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Assessment of trace metal concentrations in muscle tissue of certain commercially available fish species from Kayseri, Turkey

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Abstract Regular consumption of fish has been widely recommended by health authorities. However, it is known that some species accumulate high levels of contaminants including heavy metals (e.g., Hg, Cd, Pb, and As). In this study, Cu, Pb, Co, Ni, Cr, Mn, Cd, and Fe were determined in the muscle tissue of 11 commercially available fish species (*Sparus auratus, Dicentrarchus labrax, Mullus barbatus, Belone belone, Psetta maxima, Epinephelus aeneus, Salmothymus, Soleidae, Pomatomus saltatrix, Engraulis encrasicolus,* and *Sarda sarda*) supplied from retailers in Kayseri, Turkey. Determinations were carried out by flame atomic absorption spectrometry after the wet digestion method. The average metal concentrations of the 11 species were determined in the range of 0.54–1.79, 0.82–1.40, 2.38–4.54, 1.23–3.67, 5.01–5.97, 0.77–3.59, 0.48–1.06, and 5.05–122.8 μg/g wet weight for Cu, Pb, Co, Ni, Cr, Mn, Cd, and Fe, respectively. The permissible tolerable daily intake (PTDI) and calculated daily intake (CDI) values were compared, and the calculated daily intake values of the samples were found to be below the established values. Correlations between the metal contents in samples were investigated by performing correlation tests with SPSS 13.0 for windows.

Keywords Heavy metals · Fish species · Permissible tolerable daily intake (PTDI) · Flame atomic absorption spectrometry · Turkey

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Introduction

Fish from seas, rivers, and lakes have been recognized as nutritious; they are one of the best sources of food for people and are consumed all around the world. Fish is almost a single source of high quality protein for humans and meets 16 % of animal protein consumption all around the world (A Guide for Seafood Marketers 2004; Tidwell and Allan 2002). It is trusted by so many people that seafood is the main source of animal protein. In 2008, about 115 million tons of the world's fish production was processed as human food with an average consumption of 17 kg, and this value is equal to 81 % of the total world's fish production (FAO Food and Agriculture Organization of the United Nations 2010).

Fish is also a good source of other nutrients such as selenium, antioxidants, essential fatty acids, etc. Fish, as seafood, has an important role in the functionality of the human body in that the minerals and nutrients in fishes are helpful for improving brain development (Irish Sea Fisheries Board 2005). Due to its high protein levels, omega fatty acids, and low saturated fat content that are known to contribute to a healthy body, fish consumption has increased in significance among the health conscious (Copat et al. 2012). Researchers have discovered strong links between healthy hearts and fish consumption. A study suggested that one portion of fish per week in the diet reduces the risk of heart attack by half. Fish contains very high amount of omega 3 and less saturated fat; therefore, it helps to reduce the amount of triglycerides and cholesterol in the blood. If these two fats are in excess amount, they increase the risk of heart disease. Omega 3 fats are also natural built-in antioxidants, and damaging of artery walls may be stopped by antioxidants. Fish oil also has these advantages for heart health (A Guide for Seafood Marketers 2004).

Meanwhile, the health hazards related to the consumption of fish contaminated by heavy metals have received worldwide attention. Heavy metals are potentially accumulated in fish and are then transferred by the food chain to human beings who eat fish. Heavy metal levels change in different fish species due to their different diet and habitats. Heavy metal accumulation in fish is also size specific; metals in high concentrations are generally found in smaller species (Mendil et al. 2010; Tuzen et al. 2007; Yildirim et al. 2009). At the other hand, bioaccumulating metals like Hg is often higher in larger (older) fish of the same species. Fish that are predatory are large and at the top of the food chain and so tend to contain more Hg (Irish Sea Fisheries Board 2005).

Industrialization, urbanization, and population growth have increased heavy metal pollution (Soylak and Turkoglu 1999; Soylak et al. 1995, 2006; Mitic et al. 2013). The discharge of heavy metals into the marine environment can disrupt marine species diversity as well as ecosystems due to their toxic effects, long persistence, and accumulative nature and finally result in health risks (Ebrahimpour et al. 2011; Rahman et al. 2010; Saha and Zaman 2011).

There has been a growing interest in heavy metal pollution, and it has become an important worldwide concern (Soylak et al. 1996a, b; Suarez et al. 2000; Duran et al. 2009; Tuzen et al. 2009a, b; Citak et al. 2012; Imyim et al. 2013; Kirdar et al. 2013; Shaltout et al. 2013). For instance, Pb may cause liver damage and renal failure (Lee et al. 2011; Luckey and Venugopal 1977). Moreover, exposure to high concentrations of Pb over long periods can result in coma, mental retardation, and even death (Soylak et al. 2001, 2002; Divrikli et al. 2003; Tuzen et al. 2007; Al-Busaidi et al. 2011). Cd damages the urinary system and causes chronic toxicity symptoms, including poor reproductive capacity, impaired kidney function, tumors, hypertension, and hepatic function disability (Luckey and Venugopal 1977; Rahman and Islam 2010; Soylak et al. 2012). Some other metals (e.g. Cr, Cu, and Zn) cause nephritis and extensive lesions in the kidney (Luckey and Venugopal 1977; Rahman and Islam 2009; Soylak et al. 2013). Ever since heavy metal contamination in fish is considered as a serious problem, global attention has raised for the last several years.

