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Heavy Metal Contaminants in Tissues of the Garfish, *Belone belone* L., 1761, and the Bluefish, *Pomatomus saltatrix* L., 1766, from Turkey Waters

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Abstract Levels of contaminants in fish are of particular interest because of the potential risk to humans who consume them. Fish samples were collected through the coastal waters of Turkey and the contents of cadmium, cobalt, chrome, copper, iron, manganese, nickel, zinc and lead in the liver and muscle tissues were determined. Among the metals analyzed, copper, zinc and iron were the most abundant in the different tissues while cadmium and lead were the least abundant both in *Belone belone* and *Pomatomus saltatrix*. Metal concentrations in muscles of fish species were found 0.01–0.38 mg kg^{-1} for cadmium, 0.01–0.53 mg kg^{-1} for cobalt, 0.05–1.87 mg kg^{-1} for chromium, 0.21–5.89 mg kg^{-1} for copper, 9.99–43.3 mg kg^{-1} for iron, 0.14–1.33 mg kg^{-1} for manganese, 0.06–4.70 mg kg^{-1} for nickel, 0.09–0.81 mg kg^{-1} for lead, 3.85–15.9 mg kg^{-1} for zinc, respectively. Regional changes in metal concentration were observed in the tissues of both species, but these variations may not influence consumption advisories.

Keywords Metals · Fish · Turkish seas

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Turkey is surrounded by four different seas with 8333 km long coastal line and fishing is one of the biggest income sources for the country. The four seas around Turkey each reflect a different ecological character, salinity is 18 ppt the Black Sea, 23 ppt in the Marmara Sea, 32 ppt in the Aegean Sea and 38 ppt in the Mediterranean Sea (Türkmen et al. 2007). Over the last few decades the marine environment has been contaminated by persistent pollutants of agriculture and industrial origin. Heavy metal contamination has been identified as a concern in coastal environment, due to discharges from industrial wastes, agricultural and urban sewage. Heavy metals can be accumulated by marine organisms through a variety of pathways, including respiration, adsorption and ingestion (Zhou et al. 2001). The levels of heavy metal are known to increase drastically in marine environment through mainly anthropogenic activities. This result either with the complete extinction of some non tolerant species from these environments or they cause structural and functional damage to the organisms by interfering with their physiological and biochemical mechanisms. Biomonitors play an important role on in the assessment of the bioavailability of heavy metals in the marine environment. Fish are good indicators for the long term monitoring of metal accumulation in the marine environment. Therefore, numerous studies have been carried out on metal accumulation in different fish species (Andres et al. 2000; Tepe et al. 2007; Türkmen et al. 2005; Dural et al. 2007; Türkmen and Ciminli 2007). Many species of marine benthic fish have been shown to reflect ambient metal concentrations (Hornung and Ramelow 1987; Romeoa et al. 1999). The aim of this study was to determine the metal levels (Cd, Co, Cr, Cu, Fe, Mn, Pb, Ni and Zn) in tissues of the garfish, *B. belone*, and the bluefish, *P. saltatrix*, from the coastal water of Turkey, and to assessment for human consumption.

Materials and Methods

Fish samples were obtained from commercial fishing efforts of local fishermen along eight different stations in Turkish seas from December 2004 to July 2005. These sampling sites were coasts and offshore of Trabzon (TRB), coasts and offshore Sinop (SNP) and coasts and offshore Bartın (BRT) in the Black Sea; coasts and offshore Yalova (YLV) in the Marmara Sea; Çanakkale coast and offshore in northern Aegean Sea (NAS) and offshore and outer part of İzmir Bay in central Aegean Sea (CAS) in Aegean Sea, offshore and coasts of Antalya Bay (AB) and offshore and coasts of İskenderun Bay (IB) in Mediterranean Sea (Fig. 1). Samples (74 fish) collected during the sampling period were frozen and brought to laboratory on ice. Total body length and weight of the samples were measured to the nearest millimeter and gram prior to dissection. Approximately 1 g sample of muscle and entire liver from each fish were dissected, washed with distilled water, weighed, packed in polyethylene bags and stored at −18°C until chemical analysis.

