Determination of heavy metal contents in some freshwater fishes

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Abstract The concentrations of heavy metals in tench, pike-perch, and common carp fish caught in four different seasons from Damsa dam lake (Nevsehir) were determined. Heavy metal contents of fishes changed depending on seasons. The highest Al (20.894 mg/kg) in tench was established in winter, and the lowest Al (1.605 mg/kg) was determined in summer. Fe content of tench fish changed between 112.906 mg/kg (autumn) and 31.207 mg/kg (spring). In addition, Zn contents of tench were found between 36.0323 mg/kg (summer) and 430.586 mg/kg (winter). The results indicate that concentrations of Cu of tench varied from 0.1934 mg/kg (winter) to 15.422 mg/kg (autumn). Results indicate that concentrations varied from 2.923 mg/kg (autumn) to 32.078 mg/kg (summer) with a mean

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Department of Food Engineering, Faculty of Agriculture, Selçuk University, 42031 Konya, Turkey e-mail: mozcan@selcuk.edu.tr of 11.1893 mg/kg for Al; 0.2483 mg/kg (spring) to 3.3088 mg/kg (autumn) with a mean of 1.6189 mg/kg for Ni; 0.5325 mg/kg (spring) to 0.845 mg/kg (autumn) with a mean of 0.7234 for Pb; and 7.0464 mg/kg (winter) to 253.686 mg/kg (summer) with a mean of 133.6348 for Zn. In common carp, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Se, Ga, and Te contents were determined as 3.9623 mg/kg; 0.1293, 0.2336, 0.0526, 0.1543, 4.2406, 0.726, 1.797, 0.6216, 6.8536, 0.1783, 0.7876, and 0.371 mg/kg in autumn, respectively.

Keywords Tench \cdot Pike-perch \cdot Common carp \cdot Heavy metal \cdot ICP-AES

Introduction

Elements have an important role in human metabolism (Belitz et al. 2001). These elements can be classified as potentially toxic (aluminum, arsenic, cadmium, lead, mercury, etc.), probably essential (nickel, vanadium, and cobalt), and essential (copper, zinc, and selenium) (Çelik and Oehlenschläger 2005; Özden et al. 2010). The metals must be taken up from water, food, or sediment for the normal metabolism of fish (Özden et al. 2010). Trace minerals are a threat to public health, even at low concentrations, since long-term chronic exposure may result in the accumulation of toxic levels (Belitz et al. 2001). Fish, apart from being a good source of digestible protein, vitamins, minerals, and polyunsaturated fatty acids, are also an important source of heavy metals (Simopoulos 2002; Irwandi and Farida 2009). Marina foods are very rich sources of mineral components (Sikorski et al. 1990; Craig and Helfrich 2002; Lall 2002). Heavy metals are considered to be the most important form of aquatic pollution because of their accumulation by aquatic organisms. Metal pollution in the marine environment is not very visible but its impacts on delicate marine ecosystems and humans are drastic (Ashraf et al. 2006). Fish accumulates substantial amounts of metals in their tissues especially muscles and, thus, represent a major dietary source of these metals for humans (Kalay et al. 1999; Rose et al. 1999; Tarıq and Jaffar 1993; Ashraf et al. 2006; Alaş et al. 2014). Trace metals are significant either from the viewpoint of their essentiality or their toxicity (El-Hraiki et al. 1992; Sharif et al. 1993). Copper and zinc are known to be essential and may enter the food materials during food processing or environmental contamination (Aucoin et al. 1999; Ashraf et al. 2006). Metal contaminations in sea foods have been broadly investigated (Liang et al. 1999; Voegborlo et al. 1999; Khansari et al. 2004). The toxicants enter the food chain through edible commodities and cause severe health hazards in that area. Other elements like Na, K, and Ca are necessary for maintaining important cellular functioning (Farkas et al. 2000). The value of biological methods to monitor metals within the freshwater environment has been considered of great importance, offering an economic and sensitive way of analysis. Fish are useful organisms to study metal contamination because they explore freely the different trophic levels of the aquatic ecosystem or microbasin (Swaibuh Lwanga et al. 2003; Vives et al. 2006). Javed (2005) reported fish liver and kidney as the highest depository of metal contaminants in River Ravi fish. The aim of the current study is to determine the levels of heavy metals, such as Al, Cd, Co, Cr, Cu, Fe, Pb, Ga, Te, etc., in different edible freshwater fish varieties. This study will provide insight into the level of different heavy metals and micronutrients in freshwater fishes of Turkey. There were only a few previous studies focusing on the mineral content of local fish. The aim of the current study was to determine the mineral contents of three

