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Heavy Metal Levels in Muscle Tissues of *Solea solea*, *Mullus barbatus*, and *Sardina pilchardus* Marketed for Consumption in Mersin, Turkey

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Abstract Edible muscle tissues of *Solea solea*, *Mullus barbatus*, and *Sardina pilchardus* marketed in Mersin were analyzed for their Cr (total), Mn, Fe, Ni, Cu, Zn, As (total), Cd, Sn, and Pb levels. Metal levels of the tissues were determined using inductively coupled plasma-mass spectrophotometric (ICP-MS) methods. Muscle levels of Cr, Mn, Fe, Ni, Cu, Zn, As, Sn, and Pb were determined as 0.19–2.80, 0.08–3.88, 0.93–25.76, 0.03–0.63, 0.01–1.96, 1.28–45.95, 0.49–25.26, 0.14–4.03, and 0.02–1.37 mg kg^{-1} w.w., respectively. Cadmium levels were below detection limits in all the muscle samples taken. Mean metal levels of the tissues were compared with the provisional tolerable daily (PTDs) and weekly (PTWIs) intake limits. Mean metal levels taken by the consumption of analyzed tissues were below PTDs and PTWIs; hence, the fish species studied do not pose any risk for human consumption from the point of heavy metals.

Keywords Heavy metals · Food safety · Tolerable weekly intake · Marine fish

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1 Introduction

Demand for aquaculture products increased with increasing living standards especially after the realization of health benefits of these products on human health (Kalogeropoulos et al. 2012). Hence, apparent world fish consumption per capita increased from an average of 9.9 kg in the 1960s to 19.2 kg in 2012 (FAO 2014).

Dieticians state the need to consume aquatic products regularly since these edibles contain various high-quality proteins, minerals, essential amino acids, and fatty acids such as omega-3 (n-3) which lower risk of various kinds of cancer, type 2 diabetes, and heart attack (Guérin et al. 2011). Among the animal-based foods, however, aquatic animals are in direct contact with chemical contaminants and accumulate them to higher concentrations in their tissues (Cirillo et al. 2010).

Large water masses both fresh and marine are polluted with heavy metals mainly due to anthropogenic inputs (Bettini et al. 2006) and have become a health risk for human themselves. They can be found as dissolved, suspended in water or deposited on sediments where they are taken by aquatic organisms and transferred up to humans through food chain (Cirillo et al. 2010).

Essential elements such as Cr (III), Cu, Fe, Mn, Ni, Sn, and Zn are needed in trace amounts for various biochemical and enzymatic reactions whereas toxic metals such as As, Cd, Cr (VI), and Pb have no biological function at all (Miedico et al. 2015). Heavy metals are shown to have pathogenic effects (Cirillo et al. 2010). Cr^{+6} compounds show mutagenic effects in mammals and are known as carcinogens of circulatory system. High levels of Mn, Cu, and Zn can cause hepatic, renal, cardiovascular, and neurologic disorders in humans and similar symptoms were observed when exposed to low levels of Cd, As, and Pb (Eisler 2000).

Fish are constantly exposed to chemicals in polluted and contaminated waters and have been found to be good indicators of heavy metal contamination in aquatic systems; hence, they occupy different trophic levels and are of different sizes and ages (Ikem and Egiebor 2005). Heavy metals are shown to accumulate mainly in liver and to a less extent in muscle tissues in various fish species (Guerin et al. 2011; Kalogeropoulos et al. 2012).

Presence and the amount of toxic materials in food and their effects on human health are becoming more important in recent years. Hence, the main concern of researchers working on the subject is "food safety" and keeping food quality in acceptable limits for human consumption. Levels of Cr (total), Mn, Fe, Ni, Cu, Zn, As (total), Cd, Sn, and Pb were determined in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* marketed for consumption in Mersin and compared with tolerable daily and weekly limits together with their reliabilities as far as the human health is concerned.

2 Materials and Methods

2.1 Sample Collection and Preparation

The selected three fish species are consumed regularly by local people and were obtained from three different supermarkets. Eight samples of each species were taken from each market totaling to 72 fishes to be analyzed. Samples were taken to the laboratory and were dissected for their muscle tissues. An average of 0.5-g muscle tissue was taken from each fish which were kept at − 4 °C until metal analysis. The mean length and weight of the fish samples are given in Table 1.