Special care was taken to prevent metal contamination of the samples by the laboratory equipments, and tissues were dissected by plastic knife and all laboratory-ware was soaked in 2 M HNO_3 for 48 h, and rinsed five times with distilled water, and then five times with deionized water prior to use. All tissue samples were transferred into 100 mL Teflon beakers. There after, 10 mL ultrapure concentrated nitric acid was added slowly to the sample. The Teflon beaker was covered with a watch glass, and heated at 200°C on a hot plate for 3 h, until the solution evaporate slowly to near dryness. Two milliliters of 1 N HNO_3 was added to the residue and the solution was evaporated again on the hot plate. By repeating the additional digestion twice, all organic materials in each sample were completely digested. After cooling, 2.5 mL of 1 N HNO_3 was added to digested residue and was transferred to 25 mL volumetric flasks, then diluted to level with deionized water. Before analysis, the samples were filtered through a 0.45 μm nitrocellulose membrane filter. Sample blanks were prepared in the laboratory in a similar manner to the field samples (Alam et al. 2002). Metal contents were expressed as μg g^{-1} wet weight. All samples were analyzed three times for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Varian Model-Liberty Series II). Standard solutions were prepared from stock solutions (Merck, multi element standard). A Dorm-2 certified dogfish tissue was used as the calibration verification standard (Table 1). A logarithmic transformation was done on the data to improve normality. To test the differences between the concentrations in tissues of the samples from different sites, one way ANOVA was performed. Post hoc test (Duncan) was applied to determine statistically significant differences following ANOVA. The differences between the metal concentrations in tissues of two different species from same site were analyzed by t-test. All statistical calculations were performed with SPSS 13.0 for Windows.

Results and Discussion

Concentrations of nine elements in the muscle and liver of garfish, *B. belone* and bluefish, *P. saltatrix* from Turkish coastal waters are shown in Tables 2 and 3, respectively. Fe was highest in both muscle and liver of analyzed species in this study, followed by Zn. Regional differences in contamination of trace elements were examined using the garfish muscle of similar body size collected from six stations of Turkish coastal waters. The highest concentrations of Co, Cu and Mn were found in fish from BRT station among all the stations. Fe concentrations in garfish muscle were greater from SNP station. Also, Ni levels were higher in muscle of garfish collected from TRB, whereas

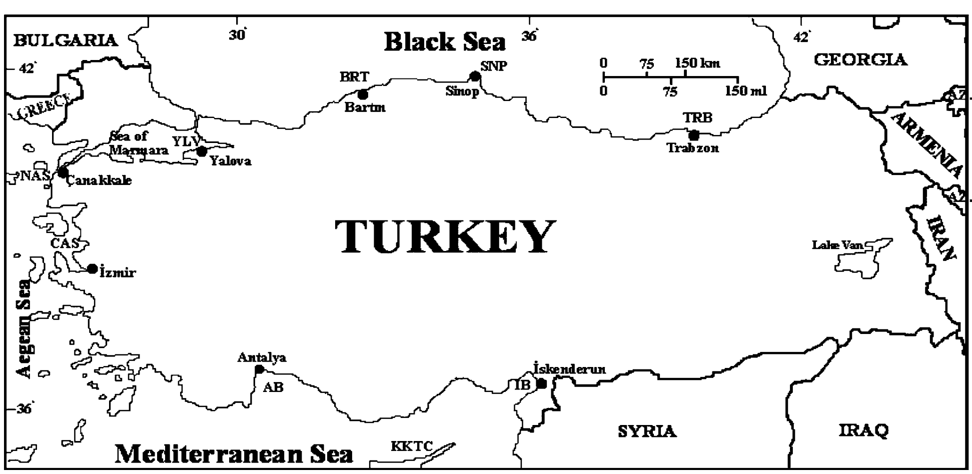

Fig. 1 The sampling locations from the coastal waters of Turkey (TRB: Trabzon, SNP: Sinop, BRT: Bartın, YLV: Yalova, NAS: northern Aegean Sea, CAS: central Aegean Sea, AB: Antalya Bay, IB: İskenderun Bay)

Table 1 Concentrations of metals found in certified reference material DORM-2 from the NRC (all data as means ± standard errors, in μg g^{-1} dry wt)