different freshwater fish species, tench (*Tinca* tinca), pike-perch (*Sander lucioperca*), and common carp (*Cyprinus carpio*).

Material and methods

Material

In this research, three different freshwater fish species, tench (*T. tinca*), pike-perch (*S. lucioperca*), and common carp (*C. carpio*), were used (Table 1). Fish samples were caught from Damsa dam lake (Nevşehir). Each fish group consists of ten fishes. These samples were transported to the laboratory in a portable fridge. Foreign substances on each fish sample were removed by washing with distilled water. Then, 0.5 g of meat with bone from fork length of each fish body was measured with a 0.01 g precision for analysis in the soonest possible time.

Determination of heavy metals

Provided fish samples were dried at 70 °C in a drying cabinet with air circulation until they reached constant weight. Later, about 0.5 g dried and ground samples were digested by using 5 ml of 65 % HNO₃ and 2 ml of

 Table 1
 Fork length and weight of tench, pike-perch, and common carp fishes

	Fork length (mm)	Weight (g)
Tench		
Autumn	345±4.582a*	725.2±31.885a
Winter	320±13.693a	$518 {\pm} 75.465 b$
Summer	306.16±8.471b	513±42.511b
Pike-perch		
Autumn	250.4±13.069b	146.4±31.341c
Winter	365.4±25.919ab	510±108.655b
Spring	$405.5 {\pm} 60.808 b$	775.75±528.297a
Summer	274.75±23.128b	179±39.874c
Common carp		
Autumn	526.3±71.988a	2826.3±1290.317a
Winter	335±136.433b	1079.2±889.336b
Spring	422.4±12.778ab	1411±143.500ab
Summer	394.5±49.735b	1352±359.249ab

*Means in this row significantly different (p < 0.05)

35 % H_2O_2 in a closed microwave system (Cem-MARS Xpress). The volumes of the digested samples were completed to 20 ml with ultradeionized water, and mineral contents were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Varian-Vista, Australia). Measurements of mineral concentrations were checked using the certified values of related minerals in the reference samples received from the National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA) (Skujins 1998).

Working conditions of ICP-A	AES:
Instrument	ICP-AES (Varian-Vista)
RF Power	0.7-1.5 kW (1.2-1.3 kW for axial)
Plasma gas flow rate (Ar)	10.5-15 l/min (radial) 15 (axial)
Auxiliary gas flow rate (Ar)	1.5
Viewing height	5–12 mm
Copy and reading time	1–5 s (max 60 s)
Copy time	3 s (max 100 s)

Statistical analyses

The average is calculated by analyzing the samples three times. Results of the research were analyzed for statistical significance by analysis of variance (Püskülcü and İkiz 1989).

Results and discussion

Fork length and weight of tench, pike-perch, and common carp fishes are presented in Table 1. Both fork length and weight values of tench fish were found high in autumn compared with other seasons (p < 0.05). In addition, fork length and weight values of pike-perch were found low in autumn. Generally, fork length and weight values of common carp fish were found high in all seasons (p < 0.05). Also, in spring period, fork length and weight values of fish partly increased. The concentrations of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Se, Ga, and Te in tench, pike-perch, and common carp fish caught in four different seasons from Damsa dam lake (Nevşehir) are given in Table 2 along with relevant statistical parameters. Element contents of fishes changed depending on seasons. Generally, Al, Fe, Cu, Ni, and Zn contents of tench fish were found high compared with other elements. While the highest Al (20.894 mg/kg) in tench is established in winter; the lowest Al (1.605 mg/kg) was determined in summer. Fe content of tench fish changed between 112.9062 mg/kg (autumn) and 31.2072 mg/kg (spring). In addition, Zn contents of tench were found between 36.0323 mg/kg (summer) and 430.586 mg/kg (winter). The results indicated that concentrations of Cu of tench varied from 0.1934 mg/kg (winter) to 15.422 mg/kg (autumn).