Table 1 Mean weight and length of *S. solea*, *M. barbatus*, and *S. pilchardus* sampled from three markets in Mersin, Turkey

Species	*S. solea* (n = 24) $\bar{X}$ ±*SD**	*M. barbatus* (n = 24) $\bar{X}$ ±*SD**	*S. pilchardus* (n = 24) $\bar{X}$ ±*SD**
Weight (g)	163.7 ± 19.7	60.94 ± 5.19	53.72 ± 6.86
Length (cm)	26.11 ± 0.87	16.29 ± 0.66	18.51 ± 0.76

n = total fish samples for each species

*$\bar{X}$ ±*SD* = mean ± standard deviation

2.2 Metal Analysis

Muscle tissue from each fish was transferred to a petri dish after being wet weighed and dried at 150 °C for 48 h. Dried tissues were reweighed and were added 2 mL nitric acid (HNO_3, % 65, S.W.: 1.40, Merck) and 1 mL perchloric acid ($HClO_4$, % 60, S.W.: 1.53, Merck) mixture in experimental tube and were wet digested on a hotplate at 120 °C for 8 h. They were then transferred to polyethylene tubes and their volumes were made up to 10 mL using deionized water. Samples were passed through a 0.45-μm membrane filter before analysis. Metal levels in tissue samples were determined using ICP-MS (Octopole Reaction System, Agilent Technologies, Agilent 7500 ce) techniques. The operating conditions of ICP-MS are given in Table 2.

Metal levels of the tissues were determined using their dry weight (mg kg^{-1} d.w.) which were then converted to wet weight values (mg kg^{-1} w.w.) by using moisture content for each sample (El-Moselhy et al. 2014). Analysis was carried out in triplicate. Control samples were prepared from fish tissue homogenate (IAEA-407) (Anon 2003) for recovery purposes and the recovery values for Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Sn, and Pb were measured as 99.64, 87.74, 96.29, 91.79, 93.63, 93.06, 99.5, 97.2, 96.07, and 96.59%, respectively. Six standards with standard linear regression were used for each metal. Validation parameters for the method used are given in Table 3.

Table 2 ICP-MS (Agilent 7500ce) operating conditions

RF power	1500 W
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1 L min^{-1}
Carrier gas flow rate	1.1 L min^{-1}
Helium collision gas flow rate	mL min^{-1} (not used)
Spray chamber T	2 °C
Sample depth	8.6 mm
Sample introduction flow rate	1 mL min^{-1}
Nebulizer pump	0.1 rps
Extract lens	1.5 V

Table 3 Validation parameters of the analytical method

Metal	LOD (ng g^{-1})	LOQ (ng g^{-1})	RSDr %	R^2
Cr	1.14	3.81	2.44	0.9999
Mn	0.23	0.78	3.28	0.9999
Fe	1.52	5.06	4.61	0.998
Ni	0.68	2.26	1.51	1
Cu	0.61	2.02	3.05	0.9999
Zn	2.48	8.27	3.77	0.9997
As	0.51	1.71	2.35	1
Cd	0.46	1.52	1.99	0.9999
Sn	0.44	1.47	2.89	1
Pb	0.35	1.16	2.04	1

2.3 Calculation of Weekly Intake (EWIs) of the Metals Analyzed

The daily intake of an element from food consumption is based on body weight and is dependent on element concentration in food and amount of food consumed. Daily amount of fish consumption for an average person (70 kg body weight) is 20 g fish/day which equals to 140 g fish/weekly in Turkey (FAO 2005). Multiplying the amount of fish consumption (140 g fish/week) by mean metal concentration (mg/kg) gives the amount of metal intake (EWI). EWI by the consumption of fish tissues sampled were calculated by using the formula;

$$\text{EWI}\ \left(\ddot{\text{E}}\text{g}\Big/\textit{week}\Big/70\ \text{kg}\ \textit{body weight}\right)\ =\ (\text{C}\times\text{FIR})\ \ \textit{where},$$
$$\text{C}(\textit{Concentration});\textit{Mean metal level in fish tissue}\ \left(\text{mg kg}^{-1}\text{w.w.}\right).$$
$$\text{FIR}\ \ (\textit{Consumption Rate})\ \ ;\ \ 140\ \ \text{g}\ \ \textit{fish}\Big/\ \ \textit{week}$$

2.4 Statistical Analysis

Data obtained from tissue analysis were analyzed by one-way ANOVA and Student Newman Keul's (SNK) Procedure using SPSS 16.0 statistical package program.

3 Results and Discussion

Mean metal levels measured in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* are given in Table 4. Cadmium levels in muscle tissues of all the species studied and chromium levels in *S. solea* samples were below detection limits. The minimum and maximum levels of the metals differed (as mg kg^{-1} w.w.) between the following ranges, respectively; Cr < 0.001–2.80, Mn 0.08–3.88, Fe 0.93–25.76, Ni 0.03–0.63, Cu 0.01–1.96, Zn 1.28–45.95, As 0.49–25.26, Cd < 0.0004, Sn 0.14–4.03, and Pb 0.02–1.37 (Table 4.)

