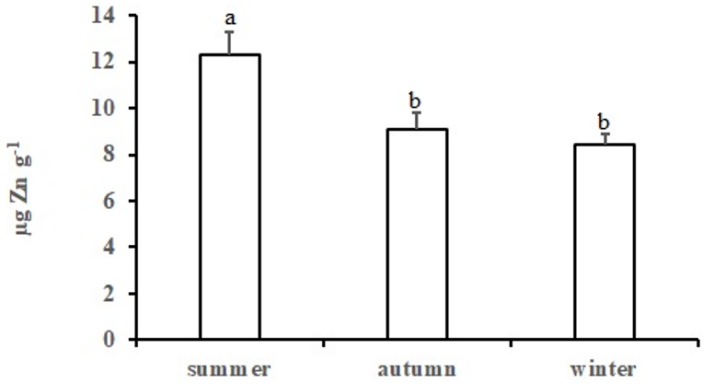

Fig. 6: The concentrations of Zn (wet wt.) in carps from Karasu Stream. a, b= The same letters beside the vertical bars in each graph indicate the values are not significantly different (p > 0.05)

of carps vary considerably among different localities (Table 3). Overall Zn was detected in higher concentrations followed by Cu. The lowest were Hg and followed by Cd. The highest Hg level was 0.12±0.005 µg g^{-1} wet wt. in Lake Sarikum[36] for carp, while similar values were found in the Lake Beysehir[21] and Altınkaya Dam Lake.[34]

Cd levels in for muscles of *C. carpio* the current study were largely in lower ranges with the literature, where it has been reported as 0.088±0.013 µg g^{-1} wet wt. from the Altınkaya Dam Lake17; 0.17±0.07 µg g^{-1} wet wt. from the Avsar Dam Lake[28] and were usually in match values with the Sır Dam Lake,[22] Menzelet Dam Lake,[22] Lake Balık –Kızılırmak,[33] Altınkaya Dam Lake,[34] Lake Sarıkum[36] and Sırakaraagaçlar Stream.[37] As the rest of literature from Table 3 gave dry wt. values, comparisons could not be made.

Pb amounts in the literature have been found in the ranged from 0.025 µg g^{-1} wet wt. from Sırakaraagaçlar Stream[37] to 7.04±1.93 µg g^{-1} dry wt. from Seyhan River.[18] In general, Pb values in this study were lower than other studies[17,18,19,20,23,24,26,27,28,30,31,32] and higher than those in studies.[33,34,36,37] However, it should be kept in mind that some studies gave values as dry wt.

Cu amounts in the current study were in good agreement with determined amounts in the literature.[17,19,20,23,26,27,31,35] Cu levels in the current study were larger than the studies.[34,36,37] Similarly our data for Zn were within the ranges reported in the literature from Table 3;[20,25,29,30,31,34] higher than those in studies.[34,36,37] The values of the current study were lower than the rest of literature in Table 3.

As it can be seen from different studies, the metal values in carps showed changes in different rivers, streams and lakes. Turkey is one of the countries facing fresh water pollution mainly due to untreated discharge of industrial, agricultural and domestic wastes into rivers, streams and lakes. The lack of waste water treatment plants has resulted in discharge of polluted wastes to the rivers, streams

Table 1: Estimated Daily Intakes of heavy metals (mg/day/70 kg body wt.) in edible tissues of *C. carpio* from the Karasu Stream

	EDI				
Season	**Hg**	**Cd**	**Pb**	**Cu**	**Zn**
Summer	8.61143E-06	1.21343E-05	8.61143E-05	0.000516686	0.004814571
Autumn	1.40914E-05	1.33086E-05	0.000113514	0.0006302	0.000598886
Winter	0.00001096	1.76143E-05	9.39429E-05	0.003562	0.003288
Mean	1.1221E-05	1.43524E-05	9.78571E-05	0.000581924	0.00388819

Table 2: THQ and TTHQ values in edible tissues of C. carpio from the Karasu Stream for consumers

	THQ					TTHQ
Season	**Hg**	**Cd**	**Pb**	**Cu**	**Zn**	
Summer	0.02870	0.01213	0.02460	0.01292	0.01605	0.09441
Autumn	0.04697	0.01331	0.03243	0.015755	0.01187	0.12034
Winter	0.03653	0.01761	0.02684	0.014972	0.01096	0.10692
Mean	0.03740	0.01435	0.02796	0.014548	0.01296	0.10722

Table 3: Comparison of the amounts of toxic metals in carps from the different locations in Turkey