For pike-perch (Table 2), results indicate that concentrations varied from 2.923 mg/kg (autumn) to 32.078 mg/kg (summer) with a mean of 11.1893 mg/kg for Al; 0.1304 mg/kg (winter) to 0.1572 (autumn) with a mean of 0.1395 mg/kg for Cd; 0.13475 mg/kg (spring) to 0.6428 mg/kg (autumn) with a mean of 0.3728 for Cr; 0.1094 mg/kg (winter) to 14.0216 mg/kg (autumn) with a mean of 3.6591 for Cu; 6.4846 mg/kg (winter) to 414.5612 mg/kg (autumn) with a mean of 122.13 for Fe; 0.1014 mg/kg (winter) to 3.5966 mg/kg (autumn) with a mean of 2.1518 mg/kg for Mn; 0.2483 mg/kg (spring) to 3.3088 mg/kg (autumn) with a mean of 1.6189 mg/kg for Ni; 0.5325 mg/kg (spring) to 0.845 mg/kg (autumn) with a mean of 0.7234 for Pb; and 7.0464 mg/kg (winter) to 253.686 mg/kg (summer) with a mean of 133.6348 for Zn. Generally, in autumn, metal contents of pike-perch fish were found high.

In common carp, while Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Se, Ga, and Te contents are determined as 3.9623, 0.1293, 0.2336, 0.0526, 0.1543, 4.2406, 0.726, 1.797, 0.6216, 6.8536, 0.1783, 0.7876, and 0.371 mg/kg in autumn, these element values were found as 1.1022, 0.129, 0.221, 0.096, 1.0408, 14.9008, 0.3968, 0.3508, 0.5312, 16.4298, 1.8058, 0.6616, and 0.3114 mg/kg in winter, respectively. While these elements in spring are measured as 5.237, 0.1294, 0.2342, 1.1438, 0.6298, 73.4632, 7.4886, 12.1498, 0.2286, 48.4998, 0.3578, 0.8084, and 0.1332 mg/kg, these values in summer season were found as 2.0208, 0.1305, 0.1973, 0.0865, 0.1958, 1.9348, 0.2608, 0.8733, 0.753, 5.9558, 0.8783, 0.758, and 250.834 mg/kg, respectively. As seen in Table 2, tellurium content of common carp in summer was found very high. Tellurium has no known biological function, although fungi can incorporate it in place of sulfur and selenium into amino acids such as tellurocysteine and telluro-methionine (Ramadan et al. 1989).

Özyurt et al. (2009) reported that pike-perch, common carp, and European catfish contained 61.25– 130.10 mg/100 g Na, 305.90–358.10 mg/100 K, 27.11–34.43 mg/100 g Mg, 0.85–1.36 mg/100 g Mo, 0.08–0.13 mg/100 mg/100 g Cu, and 1.25–1.32 mg/