3.1 Chromium

Chromium is found in divalent (Cr^2), trivalent (Cr^3), and hexavalent (Cr^6) forms (Eisler 2000); only trivalent form is an essential mineral for the use of lipids and proteins in living metabolisms (Ikem and Egiebor 2005). Oral reference doses (RfD) for Cr^{+3} and Cr^{+6} recommended by the US Environmental Protection Agency (US EPA) are 1500 and 3 µg/kg/day, respectively, and values beyond these levels would cause health problems in humans (EPA 2000a).

Chromium levels measured in muscle tissues of

Table 4 Metal concentrations (mean ± SD and range as mg kg^{-1} w.w.) in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* marketed in Mersin, Turkey

	S. solea (n = 24) $\bar{X}$ ±*SD** (min–max)	*M. barbatus* (n = 24) $\bar{X}$ ±*SD** (min–max)	*S. pilchardus* (n = 24) $\bar{X}$ ±*SD** (min–max)
Cr	< 0.001	1.54 ± 0.29 (0.23–2.80)	0.75 ± 0.12 (0.19–1.48)
Mn	1.13^{x} ± 0.23 (0.33–3.88)	0.33^{y} ± 0.04 (0.08–0.60)	0.70^{y} ± 0.12 (0.11–1.76)
Fe	13.52^{x} ± 1.61 (3.86–25.76)	10.40^{x} ± 1.36 (0.93–19.58)	10.03^{x} ± 1.24 (1.66–21.02)
Ni	0.26^{x} ± 0.05 (0.06–0.63)	0.14^{x} ± 0.01 (0.03–0.21)	0.15^{x} ± 0.03 (0.03–0.44)
Cu	0.49^{xy} ± 0.10 (0.01–1.61)	0.72^{x} ± 0.11 (0.09–1.96)	0.35^{y} ± 0.04 (0.16–0.70)
Zn	23.58^{x} ± 3.54 (5.16–45.95)	17.12^{xy} ± 2.14 (4.05–35.79)	11.75^{y} ± 1.77 (1.28–22.76)
As	6.14^{x} ± 0.60 (1.48–9.83)	10.24^{y} ± 1.14 (5.08–25.26)	3.04^{z} ± 0.61 (0.49–8.70)
Cd	< 0.0004	< 0.0004	< 0.0004
Sn	1.54^{x} ± 0.30 (0.17–4.03)	0.53^{y} ± 0.06 (0.21–1.12)	0.30^{y} ± 0.03 (0.14–0.56)
Pb	0.48^{x} ± 0.08 (0.03–0.99)	0.16^{x} ± 0.03 (0.02–0.42)	0.91^{y} ± 0.08 (0.57–1.37)

Letters x, y, and z show differences between the fish species. Data shown with different letters are significantly different at the $p < 0.05$ level

n = total fish samples for each species

$\bar{X}$ ±*SD* = mean ± standard deviation;

S. solea, *M. barbatus*, and *S. pilchardus* differed between 0 and 0.001, 0.23–2.80, and 0.19–1.48 mg kg^{-1} w.w., respectively, the highest levels being in *M. barbatus*. Mean Cr levels from Turkish Mediterranean sea were reported as 0.03–0.05 mg kg^{-1} w.w. (Ersoy and Çelik 2010) in muscle tissues of *S. solea*, 1.06–1.91 mg kg^{-1} d.w. (Kalay et al. 1999) in edible parts of *M. barbatus*, 2.22 mg kg^{-1} d.w. (Canlı and Atlı 2003) and 1.22–2.15 mg kg^{-1} d.w. (Canlı et al. 2001) in consumable parts of *S. pilchardus*.

The mean levels of chromium found in fish varied between 0.05–0.57 mg kg^{-1} w.w. in France (Guerin et al. 2011), < 0.05–0.06 mg kg^{-1} w.w. in Greece (Kalogeropoulos et al. 2012) and 0.07–0.34 mg kg^{-1} w.w. in New Jersey, USA (Burger and Gochfeld 2005). The mean levels of chromium determined in fish species from the Turkish Mediterranean, Black sea, Marmara, and Aegean seas were between 0.03–2.08 mg kg^{-1} w.w. (Ates et al. 2015), 0.95–1.98 mg kg^{-1} w.w. (Uluozlu et al. 2007), and < 0.06–0.84 mg kg^{-1} d.w. (Topcuoglu et al. 2002).

The Cr concentrations in *M. barbatus* collected from Turkish Mediterranean sea (Kalay et al. 1999) is in agreement with the present results.

3.2 Manganese

Daily intake of low doses of Mn is necessary for the normal development and growth in humans (Ikem and Egiebor 2005). US EPA reported that oral RfD of Mn is 140 μg/kg/day and that doses above this value might cause health problems (EPA 2016).