Region	Unit	Metals					Ref.
		Hg	Cd	Pb	Cu	Zn	
Altınkaya Dam Lake	μg g^{-1} – w.w.	-	0.088± 0.013	0.413± 0.059	1.04± 0.116	16.98± 1.28	17
Seyhan River	μg g^{-1} – d.w.	-	0.93± 0.27	7.04± 1.93	5.12± 2.37	-	18
Sakarya River	μg g^{-1} – d.w.	-	0.039-0.301	0.056-1.094	0.511-2.054	-	19
Atatürk Dam Lake	ppm - w.w.	ND	ND	ND	1.26-3.90	7.39-11.50	20
Lake Beysehir	μg g^{-1}	0.021–0.022	0.500–0.585	0.255–0.350	-	-	21
Sır Dam Lake	ppm - w.w.	-	0.00-1.14	-	0.00-0.87	-	22
Menzelet Dam Lake		-	0.00-0.60	-	0.53-3.34	-	
Kızılırmak	μg g^{-1} – w.w.	-	0.12	1.79	1.1	80.50	23
Sır Dam Lake	mg kg^{-1} –w..w.	-	-	0.12-0.07	-	-	24
Lake Beysehir	mg kg^{-1} – d.w.	-	-	-	BDL	7.49±4.14 11.32±3.45	25
Lake Hampınar	μg g-1 – d.w.		-	1.3 ± 0.12 1.3 ± 0.12	1.6 ± 0.14 1.2 ± 0.10	32.1 ± 3.1 37.1 ± 3.3	26
Lake Dutluca		-	-	1.2 ± 0.12 1.2 ± 0.12	1.5 ± 0.14 1.2 ± 0.12	32.9 ± 3.1 17.4 ± 1.4	
Almus Dam Lake		-	-	1.0± 0.10 0.7 ± 0.07	2.6 ± 0.18 1.9 ± 0.15	33.6 ± 2.4 37.1 ± 3.7	
Lake Bedirkale	μg g^{-1}	-	-	1.0± 0.1 1.2 ± 0.1	1.2 ± 0.1 1.4 ± 0.1	35.1 ± 3.1 42.1 ± 3.3	27
Lake Boztepe		-	-	0.8 ± 0.1 1.2 ± 0.1	1.6 ± 0.2 2.1 ± 0.2	18.7 ± 1.6 24.2 ± 2.3	
Lake Belpınarı		-	-	1.4 ± 0.1 1.8 ± 0.1	1.0± 0.1 1.3 ± 0.1	18.4 ± 1.4 38.9 ± 3.1	
Lake Avara		-	-	1.3 ± 0.1 2.8 ± 0.2	2.8 ± 0.3 3.9 ± 0.3	23.6 ± 1.1 28.5 ± 1.6	
Lake Ataköy		-	-	0.8 ± 0.1 1.0 ± 0.1	1.3 ± 0.1 3.2 ± 0.3	35.6 ± 2.4 39.1 ± 3.7	
Lake Akın		-	-	1.8 ± 0.1 2.1 ± 0.2	1.4 ± 0.1 1.9 ± 0.2	39.3 ± 3.3 48.6 ± 3.5	
Avsar Dam Lake	mg kg^{-1} – w.w.	-	0.17± 0.07	2.14±2.09	3.85±2.18	-	28
Lake Sugla	mg kg^{-1} – w.w.	-	-	BDL	0.31±0.09 0.30±0.06 0.36±0.02	11.58±1.01 9.83±1.78 10.87±0.56	29
Isıklı Dam Lake	μg g^{-1} – d.w.	-	2.00± 0.47	1.65±0.01	0.37±0.04	4.36±1.30	30
Karacaören Dam Lake		-	1.95± 0.42	1.90±0.02	1.85±1.24	13.13±2.83	

Lake Besehir	mg kg^{-1} – d.w.		2.06-2.32	1.68-4.02	1.09-2.68	9.32-15.92	31
Lake Mogan	µg g^{-1}	-	-	3.29-6.48	-	17.70-45.02	32
Lake Balık - Kızılırmak	mg kg^{-1} – w.w.	-	0.03± 0.002	0.055± 0.002	5±1	33±5	33
Altınkaya Dam Lake	mg kg^{-1} – w.w.	0.033± 0.001	0.018± 0.001	0.037± 0.002	0.90±0.011	9.85±0.33	34
Keban Dam Lake	mg kg^{-1} – d.w.	-	0.010-0.370	-	1.36- 2.21	19.07-35.85	35
Lake Sarıkum	µg g^{-1} – w.w.	0.12± 0.005	0.023± 0.004	0.088± 0.001	0.5128±0.03	5.33±0.78	36
Sırakaraagaçlar Stream	mg kg^{-1} – w.w.	-	0.015	0.025	0.6	6	37

and lakes. Little is known about the heavy metal loads in the surface water and contamination as well as toxic effects in fish residing Karasu Stream. In this study, metal amounts in carps were found for the first time in Karasu Creek.

Conclusion

Fish living in contaminated waters tend to accumulate heavy metals in their tissues. Carp is one of the most caught and consumed fish in the world, and it is a good biomonitor for determine the impacts of different contaminants on aquatic habitats. The current study was performed to determine heavy metals in the muscles of carps from Karasu Stream of Sinop Provincial. The results suggested that the studied metals are in permissible limits and their use is allowed for consumers. Estimated TTHQ of all the considered elements were below the value of 1, thus these elements in fish samples do not toxic any apparent risk to the population and carps from the Karasu Stream are healthy for consumption.

The frequent presence of heavy metals in industrial wastes and considerable bioaccumulation in freshwater fish especially common carps make them significant environmental concern. The fact that heavy metals are not biodegradable and have the ability to accumulate in the environment make them deleterious to the aquatic environment and consequently to humans who depend on fish as sources of food. Data on heavy metal amounts in fish is priority with regard to aquatic ecosystem health, wellbeing of aquatic wildlife and people consumption of fish. Therefore impact of heavy metal concentration and its effects on fish should be monitored occasionally to understand perfectly the effects of these contaminants on fish growth and the viable condition of population dynamics.

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Conflict of Interests

Authors declare that there is no conflict of interest.

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