	Al	Cd	Co	Cr	Cu	Fe	Mn
Tench							
Autumn	5.4928 ± 3.669	0.0784 ± 0.060	0.1302 ± 0.023	0.0534 ± 0.033	15.422 ± 6.508	112.9062 ± 100.985	1.2896 ± 0.341
Winter	30.8938 ± 23.563	0.1766 ± 0.076	$0.1264 {\pm} 0.788$	$0.548 {\pm} 0.344$	$0.1934{\pm}0.117$	74.6646 ± 21.404	4.8502 ± 1.683
Spring	5.3978 ± 5.809	0.1078 ± 0.025	0.2276 ± 0.015	$0.107 {\pm} 0.074$	2.7188 ± 3.260	31.2072 ± 25.605	0.6492 ± 0.675
Summer	1.605 ± 0.460	0.1225 ± 0.031	0.241 ± 0.024	0.359 ± 0.641	0.5146 ± 0.424	47.304 ± 48.508	0.8655 ± 0.811
Pike-perch							
Autumn	2.923±0.890	$0.15/2\pm0.04/$	0.0868 ± 0.00	0.6428±0.614	14.0216±12.993 0.1004±0.062	414.2612±235.974	3.0900 ± 3.010
	2.1230±2.12 2.1230±2.10	0.1204±0.002	0.0.146±0.006	010.0±0/00.0	00.0044±0.0000	0.4040±7.424	0.1014±0.115 713 C + 37240 1
Spring	0.052/2±10.554 23.078±21.081	0.128±0.000	0.2445 ± 0.020 0 1505 ± 0.036	0.134/3±0.181 0.356+0.107	0.2027.5±0.202 0.216+0.150	20.10023±43.238 11 36775+33 434	110.0±0/040.1 2000 0+2020 2
Common carn	100.16±0/0.76	U.142J ± U.U11	000.070001.0	1.2JUTU.191	0.210±012.0	+C+.CCHC//0C.1+	06777±0700.0
Autumn	3,9623±3,8225	0.1293 ± 0.001	0.2336 ± 0.007	0.0526 ± 0.043	0.1543 ± 0.116	4.2406 ± 1.314	0.726 ± 0.809
Winter	$1\ 1022+0.041$	0.129 ± 0.006	0.221 ± 0.005	0.096+0.045	1 0408+1 333	14 9008+16 927	0 3968+0 377
Spring	5.237 ± 4.934	0.1294 ± 0.014	0.2342 ± 0.046	1.1438 ± 0.661	0.6298 ± 0.246	73.4632 ± 65.675	7.4886 ± 10.071
Summer	2.02075 ± 0.705	0.1305 ± 0.003	0.19725 ± 0.004	0.0865 ± 0.023	0.19575 ± 0.170	1.93475 ± 0.346	0.26075 ± 0.134
	Ni	Pb	Zn		Se	Ga	Te
Tench							
Autumn	2.4598 ± 4.058	0.7784 ± 0.030		162.4474 ± 109.080	1.3286 ± 0.816	0.7906 ± 0.045	1.243 ± 0.041
Winter	0.8756 ± 1.561	0.9392 ± 0.350		430.586 ± 122.657	0.1416 ± 0.117	$1.0588 {\pm} 0.401$	$0.9864 {\pm} 0.080$
Spring	1.3724 ± 1.921	0.5578 ± 0.049		59.1718±50.782	0.2128 ± 0.080	0.8328 ± 0.016	0.3272 ± 0.073
Summer	1.7695 ± 1.556	0.49 ± 0.151		36.0323 ± 37.885	0.52383 ± 0.585	$0.796{\pm}0.048$	0.1048 ± 0.066
Pike-perch							
Autumn	3.3088 ± 3.900	0.845 ± 0.166		176.154 ± 124.706	2.0072 ± 1.621	0.8264 ± 0.232	1.182 ± 0.140
Winter	0.9138 ± 1.071	0.7002 ± 0.026		7.0464 ± 1.487	$0.066 {\pm} 0.041$	0.8072 ± 0.018	$0.7316 {\pm} 0.100$
Spring	0.24825 ± 0.133	0.5325 ± 0.039		97.653 ± 180.954	0.1295 ± 0.097	0.801 ± 0.029	0.18225 ± 0.094
Summer	2.005 ± 2.410	0.816 ± 0.045		253.686 ± 174.565	0.6685 ± 0.270	$0.844 {\pm} 0.065$	1.13575 ± 0.067
Common carp							
Autumn	1.797 ± 2.436	0.6216 ± 0.004		6.8536 ± 0.096	0.1783 ± 0.121	0.7876 ± 0.002	0.371 ± 0.132
Winter	$0.3508 {\pm} 0.048$	0.5312 ± 0.10	-	16.4298 ± 14.214	1.8058 ± 1.179	0.6616 ± 0.108	$0.3114 {\pm} 0.180$
Spring	12.1498 ± 11.249	0.2286±0.17	1	48.4998±51.132	$0.3578 {\pm} 0.270$	0.8084 ± 0.052	0.1332 ± 0.086
Summer	0.87325 ± 0.513	0.753 ± 0.063		5 95575+0 557	0 87825+0 286	0.758 ± 0.025	750 834+0 137