Minimum and maximum levels of manganese in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* changed between 0.33–3.88, 0.08–0.60, and 0.11–1.76 mg kg^{-1} w.w., respectively. Mean Mn levels stated as 0.20–0.41 mg kg^{-1} w.w. from Turkish Mediterranean sea (Ersoy and Çelik 2010) and 0.11 mg kg^{-1} w.w. from French markets in edible parts of *S. solea* (Guerin et al. 2011), 6.54 mg kg^{-1} d.w. from Black and Aegean seas of Turkey in consumable parts of *M. barbatus* (Uluozlu et al. 2007) and 0.64 mg kg^{-1} w.w. from French markets in muscle tissues of *S. pilchardus* (Guerin et al. 2011).

Mean Mn levels measured in edible parts of fish species in New Jersey, USA, were 0.15–0.70 mg kg^{-1} w.w. (Burger and Gochfeld 2005) and 0.37–0.83 mg kg^{-1} w.w. in Gazze, Palestine (Elnabris et al. 2013). Studies carried out in Mediteranean, Aegean, Marmara, and Black seas on the levels of Mn in muscle tissues of various fish species ranged between 0.07–3.62 mg kg^{-1} w.w. (Ates et al. 2015), 0.08–2.78 mg kg^{-1} w.w. (Türkmen et al. 2009), and 0.90–2.50 mg kg^{-1} w.w. (Tuzen and Soylak 2007).

Mn levels in muscle tissues of *S. solea* obtained from this study were higher than the results from other studies (Ersoy and Çelik 2010; Guerin et al. 2011).

3.3 Iron

Iron is an essential element in humans and its deficiency results in anemia (Ikem and Egiebor 2005). Whereas high levels of Fe causes Parkinson's disease, Alzheimer, and second type diabetes (Killilea et al. 2003). There is no oral RfD designated for iron by US EPA. However, World Health Organization (WHO) reported a value of 5600 μg/kg/week PTWI for iron (FAO/WHO 2004).

Iron levels in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* differed between 3.86–25.76, 0.93–19.58, and 1.66–21.02 mg kg^{-1} w.w., respectively. Mean Fe levels from Turkish Mediterranean sea were reported as 0.41–1.11 mg kg^{-1} w.w. (Ersoy and Çelik 2010) and 9.2–15.9 mg kg^{-1} d.w. (Çoğun et al. 2005) in muscle tissues of *S. solea*, 40.4–57.2 mg kg^{-1} d.w. (Kargın 1996) and 32.2–103.1 mg kg^{-1} d.w. (Kalay et al. 1999) in consumable parts of *M. barbatus*, 39.60 mg kg^{-1} d.w. (Canlı and Atlı 2003), 80.0–126.4 mg kg^{-1} d.w. in edible parts of *S. pilchardus* (Canlı et al. 2001).

Mean levels of iron varied between 1.35–19 mg kg^{-1} w.w. in edible tissues of fish species in French markets (Guerin et al. 2011) and 6.8–16 mg kg^{-1} w.w. in Greek markets (Kalogeropoulos et al. 2012). Mean Fe levels in muscle tissues of fish species from Mediterranean, Aegean, Marmara, and Black seas were reported as 5.31–115 mg kg^{-1} w.w. (Ates et al. 2015), 9.18–136 mg kg^{-1} w.w. (Türkmen et al. 2009), 10.2–30.3 mg kg^{-1} w.w. (Tuzen and Soylak 2007), and 68.6–163 mg kg^{-1} d.w. (Uluozlu et al. 2007).

Fe levels in *M. barbatus* obtained from this study were lower than the results from other studies (Kargın 1996; Kalay et al. 1999).

3.4 Nickel

Nickel is found in trace amounts in Earth's crust and is known to play a role as a co-factor during Fe absorption processes from intestine (Das et al. 2008). US EPA reported the oral RfD for Ni as 20 μg/kg/day above which circulation disorders and carcinogenic effects might occur (EPA 2000b).

Nickel levels in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* were determined as between 0.06–0.63, 0.03–0.21, and 0.03–0.44 mg kg^{-1} w.w., respectively. Mean Ni levels from Turkish Mediterranean sea were reported as 0.07–0.22 mg kg^{-1} w.w. (Ersoy and Çelik 2010) in consumable parts of *S. solea*, 2.88–6.07 mg kg^{-1} d.w. (Kalay et al. 1999) in muscle tissues of *M. barbatus* and 2.34–6.20 mg kg^{-1} d.w. (Canlı et al. 2001) in edible parts of *S. pilchardus*.

Levels of nickel were reported as 0.02–0.34 mg kg^{-1} w.w., < 0.08 mg kg^{-1} w.w., and 0.45–0.97 mg kg^{-1} w.w. in edible tissues of fish species in French (Guerin et al. 2011), Greek (Kalogeropoulos et al. 2012) and Gazza, Palestine (Elnabris et al. 2013) markets, respectively. Mn levels in muscle tissues of various fish species from Mediterranean, Aegean, Marmara, and Black seas changed between 0.03–3.43 mg kg^{-1} w.w. (Ates et al. 2015), 0.03–3.13 mg kg^{-1} w.w. (Türkmen et al. 2009), 0.42–0.85 mg kg^{-1} w.w. (Tuzen and Soylak 2007), and 1.92–5.68 mg kg^{-1} d.w. (Uluozlu et al. 2007).