Over the past few decades, heavy metal concentrations in fish samples have been extensively studied by different researchers in various counties around the world such as Turkey (Yildirim et al. 2009), Malaysia (Bashir et al. 2012), Palestine (Elnabris et al. 2013), Pakistan (Khan et al. 2012), India (Kumar et al. 2011), the Canary Islands (García-Montelongo et al. 1992), Jordan (Ismail and Abu-Hilal 2008), Egypt (Khaled 2004), Bangladesh (Rahman et al. 2012), Italy (Copat et al. 2013), China (Yi and Zhang 2012; Zhao et al. 2013), Bosnia and Herzegovina (Djedjibegovic et al. 2012), Spain (Herreros et al. 2008), Russia (Allen-Gil and Martynov 1995), and Tunisia (Ayed et al. 2011).

The city of Kayseri is located in the middle of Turkey, and the samples analyzed here were transported to the city from north (Black Sea), west (Sea of Marmara, Aegean Sea), and south (Mediterranean). The purpose of this study was to determine the trace metal (Cu, Pb, Co, Ni, Cr, Mn, Cd, and Fe) concentrations in the muscle tissue of 11 commercially available fish species (*Sparus auratus, Dicentrarchus labrax, Mullus barbatus, Belone belone, Psetta maxima, Epinephelus aeneus, Salmothymus, Soleidae, Pomatomus saltatrix, Engraulis encrasicolus, Sarda sarda*) supplied by retailers in Kayseri, Turkey.

Experimental

Instrumentation and chemicals

A Perkin Elmer Model 3110 flame atomic absorption spectrometer was used in this study. An air-acetylene flame was used for all measurements. The operating parameters are listed in Table 1 for working elements. All reagents were of analytical reagent grade. Distilled water was used throughout the study. All the glass and plastic materials were cleaned by soaking in a 10 % HNO_3 solution and then rinsed with distilled water before experiments. The standard solutions for

Table 1 The operating parameters for working elements for flame atomic absorption spectrometer

Element	Wave length (nm)	Slit width	Lamp current (mA)
Cu	324.8	0.7	15
Pb	283.3	0.7	15
Co	240.7	0.2	30
Ni	232.0	0.2	30
Cr	357.9	0.7	12
Mn	279.5	0.2	20
Cd	228.8	0.7	8
Fe	248.3	0.2	30

calibration were prepared by diluting a stock solution of 1,000 mg/L of the analyzed element. The HNO_3 (65 %) and H_2O_2 (30 %) used for digestion procedures were supplied by Merck. The certified standard reference material used in the experimental studies was NRCC DORM-2, Dogfish Muscle Certified Reference Material for Trace Metals.

Sample collection

Turkey, with its coastal length of 8,333 km and continental shelf of 154,080 km^2, is surrounded by the Black Sea, the Sea of Marmara, the Aegean, and the Mediterranean on three sides, all of which have their own characteristics. Samples of 11 species of fish found in these seas were collected from commercial retailers located in Kayseri, Turkey. After sample collection, they were immediately washed to remove mud-like substances and conserved with ice in polyethylene bags at −20 °C until analysis.

Analytical procedure

The muscular tissues of each fish sample were cut by using a plastic knife and were then homogenized in porcelain vessel. For this, 0.2 g of the standard reference material and 1 g of wet weight fish tissue (homogenized muscles without skin) were used. Wet digestion of the samples was performed using a 6-mL HNO_3 (65 %) and 2-mL H_2O_2 (30 %) mixture. The mixture was heated up to 150 °C on a hot plate and repeated until the sample solutions became clear. The completely digested samples were cooled at room temperature, and then distilled water was added to the sample and mixed. The residue was filtered through the blue band filter paper and diluted to 10 mL. Analytical blanks were applied using the same procedure. To test the accuracy and precision of the method, a certified reference material (NRCC DORM-2, Dogfish Muscle Certified Reference Material for Trace Metals) was analyzed for each element. The whole procedure (including digestion) was repeated three times, and metal concentrations were expressed as micrograms per gram wet weight.

Statistical analysis

To investigate correlation relationship among the metal concentrations in analyzed fish samples, the correlation test was performed with SPSS 13.0 for windows. Two-tailed Pearson's correlation coefficient matrix was applied. Experimental data were subjected to a statistical analysis, and correlation matrices were produced to analyze the relationship between the investigated metal concentrations. The correlation coefficient values between metal concentrations were calculated.

Results and discussion

For the digestion procedure, rapidity, preferable recovery, and precision were achieved with a combination of HNO_3/H_2O_2 (6:2) mixture for all samples. The accuracy of the method was evaluated by element determination in standard reference material (NRCC DORM-2, Dogfish Muscle Certified Reference Material for Trace Metals). The achieved results were in good agreement with the certified values with recovery values of 95–96 %. The results are given in Table 2.

The concentrations of Cu, Pb, Co, Ni, Cr, Mn, Cd, and Fe determined in the muscles of the 11 analyzed fish

Table 2 Results of the analysis with wet digestion procedure of NRCC DORM-2, Dogfish Muscle Certified Reference Material for Trace Metals standard reference material as micrograms per gram wet weight (n=3)

Element	Certified value (μg/g)	Our value (μg/g)	Recovery (%)
Fe	142±10	136.3±9.50	96
Cu	2.34±0.16	2.22±0.20	95
Mn	3.66±0.34	3.48±0.25	95
Cr	34.7±5.5	32.9±2.70	95
Ni	19.4±3.1	18.6±1.30	96

species are presented in Table 3 as micrograms per gram wet weight. There were vast differences among the heavy metal concentrations found in the muscles of the different fish species. The results were in the range of 0.54–1.79, 0.82–1.40, 2.38–4.54, 1.23–3.67, 5.01–5.97, 0.77–3.59, 0.48–1.06, and 5.05–122.8 μg/g wet weight for Cu, Pb, Co, Ni, Cr, Mn, Cd, and Fe, respectively. The order of mean concentrations of the heavy metals in the fish muscles were as follows: Fe (32.1)>Cr (5.42)>Co (3.25)>Ni (2.18)>Mn (1.63)>Pb (1.10)>Cu (0.92)>Cd (0.66). The highest concentrations were for Fe, and the lowest were for Pb, Cu, and Cd. No single type of fish was consistently high for all metals. While *B. belone* had the highest level of Cd, *S. sarda* had the highest levels of Cu and Mn.