Value	Cd	Cu	Cr	Pb	Zn	Ni	Mn	Fe	Co
Certified	0.043	2.34	34.7	0.065	26.6	19.4	3.66	142	0.182
SE	0.008	0.16	5.5	0.007	2.3	3.1	0.34	10	0.031
Observed[a]	0.048	2.41	32.7	0.072	25.5	21.1	3.41	139	0.169
SE	0.011	0.31	6.533	0.015	3.72	3.69	0.63	14.4	0.039
Recovery (%)	112	103	94	110	96	109	93	98	93

[a] Each value is the average of eight determinations

all other metal levels in this station were no more than other stations. These results suggest that local sources of pollution for these elements may be present in Black Sea coastal areas of Turkey. On the contrary, Cr and Pb levels in garfish muscle and liver were greater in IB station, reflecting natural Cr ore. Differences among stations were also examined by using the metal concentrations of bluefish muscle. Zn and Cu concentrations were higher in bluefish from SNP station than other stations. Ni, Co and Cr concentrations in bluefish were higher in AB and IB compared with other stations. Fe and Mn concentrations in bluefish were not changed significantly station by station. The concentrations of several elements in the fish were significantly different among the species in each station. Compared within the same station, metal concentrations in the muscle of bluefish and garfish were different as follow; Mn in TRB samples, Co and Cu in SNP samples, Cr, Mn, Zn in BRT samples. Comparison were made between the level of metals in liver of two species within the same station and differences between Cd, Co, Zn levels in SNP, Cd, Co, Cu, Zn levels in BRT, Cd and Cu levels in IB were found significant ($p < 0.05$). Muscles and livers were chosen as target organs for assessing metal accumulation.

Cd levels found in muscles of fish in the present study ranged from 0.01 to 0.07 μg g^{-1} for garfish and from 0.01 to 0.38 μg g^{-1} for bluefish, respectively. Cd concentrations in the literature were between 0.09 and 0.48 μg g^{-1} in fish from middle Black Sea (Tüzen 2003), 0.02–0.37 μg g^{-1} for fish caught from Marmara, Aegean and Mediterranean seas (Türkmen et al. 2008). Our values were in agreement with literature. Co levels found in the present study ranged from 0.01 to 0.10 μg g^{-1} wet wt for garfish and from 0.03 to 0.53 μg g^{-1} for bluefish, respectively. In literature, Co levels were reported as <0.05 – 0.40 μg g^{-1} in fish from coastal waters of Black Sea (Topcuoğlu et al. 2002), 0.03–0.44 μg g^{-1} in fish from Turkish seas (Tepe et al. 2007). These Co levels were agreement with our results. On the other hand, Co levels were reported as 1.42 μg g^{-1} (Türkmen et al. 2005) and 0.73–1.91 μg g^{-1} (Türkmen et al. 2006) in fish from İskenderun Bay. Our Co levels were lower than them. Cr concentrations found in the present study ranged from 0.05 to 0.42 μg g^{-1} for garfish and from 0.06 to 1.87 μg g^{-1} for bluefish, respectively. Cr levels in literature were 0.26–0.82 μg g^{-1} for fish from Tuzla Lagoon in Mediterranean region (Dural et al. 2007), 0.10–1.60 μg g^{-1} for fish from Turkish seas (Tepe et al. 2007) and <0.06–0.84 μg g^{-1} for fish from coastal waters of Black Sea (Topcuoğlu et al. 2002). These reported Cr levels were agreement with our results. Cu levels found in the present study ranged from 0.21 to 5.89 μg g^{-1} for garfish and from 0.52 to 2.97 μg g^{-1} for bluefish, respectively. Cu levels in literature ranged from 1.01 to 4.54 μg g^{-1} for fish from coastal waters of Black Sea (Topcuoğlu et al. 2002), from 0.74 to 2.24 μg g^{-1} for fish from İskenderun Bay (Türkmen et al. 2006) and from 0.15 to 5.06 μg g^{-1} for fish from Turkish seas (Tepe et al. 2007). In general, these values reported in literature for Turkish seas were agreement our results.