Determined Ni concentrations in *M. barbatus* and *S. pilchardus* in the present study were lower than the results from other studies (Kalay et al. 1999; Canlı et al. 2001).

3.5 Copper

Copper is a common element in nature and is essential for the development and growth of all organisms (Eisler 2000). It causes liver and kidney dysfunctions above certain concentrations (Duruibe et al. 2007). There is no oral RfD determined for Cu by US EPA. The WHO, however, reported a PTWI value of 3500 μg/kg/week for Cu (FAO/WHO 2004).

The muscle tissue levels of Cu differed between 0.01–1.61 mg kg^{-1} in *S. solea*, 0.09–1.96 mg kg^{-1} in *M. barbatus*, and 0.16–0.70 mg kg^{-1}in *S. pilchardus* on wet weight basis. Mean Cu levels from Turkish Mediterranean sea were reported as 1.06–1.54 mg kg^{-1} w.w. (Ersoy and Çelik 2010) and 4.7–8.3 mg kg^{-1} d.w. (Çoğun et al. 2005) in consumable parts of *S. solea*, 9.9–14.2 mg kg^{-1} d.w. (Kargın 1996) and 2.26–5.88 mg kg^{-1} d.w. (Kalay et al. 1999) in muscle tissues of *M. barbatus*, 4.17 mg kg^{-1} d.w. (Canlı and Atlı 2003), 6.04–14.53 mg kg^{-1} d.w. in edible parts of *S. pilchardus* (Canlı et al. 2001).

Mean levels of copper in muscle tissues of fish species were 0.06–2.01 mg kg^{-1} w.w. marketed in France (Guerin et al. 2011), 0.24–1.4 mg kg^{-1} w.w. in Greece (Kalogeropoulos et al. 2012), 0.25–0.90 mg kg^{-1} w.w. in Gazza, Palestine (Elnabris et al. 2013), 0.13–1.47 mg kg^{-1} w.w. in coastal sites of Croatia (Bilandžić et al. 2011) and < 0.003–8.30 mg kg^{-1} d.w. in Alexandria, Algeria (Abdallah 2008). The reported levels of Cu in muscle tissues of fish species from Mediterranean, Aegean, Marmara, and Black seas changed between 0.34–7.05 mg kg^{-1} w.w, (Türkmen et al. 2009), 1.10–2.50 mg kg^{-1} w.w. (Tuzen and Soylak 2007), and 0.73–1.83 mg kg^{-1} d.w. (Uluozlu et al. 2007).

Cu levels in *S. solea*, *M. barbatus*, and *S. pilchardus* determined this study were lower than the results from other studies (Kargın 1996; Kalay et al. 1999; Canlı and Atlı 2003; Çoğun et al. 2005; Ersoy and Çelik 2010).

3.6 Zinc

Zinc is found in coal and many manufactured products such as motor oils, lubricants, tires, and fuel oil (Eisler 2000). Excess levels of zinc are known to cause harmful effects. US EPA reported oral RfD of Zn as 300 μg/kg/day above which its adverse effects on growth, survival, and reproduction are observed (EPA 2005).

Minimum and maximum levels of Zn in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* were 5.16–45.95, 4.05–35.79, and 1.28–22.76 mg kg^{-1} w.w., respectively. Mean Zn levels from Turkish Mediterranean sea were reported as 2.09–2.76 mg kg^{-1} w.w. (Ersoy and Çelik 2010) and 22.7–33.8 mg kg^{-1} d.w. (Çoğun et al. 2005) in edible parts of *S. solea*, 26.64–39.2 mg kg^{-1} d.w. (Kargın 1996) and 16.1–25.8 mg kg^{-1} d.w. (Kalay et al. 1999) in muscle tissues of *M. barbatus*, 34.58 mg kg^{-1} d.w. (Canlı and Atlı 2003), 24–42.4 mg kg^{-1} d.w. in consumable parts of *S. pilchardus* (Canlı et al. 2001).

Mean zinc levels in consumable parts of various fish species were 1.36–25.1 mg kg^{-1} w.w. in France (Guerin et al. 2011), 4.1–62 mg kg^{-1} w.w. in Greece (Kalogeropoulos et al. 2012), 7.4–43.9 mg kg^{-1} d.w. in Alexandria, Egypt (Abdallah 2008), 3.70–20.53 mg kg^{-1} w.w. in Gazza, Palestine (Elnabris et al. 2013). Zinc levels in fish species from Turkey were reported as 3.51–53.5 mg kg^{-1} w.w. (Türkmen et al. 2009), 7.57–34.4 mg kg^{-1} w.w. (Tuzen and Soylak 2007), and 35.4–106 mg kg^{-1} d.w. (Uluozlu et al. 2007).