Cu is an essential part of several enzymes. It is essential for hemoglobin synthesis (Sivaperumal et al. 2007). However, high intake of Cu has been recognized to cause adverse health problems (Gorell et al. 1997). Cu concentration in *S. sarda* was significantly higher than in all other fish species with a value of 1.79±0.09 μg/g followed by *S. auratus* with a value of 1.22±0.16 μg/g. The pattern of the Cu concentration in the muscles of the remaining fish types in order of decreasing content was as follows: *M. barbatus*>*D. labrax*=*E. encrasicolus*>*P. maxima*=*P. saltatrix*>*Soleidae*>*E. aeneus*>*Salmothymus*=*B. belone*. Results in micrograms per gram are shown in Table 3. In the literature, Cu levels in fish samples have been reported in the range of 0.11–0.97 μg/g (Celik and Oehlenschlager 2007), 0.065–4.36 μg/g (Yilmaz et al. 2007), 0.04–5.43 μg/g dry weight in fish species from Iskenderun Bay (Turkmen et al. 2005), and 0.73–1.83 μg/g (Uluozlu et al. 2007). There is no limit for Cu in Turkish Standards; however, the FAO/WHO has a limit of 30 μg/g, and the UK and Saudi Arabia have a limit of 20 μg/g for Cu as shown in Table 4.

Pb is one of the most ubiquitous metals known to humans. It is detectable practically in all biological systems and environments (Castro-Gonzalez and Mendez-Armenta 2008). To eat fish is an obvious means of exposure to metals because their tissues and muscles accumulate substantial amounts of metals. Metal concentration of Pb was as follows: *S. auratus*=*Salmothymus*>*M. barbatus*>*E. aeneus*=*B. belone*>*D. labrax*>*Soleidae*>*S. sarda*=*P. saltatrix*>*P. maxima*>*E. encrasicolus* with values of 1.40±0.11, 1.40±0.11, 1.33±0.22, 1.20±0.11, 1.20±0.11, 1.07±0.19, 1.01±0.11, 0.95±0.11, 0.95±0.11, 0.82±0.11, and 0.75±0.11 μg/g, respectively. Pb contents in the literature have been reported in the range of 0.09–6.95 μg/g (Turkmen et al. 2005), 0.22–0.85 μg/g dry weight in fish samples from the Black Sea (Tuzen 2003), 0.068–0.874 μg/g (Yilmaz et al. 2007), and 0.33–0.93 μg/g (Uluozlu et al. 2007). The permitted Pb level for fish is 0.30 μg/g in Turkish Standards, and determined values in this study were found to be higher than this. However, the UK's and Saudi Arabia's maximum limit standards for Pb are higher than the other cited international standards and our results, as given in Table 4.

As part of vitamin B_{12}, Co is essential to red blood cell formation and is also helpful to other cells. Ocean fish and sea vegetables contain Co. The greatest value of

Table 3 Heavy metal concentrations (μg/g wet weight) in fish samples determined by AAS after wet digestion procedure (*n*=3)

Fish species	Cu	Pb	Co	Ni	Cr	Mn	Cd	Fe
Sparus auratus	1.22±0.16	1.40±0.11	3.64±0.54	1.23±0.23	5.23±0.32	0.83±0.12	0.64±0.09	10.4±0.69
Dicentrarhus labrax	1.01±0.09	1.07±0.19	4.54±0.31	2.32±0.41	5.41±0.32	0.97±0.12	0.85±0.09	12.8±0.91
Mullus barbatus	1.11±0.09	1.33±0.22	2.38±0.31	1.37±0.23	5.03±0.02	0.77±0.12	0.54±0.09	11.0±0.34
Belone belone	0.54±0.09	1.20±0.11	2.74±0.31	2.86±0.24	5.78±0.32	1.03±0.12	1.06±0.16	47.4±0.59
Psetta maxima	0.80±0.09	0.82±0.11	2.38±0.31	2.59±0.23	5.23±0.32	0.83±0.12	0.54±0.09	92.3±2.93
Epinephelus aeneus	0.64±0.09	1.20±0.11	3.46±0.31	1.64±0.24	5.97±0.32	0.77±0.12	0.85±0.09	122.8±0.59
Salmothymus	0.54±0.09	1.40±0.11	3.82±0.31	2.18±0.24	5.78±0.32	1.64±0.12	0.48±0.09	11.0±0.69
Soleidae	0.70±0.09	1.01±0.11	3.28±0.31	2.05±0.24	5.03±0.02	3.32±0.20	0.64±0.09	5.05±0.69
Pomatomus saltatrix	0.80±0.09	0.95±0.11	2.38±0.31	1.23±0.23	5.01±0.02	2.31±0.20	0.48±0.09	6.44±0.59
Engraulis encrasicolus	1.01±0.09	0.75±0.11	2.92±0.31	3.67±0.23	5.78±0.32	1.84±0.12	0.48±0.09	8.41±0.69
Sarda sarda	1.79±0.09	0.95±0.11	4.18±0.54	2.86±0.24	5.41±0.32	3.59±0.12	0.70±0.09	25.4±0.59

Table 4 Maximum permitted concentrations (μg/g wet weight) of certain heavy metals in fishes for different international standards and concentration range in fish samples determined in this study

International standards	Heavy metals			References
	Cu	Pb	Cd	
European Commission	–	0.30	0.05	EC (2006)
Turkish Food Codex	–	0.30	0.05	Turkish Food Codex (2008)
Australia Food Standards	–	0.50	2	FSANZ (2011)
FAO/WHO Limits	30	0.50	0.50	FAO/WHO (1989)
England	20	2.0	0.20	MAFF (2000)
Codex Standard	–	0.30	–	CODEX (2012)
Saudi Arabia	20	2.0	0.5	SASO (1997)
Range in this study	0.54–1.79	0.82–1.40	0.48–1.06	This study

Co was detected in the *D. labrax* species with a concentration of 4.54±0.31 followed by *S. sarda* and *Salmothymus* with concentrations of 4.18±0.54 and 3.82±0.31 μg/g, respectively. No significant difference was detected among these fish species. Turkish Standards do not cover information about maximum Co levels in fish samples.