Fe levels ranged from 9.99 to 43.3 μg g^{-1} for garfish and from 11.6 to 41.2 μg g^{-1} for bluefish, respectively. Fe levels for fish from Turkish seas were between 9.52–32.4 μg g^{-1} (Tüzen 2003), 30–60 μg g^{-1} (Topcuoğlu et al. 2002) and 7.46–40.1 μg g^{-1} (Türkmen et al. 2008). In general, these values were agreement our results. Mn concentrations ranged from 0.25 to 1.33 μg g^{-1} for garfish and from 0.14 to 0.85 μg g^{-1} for bluefish, respectively. Mn concentrations in fish from Turkish seas were between 0.69 and 3.56 μg g^{-1} (Topcuoğlu et al. 2002), 0.08–1.12 μg g^{-1} (Tepe et al. 2007) and 0.10–0.99 μg g^{-1} (Türkmen et al. 2008). Our findings were generally agreement with literature. Ni levels ranged from 0.06 to 0.92 μg g^{-1} for garfish and from 0.44 to 4.70 μg g^{-1} for bluefish, respectively. Ni levels in fish from Turkish seas were reported as <0.01–2.04 μg g^{-1} (Topcuoğlu et al. 2002), 2.90 μg g^{-1} (Türkmen et al. 2005), 0.66–1.59 μg g^{-1} (Türkmen et al. 2006) and 0.02–4.22 μg g^{-1} (Tepe et al. 2007), 0.01–2.78 μg g^{-1} (Türkmen et al. 2007). In general, these values reported in literature for Turkish seas were agreement our results. Pb concentrations ranged from 0.19 to 0.81 μg g^{-1} for garfish and from 0.09 to 0.62 μg g^{-1} for bluefish, respectively. Pb levels for fish in Turkish seas were reported as 0.22–0.85 μg g^{-1} (Tüzen 2003), 0.40–2.44 μg g^{-1} (Dural et al. 2007), 0.11–1.00 μg g^{-1} (Türkmen et al. 2007) and 0.33–0.86 μg g^{-1} (Türkmen et al. 2008). These reported Pb levels were generally agreement with our results. Zn concentrations in the muscles of fish ranged from 8.08 to 15.0 μg g^{-1} for garfish and from 3.85 to 15.9 μg g^{-1} for bluefish, respectively. Zn concentrations in fish from Turkish seas were 9.5–22.9 μg g^{-1} (Tüzen 2003), 3.20–8.03 μg g^{-1} (Türkmen et al. 2005), 8.27–76.9 μg g^{-1} (Dural et al. 2007) and 3.15–12.9 μg g^{-1} (Tepe et al. 2007). In general, these values reported in literature for Turkish seas were agreement our results.

Table 2 Mean metal levels with SE in the tissues of the garfish, *B. belone*, from the coastal waters of Turkey and comparison of different sites (μg g^{-1} wet wt)[a]