Zn levels in muscle tissues of *M. barbatus* obtained from this study were similar to the results from other studies (Kargın 1996; Kalay et al. 1999).

3.7 Arsenic

Arsenic is widely distributed on Earth in a number of valences which is a highly toxic as well as an essential dietary element (Jain and Ali 2000). Water and food are the main routes in which As enter organisms. Oral RfD reported for As is 0.3 μg/kg/day above which dermatitis, lowered neuron transmission and liver carcinoma may develop (EPA 2000c).

Arsenic levels in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* were between 1.48–9.83, 5.08–25.26, and 0.49–8.70 mg kg^{-1} w.w., respectively. Mean levels of As determined in various marketed fish species differed between 0.03–0.12 mg kg^{-1} in China (Wu et al. 2014), 0.59–5.70 mg kg^{-1} in Brazil (Morgano et al. 2011), 0.43–5.91 mg kg^{-1} in coastal sites of Croatia (Bilandžić et al. 2011), 0.23–3.30 mg kg^{-1} in New Jersey, USA (Burger and Gochfeld 2005), and 30.76–59.91 mg kg^{-1} in Adriatic Sea Italy (Perugini et al. 2014) on wet weight basis.

The obtained As concentrations in *M. barbatus* from this study were higher than the results from other studies (Burger and Gochfeld 2005; Morgano et al. 2011; Wu et al. 2014).

3.8 Cadmium

Cadmium is generally found at low levels in nature and is obtained as a byproduct from zinc, lead, and copper mining (Eisler 2000). The main source of cadmium for non-smokers are water and food (Cirillo et al. 2010). US EPA reported oral RfD of Cd as 1 μg/kg/day above which abnormalities in kidney, liver, skeleton, and reproductive functions are observed (EPA 2000d).

Cadmium levels in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* were below 0.0004 mg kg^{-1} w.w. Mean Cd levels from Turkish Mediterranean sea were reported as 0.03–0.11 mg kg^{-1} w.w. (Ersoy and Çelik 2010) and 2.1–3.5 mg kg^{-1} d.w. (Çoğun et al. 2005) in edible parts of *S. solea*, 5.4–10.2 mg kg^{-1} d.w. (Kargın 1996) and 1.07–1.43 mg kg^{-1} d.w. (Kalay et al. 1999) in muscle tissues of *M. barbatus*, 0.55 mg kg^{-1} d.w. (Canlı and Atlı 2003), 0.96–1.26 mg kg^{-1} d.w. in consumable parts of *S. pilchardus* (Canlı et al. 2001).

Mean levels of Cd determined in various fish species differed between 0.004–0.07 mg kg^{-1} in Spain (Yusa et al. 2008), 0.003–0.04 mg kg^{-1} w.w. (Cirillo et al. 2010) and 0.009–0.16 mg kg^{-1} w.w in Italy (Miedico et al. 2015), 0.003–0.25 mg kg^{-1} w.w. in Greece (Kalogeropoulos et al. 2012), 0.000–0.03 mg kg^{-1} w.w in New Jersey, USA (Burger and Gochfeld 2005), 0.002–0.006 mg kg^{-1} w.w. in coastal sites of Croatia (Bilandžić et al. 2011), and 0.000–2.80 mg kg^{-1} d.w. in Alexandria, Egypt (Abdallah 2008). Minimum and maximum levels of Cd determined in various fish species from Mediterranean, Aegean, Marmara, and Black seas were between < 0.01–0.39 mg kg^{-1} w.w. (Türkmen et al. 2009), 0.06–0.25 mg kg^{-1} w.w. (Tuzen and Soylak 2007), and 0.45–0.90 mg kg^{-1} d.w. (Uluozlu et al. 2007).

Cd levels in all analyzed tissues of fish were lower than the results from other studies (Kargın 1996; Kalay et al. 1999; Canlı and Atlı 2003; Çoğun et al. 2005; Ersoy and Çelik 2010).

3.9 Tin

Uptake of Sn by humans is generally via conserved products, tooth pastes, or by consumption of aquatic products (Eisler 2000). High levels of Sn have been reported to cause kidney and liver dysfunctions, gastrointestinal irritation, diarrhea, nausea, vomit, and anemia (Ikem and Egiebor 2005). There is no oral RfD value determined for Sn by US EPA. However, the WHO reported the PTWI value of 14,000 μg/kg/week for Sn (FAO/WHO 2004).