Ni normally occurs at very low levels in the environment. Lung inflammation, tumors, emphysema, and fibrosis are some of the pulmonary negative health effects that it causes (Forti et al. 2011). The Ni level should be as low as possible because it is a cumulative body poison. The Ni levels determined were as follows: *E. encrasicolus*>*B. belone*=*S. sarda*>*P. maxima*>*D. labrax*>*Salmothymus*>*Soleidae*>*E. aeneus*>*S. auratus*=*P. saltatrix* with concentrations of 3.67±0.23, 2.86±0.24, 2.86±0.24, 2.59±0.23, 2.32±0.41, 2.18±0.24, 2.05±0.24, 1.64±0.24, 1.37±0.23, 1.23±0.23, and 1.23±0.23 μg/g, respectively. There is no available information about maximum Ni levels in fish samples in Turkish Standards.

Cr does not accumulate in fish normally. Hence, only low concentrations have been reported even from the industrialized areas of the world. The uptake rate is higher in young fish, but the body burden of Cr declines with advancing age (Dara 1995). There were no significant differences in Cr concentrations among the studied fish species. *E. aeneus* had the highest value of 5.97±0.32 μg/g, and *P. saltatrix* has the lowest value of 5.01±0.02 μg/g. Cr contents in the literature have been reported in the range of 0.07–6.46 μg/g (Turkmen et al. 2005), 0.97–1.70 μg/g (Tuzen and Soylak 2007), and 0.95–1.98 μg/g (Uluozlu et al. 2007). There is no information about maximum Cr levels in fish samples in Turkish Standards.

Mn has low toxicity; however, it has considerable biological importance. No maximum limit is identified for Mn in fish samples. In our samples, 5.41±0.32 μg/g was the highest determined value for Mn in *S. sarda*, and 0.77±0.12 μg/g was the lowest in *M. barbatus* and *E. aeneus*. Mn contents in the literature have been reported in the range of 1.56–3.76 μg/g (Tuzen 2003), 0.05–4.64 μg/g (Turkmen et al. 2005), 8.8–23.5 μg/g (Begum et al. 2005), and 1.28–7.40 μg/g (Uluozlu et al. 2007). There is no information about Mn levels in Turkish Standards. The WHO recommends 2–9 mg per day for adults (WHO World Health Organization 1994).

Cd is an environmental and industrial pollutant that negatively affects a number of organs in humans. Many years ago, it was established that Cd occurs in the marine environment and aquatic organisms only in trace concentrations, but speciation is affected by the salinity and temperature (Ray, 1986). Cd contamination in fish is of considerable interest because fish consumption is an important source of Cd intake for the general population. Most of its concentration in fish is highly absorbable in $CdCl_2$ form. For humans, the gastrointestinal absorption efficiency of Cd has been reported to be approximately 3–8 % of the ingested value. The concentrations in muscles are low; it is especially accumulated in kidneys (ATSDS Agency for Toxic Substance and Disease Registry 2003). The concentration of Cd can be ordered as follows: *B. belone*>*E. aeneus*=*D. labrax*>*S. sarda*>*Soleidae*=*S. auratus*>*P. maxima*=*M. barbatus*>*E. encrasicolus*=

Table 5 Comparison of permissible tolerable daily and weekly intake with calculated values in fish species

	Cu	Pb	Co	Ni	Cr	Mn	Cd	Fe
Sparus auratus (CDI)	24.4	27.9	72.8	24.7	104.5	16.7	12.9	207.8
Dicentrarhus labrax (CDI)	20.2	21.5	90.8	46.3	108.3	19.3	17.0	255.3
Mullus barbatus (CDI)	22.3	26.6	47.6	27.3	100.5	15.3	10.7	219.7
Belone belone (CDI)	10.7	24.1	54.8	57.1	115.7	20.7	21.2	948.0
Psetta maxima (CDI)	16.0	16.3	47.6	51.7	104.5	16.7	10.7	1846.4
Epinephelus aeneus (CDI)	12.9	24.1	69.2	32.7	119.3	15.3	17.0	2456.0
Salmothymus (CDI)	10.7	27.9	76.4	43.7	115.7	32.8	9.7	219.7
Soleidae (CDI)	13.9	20.2	65.6	40.9	100.5	66.4	12.9	101.0
Pomatomus saltatrix (CDI)	16.0	18.9	47.6	24.7	100.3	46.2	9.7	128.7
Engraulis encrasicolus (CDI)	20.2	15.1	58.4	73.5	115.7	36.9	9.7	168.3
Sarda sarda (CDI)	35.9	18.9	83.6	57.1	108.3	71.7	13.9	508.6
PTWI (μg/week/kg body weight)	3,500	25	–	35	–	980	7	5,600
PTDI (μg/day/70 kg body weight)	35,000	250	–	350	–	9,800	70	56,000
PTWI (μg/week/70 kg body weight)	245,000	1750	–	2450	–	68600	490	392,000