		Sites					
Met.	T.	TRB	SNP	BRT	YLV	CAS	IB
Cd	M.	0.02 ± 0.01^{a}	0.01 ± 0.00^{ab}	0.06 ± 0.02^{ab}	0.02 ± 0.01^{ab}	0.03 ± 0.01^{ab}	0.07 ± 0.03^{b}
	L.	0.04 ± 0.01^{a}	0.03 ± 0.00^{a}	1.13 ± 0.40^{b}	0.07 ± 0.01^{a}	0.09 ± 0.02^{a}	0.21 ± 0.05^{a}
Co	M.	0.04 ± 0.01^{ab}	0.08 ± 0.03^{ab}	0.10 ± 0.04^{b}	0.03 ± 0.01^{ab}	0.01 ± 0.00^{a}	0.05 ± 0.02^{ab}
	L.	0.23 ± 0.06^{a}	0.16 ± 0.03^{a}	0.65 ± 0.11^{b}	0.09 ± 0.02^{a}	0.14 ± 0.04^{a}	0.24 ± 0.10^{a}
Cr	M.	0.05 ± 0.03^{a}	0.12 ± 0.06^{a}	0.21 ± 0.09^{ab}	0.16 ± 0.04^{ab}	0.10 ± 0.02^{a}	0.42 ± 0.14^{b}
	L.	0.76 ± 0.15^{a}	0.39 ± 0.08^{a}	0.89 ± 0.21^{a}	0.42 ± 0.06^{a}	0.30 ± 0.12^{a}	5.01 ± 1.00^{b}
Cu	M.	0.80 ± 0.13^{a}	0.91 ± 0.09^{a}	5.89 ± 1.43^{b}	0.26 ± 0.07^{a}	0.21 ± 0.06^{a}	1.15 ± 0.11^{a}
	L.	1.41 ± 0.33^{a}	1.85 ± 0.67^{a}	34.3 ± 13.9^{b}	1.89 ± 0.64^{a}	2.03 ± 0.21^{a}	3.81 ± 0.65^{a}
Fe	M.	16.5 ± 3.61^{ab}	43.3 ± 16.3^{b}	20.2 ± 6.07^{ab}	9.99 ± 2.25^{a}	14.6 ± 3.53^{ab}	23.7 ± 5.95^{ab}
	L.	211 ± 44.8^{b}	72.1 ± 17.8^{a}	160 ± 33.9^{ab}	109 ± 27.1^{ab}	102 ± 7.44^{ab}	97.4 ± 20.9^{ab}
Mn	M.	0.41 ± 0.08^{a}	0.46 ± 0.09^{a}	1.33 ± 0.31^{b}	0.25 ± 0.09^{a}	0.39 ± 0.07^{a}	0.44 ± 0.09^{a}
	L.	1.45 ± 0.38^{a}	0.76 ± 0.25^{a}	9.18 ± 1.45^{b}	0.38 ± 0.13^{a}	1.04 ± 0.14^{a}	0.79 ± 0.17^{a}
Ni	M.	0.92 ± 0.18^{b}	0.44 ± 0.16^{a}	0.34 ± 0.12^{a}	0.06 ± 0.01^{a}	0.06 ± 0.02^{a}	0.12 ± 0.04^{a}
	L.	3.19 ± 0.61^{a}	4.20 ± 0.48^{a}	1.37 ± 0.16^{b}	0.12 ± 0.01^{b}	1.22 ± 0.37^{b}	1.04 ± 0.22^{b}
Pb	M.	0.26 ± 0.07^{a}	0.48 ± 0.13^{ab}	0.35 ± 0.10^{ab}	0.19 ± 0.03^{a}	0.30 ± 0.07^{a}	0.81 ± 0.28^{b}
	L.	0.82 ± 0.38^{a}	1.82 ± 0.81^{ab}	4.70 ± 0.70^{b}	0.35 ± 0.04^{a}	0.57 ± 0.04^{a}	2.43 ± 0.48^{b}
Zn	M.	8.08 ± 1.28^{a}	15.0 ± 1.58^{a}	13.1 ± 6.02^{a}	10.0 ± 1.14^{a}	9.91 ± 0.94^{a}	8.17 ± 1.06^{a}
	L.	26.0 ± 7.05^{a}	23.9 ± 6.58^{a}	136 ± 12.0^{b}	14.8 ± 2.92^{a}	30.7 ± 7.62^{a}	19.5 ± 4.13^{a}

[a] Horizontally, letters *a*, *b* and *c* show differences among sites. Means with the same letter are not statistically significant, $p > 0.05$ (Met.: Metal, T.: Tissue, M.: Muscle, L.: Liver, SE: Standard error)

Table 3 Mean metal levels with SE in the tissues of the bluefish, *P. saltatrix*, from the coastal waters of Turkey and comparison of different sites (μg g^{-1} wet wt)[a]