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100 g Zn, respectively. The magnesium content of freshwater fish species was reported as 18-36 mg/ 100 g by Otitologbon et al. (1997) and 16-113 mg/ 100 g by Lall and Parazo (1995). The Mn content was reported as 0.1-4.6 mg/100 g in pink salmon, 0.1-0.4 mg/100 g in red salmon, and 0.8-6.3 mg/100 g in tuna (Ikem and Egiebor 2005). Cd, Cu, and Zn levels were found to be 0.18, 0.43, and 4.82 mg/kg in gold band goatfish and 0.25, 0.20, and 4.55 in striped red mullet, respectively (Öksüz et al. 2011). Zn levels were previously reported to be 45.1 μ g/g in cultured sea bass and 43.6 μ g/g in wild sea bass by Alasalvar et al. (2002). Öksüz et al. (2009) reported magnesium values of 38.2 and 57.9 mg/100 g wet samples for rose shrimp and red shrimp samples, which were significantly lower compared to the current findings. Fawole et al. (2007) determined that Oreochromis niloticus, Sarotherodon galilaeus, Clarias gariepinus, and Heterotis niloticus contained 0.22-0.30 % Mg, 0.10-0.14 % Fe, and 0.30-0.43 % Zn in freshwater fishes in Nigeria. Several studies have considered fish as a major source of Fe for children and adults (Fraga 2005). Stecycka et al. (2003) indicated that nonpredatory fish contained 8.66 mg/kg Zn and 0.32 mg/kg Mn wet weight, whereas the content of zinc and manganese in predatory fish was 5.11 and 0.25 mg/kg wet weight. Alaş et al. (2014) reported that while the Cd content of some fishes ranges between 0.019 ppm and 0.104 mg/kg, Cr content changed between 1.32 and 4.20 mg/kg. Ashraf et al. (2006) reported that the levels of Pb ranged from 0.03 to 1.20 μ g/g for salmon, 0.03 to 0.51 μ g/g for tuna, and 0.13 to 1.97 μ g/ g for sardines. The levels of Cd ranged from 0.02 to 0.38 μ g/g for salmon, 0.07 to 0.64 μ g/g for tuna, and 0.010 to 0.690 μ g/g for sardines in canned fish. Nawaz et al. (2010) determined the levels of As, Cd, Pb, Hg, Zn, and Cu as 35.74-45.33, 0.35-0.45, 2.1-3.0, 83.03-92.35, 37.85-40.74, and 1.39-2.93 ppm in freshwater fish species of the River Ravi in Pakistan. Uluözlü et al. (2007) determined chromium content of red mullet at 1.63 mg/kg. Selenium content of common sole ranged from between 0.307 mg/kg (summer) and 0.641 mg/kg (winter) through the year (Özden et al. 2010). Our results showed differences when compared with literature values. These differences can be due to species, growing conditions, climatic factors, and analytical conditions.

Trace element composition showed variations through the year. The most of microelements levels of fish samples were found sufficient for recommended daily allowance. The limit of acceptability of Cd and Pb content of tench, pike-perch, and common carp fish were decreased in all seasons. These toxic elements of fish and fishery products are suggestible periodically by monitoring studies. The results showed a positive evaluation of the nutritional quality of fish types. It can be concluded that all fish species studied are safe to be consumed. All samples were good source of microelements and could provide multihealth benefits if consumed in recommended amounts. In conclusion, the findings of the current work can be used in the studies on human nutrition and food composition.

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