CDI calculated daily intake (μg/day/70 kg body weight), *PTWI* permissible tolerable weekly intake (μg/week/kg body weight), *PTDI* permissible tolerable daily intake for 70 kg adult person (μg/day/70 kg body weight), *PTWI* permissible tolerable weekly intake for 70 kg adult person (μg/week/70 kg body weight)

P. saltatrix=*Salmothymus* with values of 1.06±0.16, 0.85±0.09, 0.85±0.09, 0.70±0.09, 0.64±0.09, 0.64±0.09, 0.54±0.09, 0.54±0.09, 0.48±0.09, 0.48±0.09, and 0.48±0.09 μg/g, respectively. Cd levels have been reported in the range of 0.01–4.16 μg/g (Turkmen et al. 2005), 0.09–0.48 μg/g (Tuzen 2003), 0.010–0.084 μg/g (Yilmaz et al. 2007), and 0.45–0.90 μg/g (Uluozlu et al. 2007). According to the Turkish Food Codex, the maximum Cd level permitted for fish is 0.05 μg/g (Turkish Food 2008). Levels in analyzed samples were found to be higher than those in Turkish Standards; however, the Australian Food Standards permitted limit for Cd is higher than the other cited international standards given in Table 4.

Fe levels are not high in oil rich fish, but since Fe is absorbed easily from these species, it is a useful dietary source (Irish Sea Fisheries Board 2005). Fe concentration had the highest value in all the fish species studied. The order was as follows: *E. aeneus*>*P. maxima*>*B. belone*>*S. sarda*>*D. labrax*>*Salmothymus*=*M. barbatus*>*S. auratus*>*E. encrasicolus*>*P. saltatrix*>*Soleidae* with values of 122.8±0.59, 92.3±2.93, 47.4±0.59, 25.4±0.59, 12.8±0.91, 11.0±0.69, 11.0±0.34, 10.4±0.69, 8.41±0.69, 6.44±0.59, and 5.05±0.69 μg/g, respectively. Fe contents in the literature have been reported in the range of 0.82–27.4 μg/g (Turkmen et al. 2005), 9.52–2.34 μg/g (Tuzen 2003), 71–186 μg/g (Begum et al. 2005), and 68.6–163 μg/g

Table 6 Correlation coefficient between metal concentrations in fish samples

	Cu	Pb	Co	Ni	Cr	Mn	Cd	Fe
Cu	1.000							
Pb	−0.169	1.000						
Co	0.350	0.216	1.000					
Ni	0.100	−0.594	0.112	1.000				
Cr	−0.294	0.098	0.291	0.486	1.000			
Mn	0.360	−0.410	0.208	0.231	−0.253	1.000		
Cd	−0.129	0.199	0.302	0.132	0.407	−0.219	1.000	
Fe	−0.285	−0.087	−0.150	0.029	0.440	−0.409	0.376	1.000

(Uluozlu et al. 2007). There is no information on the Fe limit for fish in Turkey.

A linear correlation test was performed for the correlations among metal concentrations in the analyzed fish species. Experimental data were subjected to a statistical analysis, and correlation matrices were produced to analyze the relationship among the investigated metal concentrations. The correlation coefficient values among the metal concentrations are shown in Table 6. The correlation among Cr and Ni is significant at the 0.05 level, and there are positive correlations for Co–Cu, Co–Pb, Cr–Co, Mn–Cu, Mn–Co, Mn–Ni, Cd–Co, Cd–Cr, Fe–Cr, Fe–Cd, with corresponding *r* values of 0.350, 0.216, 0.291, 0.360, 0.208, 0.231, 0.302, 0.407, 0.440, and 0.376, respectively. These positive correlations may show that the origin of the metals in the samples is highly related to the differences in the aquatic environments concerning chemical form of metal in the water, the level and type of water pollution, water temperature, pH value, and dissolved oxygen concentration. Ni–Cu, Ni–Co, Cr–Pb, Cd–Pb, and Cd–Ni are correlated weakly. The lowest negative correlation is between Fe and Ni with the value of 0.029.

A comparison of the permissible tolerable daily and weekly intake with calculated values in fish species is shown in Table 5. The average daily fish consumption in Turkey is 20 g per person assuming an average body weight of 70 kg (FAO Food and Agriculture Organization of the United Nations 2005; Turkmen et al. 2009). By multiplying this consumption value by the average concentration of each metal in analyzed fish species, the average daily intake of metals per person can be calculated. The calculated metal intakes were compared with the respective permissible tolerable daily intake (PTDI) for a 70-kg person. Given in Table 5, the values of calculated daily intake (CDI) of metals in the muscles of fish analyzed in this study are well below their corresponding permissible tolerable daily intake values. The dose of a toxic metal that one obtains from fish, however, not only depends on the concentration of a specific metal in the fish but also on the quantity of fish consumed. Considering normal consumption habits, we can firmly state that the calculated daily intake of fish is far below the actual daily amount of fish consumed. Therefore, there is no risk for human health in those with normal fish consumption levels who obtain fish from local retailers in Kayseri.

Conclusions

In conclusion, this study provided new data dealing with a limited number of fish species. Since this data belong to limited fish species, period of time, and regions, it would not be right to claim to specify a heavy metal accumulation trend. Therefore, more data including different conditions are necessary. The values are lower than those reported by some other international standards, such as those from Australia, the UK, and Saudi Arabia. The results of the heavy metals analyzed in this study showed an uneven distribution in the fish species (Table 6). Their concentrations are above the European Commission's and Turkish Food Codex's maximum permissible levels (Table 4). Non-essential heavy metals, such as Cd and Pb, have no biological function, but are rather harmful to fish and humans even at very low concentrations.