Tin levels in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* differed between 0.17–4.03, 0.21–1.12, and 0.14–0.56 mg kg^{-1} w.w., respectively. Mean tin levels in conserved fish products were 0.33–11.57 mg kg^{-1} w.w. in Georgia (Ikem and Egiebor 2005), 0.001–0.02 mg kg^{-1} w.w. in Spain (Olmedo et al. 2013), and 0.08–0.47 mg kg^{-1} w.w. in Iran (Pourjafar et al. 2014). Tin levels in conserved fish and marine products were reported as 0.02–0.06 mg kg^{-1} w.w. (Mol 2011a), and 0.02–0.13 mg kg^{-1} w.w. (Mol 2011b) in Turkey.

Sn levels in all analyzed tissues of fish were higher than the results from other studies (Mol 2011a, b).

3.10 Lead

Lead is known to cause memory lapses, mental deficiencies, abnormal neurotransmitter functions, cardiovascular diseases, and kidney and liver damages (Ikem and Egiebor 2005). No RfD value was reported for Pb by US EPA, but the PTWI value for Pb was reported as 25 μg/kg/week by the WHO (FAO/WHO 2004).

Minimum and maximum levels of Pb in muscle tissues of *S. solea*, *M. barbatus*, and *S. pilchardus* were 0.03–0.99, 0.02–0.42, and 0.57–1.37 mg kg^{-1} w.w., respectively. Mean Pb levels from Turkish Mediterranean sea were reported as 0.13–0.38 mg kg^{-1} w.w. (Ersoy and Çelik 2010) and 14.0–26.6 mg kg^{-1} d.w. (Çoğun et al. 2005) in edible parts of *S. solea*, 18.4–28.5 mg kg^{-1} d.w. (Kargın 1996) and 5.34–9.11 mg kg^{-1} d.w. (Kalay et al. 1999) in muscle tissues of *M. barbatus*, 5.57 mg kg^{-1} d.w. (Canlı and Atlı 2003), 5.28–7.67 mg kg^{-1} d.w. in consumable parts of *S. pilchardus* (Canlı et al. 2001).

Mean lead levels in edible parts of fish various fish species were 0.003–0.04 mg kg^{-1} w.w. in France (Guerin et al. 2011), 0.04–0.17 mg kg^{-1} w.w. in Greece (Kalogeropoulos et al. 2012), 0.03–0.05 mg kg^{-1} w.w. in Spain (Yusa et al. 2008), 0.06–0.12 mg kg^{-1} w.w. (Cirillo et al. 2010) and 0.02–0.14 mg kg^{-1} w.w. (Miedico et al. 2015) in Italy, and 0.04–0.14 mg kg^{-1} w.w. in New Jersey, USA (Burger and Gochfeld 2005). Lead levels in fish species from Turkey were reported as 0.14–1.28 mg kg^{-1} w.w. (Türkmen et al. 2009), 0.09–0.40 mg kg^{-1} w.w. (Tuzen and Soylak 2007), and 0.33–0.93 mg kg^{-1} d.w. (Uluozlu et al. 2007).

The Pb concentrations obtained were in agreement with the results of other studies in *S. solea*, *M. barbatus*, and *S. pilchardus (*Uluozlu et al. 2007; Türkmen et al. 2009; Kalogeropoulos et al. 2012).

3.11 Human Health and Risk Evaluation of Fish Consumption in Mersin

The highest levels of Mn, Fe, Ni, Zn, and Sn were measured in *S. solea*, whereas Cr, Cu, and As levels were higher in *M. barbatus* and that of Pb in *S. pilchardus*.

A number of organizations brought some limitations on the presence of heavy metals in food products and set maximum acceptable limits. These maximum acceptable limits adopted by various organizations for some metals are given in Table 5 together with the mean levels measured in the present study.

Mean metal levels measured in muscle tissues of the three species studied were below the upper limits proposed by Turkish Food Codex (TFC) (Elnabris et al. 2013). Lead levels, however, in three out of 24 specimens of *S. pilchardus* were above the 1 mg kg^{-1} w.w. upper limit of TFC. Moreover, mean levels of Pb were above the limits for *S. solea* and *S. pilchardus* adopted by EC (2005).

The provisional and estimated daily and weekly intake of metals by adult consumption of muscle tissues of the three species studied are given in Table 6. Possible risks of consuming fish marketed in Mersin markets were evaluated by comparing mean metal levels determined from the present results with the provisional daily and weekly intakes for these metals.

Tolerable daily intake (EDI) is the amount of a substance that can be consumed every day throughout the life span without any risk. EDI is based on the body weight and it differs depending on the concentration of metal in the food consumed and on the amount of food consumed. Daily fish consumption per person in Turkey is 20 g according to FAO (2005) and TFC, which equals to 140 g of fish per week. Assuming 20 g of daily or 140 g of weekly fish consumption, the amount of metal intake by a 70 kg person were calculated and data obtained were compared with provisional tolerable daily intake (PTDI) and weekly intakes (PTWI) of metals. The EWI's of Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Sn, and Pb for *S. solea*, *M. barbatus*, and *S. pilchardus* varied between < 0.14–215.6, 46.2–158.2, 1404.2–1892.8, 19.6–36.4, 49–100.8, 1645–3301.2, 14.89–50.17, < 0.05, 42–215.6, and 22.4–127.4 μg/week/70 kg body weight. EWI's of selected metals for a 70 kg person consuming fish included in this study is well below the PTWI values (Table 6).

4 Conclusion

S. solea, *M. barbatus*, and *S. pilchardus* are economically important and highly consumed fish species in Turkey. Our results showed that the amount of metal intake by the consumption of analyzed fish samples are far below the PTDI and PTWI values and that consumption of these three fish species from Mersin markets would pose no harm as far as the human health is concerned.

Table 5 Comparison of present results with maximum permissible limits (MPL) of heavy metals in muscle tissues of fish (mg kg^{-1} w.w.) according to international standards

Organization/country	Metal										Reference
	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Sn	Pb	
FAO (1983)	–	–	–	–	30	30	–	0.05	–	0.5	FAO (1983)
South African Department of Health (DOH)	–	–	–	–	–	–	3	1	50	0.5	Bosch et al. (2015)
European Com. (EC)	–	–	–	–	–	–	–	0.05 (0.1)[a]	–	0.2 (0.4-)[a]	EC (2005)
England	–	–	–	–	20	50	–	0.2	–	2.0	MAFF (2000)
Turkish Food Codex	–	20	–	–	20	50	–	0.1	–	1	Elnabris et al. (2013)
S. solea[b]	< 0.001	1.13	13.52	0.26	0.49	23.58	6.14	< 0.0004	1.54	0.48	
M. barbatus[b]	1.54	0.33	10.40	0.14	0.72	17.12	10.24	< 0.0004	0.53	0.16	
S. pilchardus[b]	0.75	0.70	10.03	0.15	0.35	11.75	3.04	< 0.0004	0.30	0.91	

– data not available

[a] MPL of Cd and Pb for *S. pilchardus* according to EC (2005)

[b] Mean metal levels in muscle tissues of the species studied (mg kg^{-1} w.w.)

Table 6 The estimated daily and weekly intake of metals by consumption of *S. solea*, *M. barbatus*, and *S. pilchardus* by adult people in Mersin, Turkey

Metal	PTWI[a]	PTWI[b]	PTDI[c]	*S. solea* EWI[d] (EDI[e])	*M. barbatus* EWI[d] (EDI[e])	*S. pilchardus* EWI[d] (EDI[e])
Cr^{+3}	10500[x]	735,000	105,000	< 0.14 (0.02)	215.6 (30.8)[w]	105 (15)[w]
Cr^{+6}	21[x]	1470	210	< 0.14 (0.02)	215.6 (30.8)[w]	105 (15)[w]
Mn	980[x]	68,600	9800	158.2 (22.6)	46.2 (6.6)	98 (14)
Fe	5600[t]	392,000	56,000	1892.8 (270.4)	1456 (208)	1404.2 (200.6)
Ni	140[x]	9800	1400	36.4 (5.2)	19.6 (2.8)	21 (3)
Cu	3500[t]	245,000	35,000	68.6 (9.8)	100.8 (14.4)	49 (7)
Zn	7000[t]	490,000	70,000	3301.2 (471.6)	2396.8 (342.4)	1645 (235)
As[y]	2.1[x]	147	21	30.08 (4.29)[z]	50.17 (7.16)[z]	14.89 (2.12)[z]
Cd	7[t]	490	70	< 0.05 (0.007)	< 0.05 (0.007)	< 0.05 (0.007)
Sn	14000[t]	980,000	140,000	215.6 (30.8)	74.2 (10.6)	42 (6)
Pb	25[t]	1750	250	67.2 (9.6)	22.4 (3.2)	127.4 (18.2)

[a] Provisional permissible tolerable weekly intake (PTWI) in μg/week/kg body weight

[b] PTWI for 70 kg adult person (μg/week/70 kg body weight)

[c] PTDI, permissible tolerable daily intake (μg/day/70 kg body weight)

[d] EWI, estimated weekly intake in μg/week/70 kg body weight

[e] EDI, estimated daily intake in μg/day/70 kg body weight

[x] EPA recommends RfD for each metal

[t] (FAO/WHO 2004)

[y] PTWI for inorganic arsenic

[w] Chromium concentrations in tissue samples were calculated assuming total Cr^{+3} or total Cr^{+6}

[z] Arsenic concentrations determined as total arsenic and 3.5 conversation factor used for inorganic arsenic conversation (Panel, 2009)

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