On the other hand, although heavy metal levels determined from studied samples are above the international standards, the permissible tolerable daily intake values show that calculated daily intakes are far below the recommended values in Turkey. So, it may be concluded that consumption of these species from different seas does not pose a problem to human health.

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References

A Guide for Seafood Marketers (2004). What's so healthy about seafood? Second Edition. Australian Government Fisheries Research and Development Corporation

Al-Busaidi, M., Yesudhason, P., Al-Mughairi, S., Al-Rahbi, W. A., Al-Harthy, K. S., Al-Mazrooei, N. A., et al. (2011). Toxic metals in commercial marine fish in Oman with reference to national and international standards. *Chemosphere, 85*(1), 67–73.

Allen-Gil, S. M., & Martynov, V. G. (1995). Heavy metal burdens in nine species of freshwater and anadromous fish from the Pechora River, northern Russia. *Science of The Total Environment, 160–161*, 653–659.

ATSDS (Agency for Toxic Substance and Disease Registry) (2003). Toxicological Profile for Cadmium, U.S. Department of Health and Humans Services, Public Health Service, Centres for Diseases Control, Atlanta

Ayed, N., Faure, E., Quignard, J.-P., & Trabelsi, M. (2011). Determination of P, Ca, Zn, Cd and Pb concentrations in muscle, gills, liver, gonads and skeletons of two natural populations of *Atherina lagunae* in North Tunis Lake, Tunisia. *Journal of Water Resource and Protection, 3*(6), 421–428.

Bashir, F. A., Shuhaimi-Othman, M., & Mazlan, A. G. (2012). Evaluation of trace metal levels in tissues of two commercial fish species in Kapar and Mersing coastal waters, Peninsular Malaysia. *Journal of Environmental and Public Health, 2012*, 1–10.

Begum, A., Amin, M. N., Kaneco, S., & Ohta, K. (2005). Selected elemental composition of the muscle tissue of three species of fish, *Tilapia nilotica*, *Cirrhina mrigala* and *Clarius batrachus*, from fresh water Dhanmondi Lake in Bangladesh. *Food Chemistry, 93*(3), 439–443.

Castro-Gonzalez, M. I., & Mendez-Armenta, M. (2008). Heavy metals: implications associated to fish consumption. *Environmental Toxicology and Pharmacology, 26*(3), 263–271.

Celik, U., & Oehlenschlager, J. (2007). High contents of cadmium, lead, zinc and copper in popular fishery products sold in Turkish supermarkets. *Food Control, 18*(3), 258–261.

Citak, D., Silici, S., Tuzen, M., & Soylak, M. (2012). Determination of toxic and essential elements in sunflower honey from Thrace Region, Turkey. *International Journal of Food Science & Technology, 47*(1), 107–113.

CODEX (Codex Standard 193–1995) (2012). Codex General Standard For Contaminants And Toxins In Food And Feed.

Copat, C., Bella, F., Castaing, M., Fallico, R., Sciacca, S., & Ferrante, M. (2012). Heavy metals concentrations in fish from Sicily (Mediterranean Sea) and evaluation of possible health risks to consumers. *Bulletin of Environmental Contamination and Toxicology, 88*(1), 78–83.

Copat, C., Arena, G., Fiore, M., Ledda, C., Fallico, R., Sciacca, S., et al. (2013). Heavy metals concentrations in fish and shellfish from eastern Mediterranean Sea: consumption advisories. *Food and Chemical Toxicology, 53*, 33–37.

Dara, S. S. (1995). *Environmental chemistry and pollution control*. New Delhi: S. Chand and Company Ltd.

Divrikli, U., Soylak, M., Elci, L., & Dogan, M. (2003). The investigation of trace heavy metal concentrations in the street dust samples collected from Kayseri, Turkey. *Journal of Trace and Microprobe Techniques, 21*(4), 713–720.

Djedjibegovic, J., Larssen, T., Skrbo, A., Marjanović, A., & Sober, M. (2012). Contents of cadmium, copper, mercury and lead in fish from the Neretva river (Bosnia and Herzegovina) determined by inductively coupled plasma mass spectrometry (ICP-MS). *Food Chemistry, 131*(2), 469–476.

Duran, A., Tuzen, M., & Soylak, M. (2009). Trace metal contents in chewing gums and candies marketed in Turkey. *Environmental Monitoring and Assessment, 149*(1–4), 283–289.

Ebrahimpour, M., Pourkhabbaz, A., Baramaki, R., Babaei, H., & Rezaei, M. (2011). Bioaccumulation of heavy metals in freshwater fish species, Anzali, Iran. *Bulletin of Environmental Contamination and Toxicology, 87*(4), 386–392.

EC (European Commission) (2006). Official Journal of the European Union. Commission Regulation (EC) No: 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs.

Elnabris, K. J., Muzyed, S. K., & El-Ashgar, N. M. (2013). *Journal of the Association of Arab Universities for Basic and Applied Sciences, 13*(1), 44–51.

FAO (Food and Agriculture Organization of the United Nations) (2005). Statistics division, food security statistics, food consumption.

FAO (Food and Agriculture Organization of the United Nations). (2010). *The State of World Fisheries and Aquaculture 2010*. Rome: Fisheries and Aquaculture Department.

FAO/WHO (Food and Agriculture Organization of the United Nations/World Health Organization) (1989). Evaluation of certain food additives and the contaminants mercury, lead and cadmium. WHO Technical . Report. Series No: 505

Forti, E., Salovaara, S., Cetin, Y., Bulgheroni, A., Tessadri, R., Jennings, P., et al. (2011). In vitro evaluation of the toxicity induced by nickel soluble and particulate forms in human airway epithelial cells. *Toxicology in Vitro, 25*(2), 454–461.

FSANZ (Food Standards Australia New Zealand) (2011). Australia New Zealand Food Standards Code-Standard 1.4.1-Contaminants and Natural Toxicants, (Proposal P1013-Code Maintenance IX) Variation, Administered by: Health and Ageing, Prepared 11 Jul 2011 by Agency.

García-Montelongo, F., Díaz, C., Galindo, L., Larrechi, M. S., & Rius, X. (1992). Heavy metals in three fish species from the coastal waters of Santa Cruz de Tenerife (Canary Islands). *Scientia Marina, 58*(3), 179–183.

Gorell, J. M., Johnson, C. C., Rybicki, B. A., Peterson, E. L., Kortsha, G. X., & Brown, G. G. (1997). Occupational exposures to metals as risk factors for Parkinson's disease. *Neurology, 48*(3), 650–658.

Herreros, M. A., Iñigo-Nuñez, S., Sanchez-Perez, E., Encinas, T., & Gonzalez-Bulnes, A. (2008). Contribution of fish consumption to heavy metals exposure in women of childbearing age from a Mediterranean country (Spain). *Food and Chemical Toxicology, 46*(5), 1591–1595.

Imyim, A., Daorattanachai, P., & Unob, F. (2013). Determination of cadmium, nickel, lead, and zinc in fish tissue by flame and graphite furnace atomic absorption after extraction with pyrrolidine dithiocarbamate and activated carbon. *Analytical Letters, 46*(13), 2101–2110.

Irish Sea Fisheries Board. (2005). *Nutritional aspects of fish*. Dublin: Bord Iascaigh Mhrara.

Ismail, N. S., & Abu-Hilal, A. H. (2008). Heavy metals in three commonly available coral reef fish species from the Jordan Gulf of Aqaba, Red Sea. *Jordan Journal of Biological Sciences, 1*(2), 61–66.

Khaled, A. (2004). Heavy metals concentrations in certain tissues of five commercially important fishes from El-Mex. *Egyptian Journal of Aquatic Biology and Fisheries, 8*(1), 51–64.

Khan, B., Khan, H., Muhammad, S., & Khan, T. (2012). Heavy metals concentration trends in three fish species from Shah Alam River (Khyber Pakhtunkhwa Province, Pakistan). *Journal of Natural and Environmental Sciences, 3*(1), 1–8.

Kirdar, S. S., Ocak, E., Kose, S., & Ozer, E. (2013). Seasonal changes in mineral and trace elements of canak cheese. *Asian Journal of Chemistry, 25*, 6177–6180.

Kumar, B., Mukherjee, D. P., Kumar, S., Mishra, M., Prakash, D. S., Singh, K., et al. (2011). Bioaccumulation of heavy metals in muscle tissue of fishes from selected aquaculture ponds in east Kolkata wetlands. *Annals of Biological Research, 2*(3), 125–134.

Lee, K. G., Kweon, H., Yeo, J. H., Woo, S., Han, S., & Kim, J. H. (2011). Characterization of tyrosine-rich *Antheraea pernyi* silk fibroin hydrolysate. *International Journal of Biological Macromolecules, 48*(1), 223–226.

Luckey, T. D., & Venugopal, B. (1977). *Metal toxicity in mammals: physiologic and chemical basis for metal toxicity*. New York: Plenum.

MAFF (Ministry of Agriculture, Fisheries and Food) (2000). Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea. In Aquatic Environment Monitoring Report No: 52. Center for Environment, Fisheries and Aquaculture Science, Lowestoft, UK

Mendil, D., Ünal, Ö. F., Tuzen, M., & Soylak, M. (2010). Determination of trace metals in different fish species and sediments from the River Yeşilırmak in Tokat, Turkey. *Food and Chemical Toxicology, 48*(5), 1383–1392.

Mitic, S. S., Pavlovic, A. N., Tosic, S. B., Stojanovic, B. T., Mitic, M. N., & Stojkovic, M. B. (2013). Elemental composition of various apple cultivars grown in Serbia. *Asian Journal of Chemistry, 25*, 6027–6032.

Rahman, M. S., & Islam, M. R. (2009). Effects of pH on isotherms modeling for Cu(II) ions adsorption using maple wood sawdust. *Chemical Engineering Journal, 149*(1–3), 273–280.

Rahman, M. S., & Islam, M. R. (2010). Adsorption of Cd(II) Ions from synthetic waste water using maple sawdust. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 32*(3), 222–231.

Rahman, M. S., Molla, A. H., & Arafat, S. M. Y. (2010). Status of pollution around Dhaka export processing zone and its impact on Bangshi River water, Bangladesh. *Journal of Nature Science and Sustainable Technology, 4*(2), 91–110.

Rahman, M. S., Molla, A. H., Saha, N., & Rahman, A. (2012). Study on heavy metals levels and its risk assessment in some edible fishes from Bangshi River, Savar, Dhaka, Bangladesh. *Food Chemistry, 134*(4), 1847–1854.

Ray, S. (1986). Bioaccumulation of cadmium in marine organisms. *Experientia. Supplementum, 50*, 65–75.

Saha, N., & Zaman, M. R. (2011). Concentration of selected toxic metals in groundwater and some cereals grown in Shibganj area of Chapai Nawabganj, Rajshahi, Bangladesh. *Current Science, 101*(3), 427–431.

SASO (Saudi Arabian Standards Organization) (1997). Maximum limits of contaminating metallic elements in foods. Riyadh, Saudi Arabia

Shaltout, A. A., Abdel-Aal, M. S., Welz, B., & Castilho, I. N. B. (2013). Determination of Cd, Cu, Ni, and Pb in black tea from Saudi Arabia using graphite furnace atomic absorption spectrometry after microwave-assisted acid digestion. *Analytical Letters, 46*(13), 2089–2100.

Sivaperumal, P., Sankar, T. V., & Nair, P. G. V. (2007). Heavy metal concentrations in fish, shellfish and fish products from internal markets of India vis-a-vis international standards. *Food Chemistry, 102*(3), 612–620.

Soylak, M., & Turkoglu, O. (1999). Trace metal accumulation caused by traffic in agricultural soil near a motorway in Kayseri-Turkey. *Journal of Trace and Microprobe Techniques, 17*, 209–217.

Soylak, M., Saraymen, R., & Dogan, M. (1995). Investigation of lead, chromium, cobalt and molybdenum concentrations in hair samples collected from diabetic patients. *Fresenius Environmental Bulletin, 4*, 485–490.

Soylak, M., Elci, L., & Dogan, M. (1996a). Determination of some trace metal impurities in refined and unrefined salts after preconcentration onto activated carbon. *Fresenius Environmental Bulletin, 5*, 148–155.

Soylak, M., Sahin, U., & Elci, L. (1996b). Spectrophotometric determination of molybdenum in steel samples utilising selective sorbent extraction on amberlite XAD-8 resin. *Analytica Chimica Acta, 322*(1–2), 111–115.

Soylak, M., Uzun, A., & Elci, L. (2001). Chemical analysis of industrial waste water samples from some metal and textile plants in the organized industrial region of Kayseri-Turkey. *Kuwait Journal of Science and Engineering, 28*, 151–160.

Soylak, M., Divrikli, U., Elci, L., & Dogan, M. (2002). Preconcentration of Cr(III), Co(II), Cu(II), Fe(III) and Pb(II) as calmagite chelates on cellulose nitrate membrane filter prior to their flame atomic absorption spectrometric determinations. *Talanta, 56*, 565–570.

Soylak, M., Colak, H., & Turkoglu, O. (2006). Heavy metal content of some cereals, spices and pulses from Middle Anatolia Region of Turkey. *Fresenius Environmental Bulletin, 15*, 345–348.

Soylak, M., Cihan, Z., & Yilmaz, E. (2012). Evaluation of trace element contents of some herbal plants and spices retailed in Kayseri, Turkey. *Environmental Monitoring and Assessment, 184*(6), 3455–3461.

Soylak, M., Cihan, Z., & Yilmaz, E. (2013). Heavy metal contents of organically produced, harvested, and dried fruit samples from Kayseri, Turkey. *Environmental Monitoring and Assessment, 185*(3), 2577–2583.

Suarez, M. F., Mills, A., Egdell, R. G., & Compton, R. G. (2000). Anodic stripping voltammetry with photochemical preconcentration at nanocrystalline TiO_2 films: detection of Ag^+ and Hg^{2+}. *Electroanalysis, 12*(6), 413–419.

Tidwell, J. H., & Allan, G. L. (2002). Fish as food: aquaculture's contribution. Ecological and economic impacts and contributions of fish farming and capture fisheries. *EMBO Reports, 2*(11), 958–963.

Turkish Food Codex (2008). Gıda Maddelerindeki Bulaşanların Maksimum Limitleri Hakkında Tebliğ. 17.05.2008- 26879, No: 2008/26.

Turkmen, A., Turkmen, M., Tepe, Y., & Akyurt, İ. (2005). Heavy metals in three commercially valuable fish species from İskenderun Bay, Northern East Mediterranean Sea, Turkey. *Food Chemistry, 91*(1), 167–172.

Turkmen, M., Turkmen, A., Tepe, Y., Töre, Y., & Ateş, A. (2009). Determination of metals in fish species from Aegean and Mediterranean seas. *Food Chemistry, 113*(1), 233–237.

Tuzen, M. (2003). Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. *Food Chemistry, 80*(1), 119–123.

Tuzen, M., & Soylak, M. (2007). Determination of trace metals in canned fish marketed in Turkey. *Food Chemistry, 101*(4), 1378–1382.

Tuzen, M., Silici, S., Mendil, D., & Soylak, M. (2007). Trace element levels in honeys from different regions of Turkey. *Food Chemistry, 103*, 325–330.

Tuzen, M., Citak, D., Mendil, D., & Soylak, M. (2009a). Arsenic speciation in natural water samples by coprecipitation-hydride generation atomic absorption spectrometry combination. *Talanta, 78*(1), 52–56.

Tuzen, M., Verep, B., Ogretmen, A. O., & Soylak, M. (2009b). Trace element content in marine algae species from the Black Sea, Turkey. *Environmental Monitoring and Assessment, 151*, 363–368.

Uluozlu, O. D., Tuzen, M., Mendil, D., & Soylak, M. (2007). Trace metal content in nine species of fish from the Black and Aegean Seas, Turkey. *Food Chemistry, 104*(2), 835–840.

WHO (World Health Organization) (1994). Quality directive of potable water (2nd ed.).

Yi, Y. J., & Zhang, S. H. (2012). The relationships between fish heavy metal concentrations and fish size in the upper and middle reach of Yangtze River. *Procedia Environmental Sciences, 13*, 1699–1707.

Yildirim, Y., Gonulalan, Z., Narin, I., & Soylak, M. (2009). Evaluation of trace heavy metal levels of some fish species sold at retail in Kayseri, Turkey. *Environmental Monitoring and Assessment, 149*(1–4), 223–228.

Yilmaz, F., Ozdemir, N., Demirak, A., & Tuna, A. L. (2007). Heavy metal levels in two fish species *Leuciscus cephalus* and *Lepomis gibbosus*. *Food Chemistry, 100*(2), 830–835.

Zhao, L., Yang, F., & Yan, X. (2013). Concentrations of selected trace elements in marine bivalves and the dietary risk to residents of Dalian City, Northern China. *Human and Ecological Risk Assessment, 19*(1), 145–150.