		Sites					
Met.	T.	TRB	SNP	BRT	NAS	AB	IB
Cd	M.	0.01 ± 0.00^{a}	0.03 ± 0.01^{a}	0.02 ± 0.00^{a}	0.01 ± 0.00^{a}	0.33 ± 0.05^{b}	0.38 ± 0.07^{a}
	L.	0.06 ± 0.02^{a}	0.09 ± 0.03^{a}	0.14 ± 0.04^{a}	0.03 ± 0.01^{a}	0.80 ± 0.11^{b}	0.77 ± 0.12^{b}
Co	M.	0.03 ± 0.01^{a}	0.21 ± 0.05^{ab}	0.03 ± 0.00^{a}	0.04 ± 0.01^{a}	0.53 ± 0.10^{c}	0.42 ± 0.07^{bc}
	L.	0.15 ± 0.06^{a}	0.46 ± 0.14^{abc}	0.21 ± 0.05^{ab}	0.11 ± 0.04^{a}	0.84 ± 0.08^{bc}	0.88 ± 0.06^{c}
Cr	M.	0.21 ± 0.03^{a}	0.18 ± 0.04^{a}	0.07 ± 0.02^{a}	0.06 ± 0.01^{a}	1.82 ± 0.42^{b}	1.87 ± 0.15^{b}
	L.	1.03 ± 0.05^{b}	0.30 ± 0.08^{a}	0.68 ± 0.17^{b}	0.14 ± 0.05^{a}	2.86 ± 0.32^{c}	3.69 ± 0.43^{d}
Cu	M.	0.52 ± 0.13^{a}	2.97 ± 0.47^{b}	1.58 ± 0.31^{ab}	0.68 ± 0.10^{a}	0.69 ± 0.18^{a}	0.22 ± 0.08^{a}
	L.	2.59 ± 1.11^{a}	7.60 ± 2.15^{a}	2.85 ± 0.52^{a}	3.57 ± 0.21^{a}	1.67 ± 0.48^{a}	0.59 ± 0.07^{a}
Fe	M.	41.2 ± 5.86^{a}	40.3 ± 8.67^{a}	33.4 ± 5.67^{a}	11.6 ± 2.78^{a}	25.4 ± 5.22^{a}	13.4 ± 2.17^{a}
	L.	206 ± 31.3^{b}	124 ± 27.3^{ab}	238 ± 26.8^{b}	151 ± 35.5^{ab}	123 ± 21.4^{ab}	43.3 ± 7.13^{a}
Mn	M.	0.20 ± 0.03^{a}	0.80 ± 0.21^{a}	0.31 ± 0.08^{a}	0.14 ± 0.04^{a}	0.62 ± 0.07^{a}	0.85 ± 0.09^{a}
	L.	1.01 ± 0.04^{a}	1.59 ± 0.41^{a}	1.48 ± 0.35^{a}	1.34 ± 0.14^{a}	1.49 ± 0.19^{a}	1.94 ± 0.43^{a}
Ni	M.	0.60 ± 0.16^{a}	0.57 ± 0.19^{a}	0.44 ± 0.16^{a}	0.80 ± 0.18^{a}	4.02 ± 0.71^{b}	4.70 ± 0.37^{b}
	L.	2.99 ± 0.61^{ab}	1.63 ± 0.42^{a}	4.02 ± 0.67^{b}	1.66 ± 0.40^{a}	8.13 ± 0.92^{c}	9.56 ± 1.07^{c}
Pb	M.	0.09 ± 0.03^{a}	0.36 ± 0.12^{ab}	0.11 ± 0.02^{a}	0.24 ± 0.11^{ab}	0.53 ± 0.13^{b}	0.62 ± 0.16^{b}
	L.	0.45 ± 0.12^{a}	0.72 ± 0.19^{a}	1.71 ± 0.51^{a}	0.90 ± 0.23^{a}	1.71 ± 0.48^{a}	1.43 ± 0.14^{a}
Zn	M.	3.85 ± 1.09^{a}	15.9 ± 2.38^{b}	6.93 ± 0.65^{a}	5.26 ± 1.55^{a}	8.33 ± 2.08^{a}	4.78 ± 0.81^{a}
	L.	19.3 ± 2.44^{ab}	24.5 ± 1.67^{b}	23.7 ± 2.76^{b}	18.1 ± 1.06^{ab}	20.9 ± 2.54^{ab}	12.2 ± 1.68^{a}

[a] Horizontally, letters *a*, *b* and *c* show differences among sites. Means with the same letter are not statistically significant, $p > 0.05$ (Met.: Metal, T.: Tissue, M.: Muscle, L.: Liver, SE: Standard error)

Trace element levels are known to vary in fish depending on various factors such as its habitat, feeding behavior and migration even in the same area (Romeoa et al. 1999; Andres et al. 2000; Anan et al. 2005). In the two fish species analyzed in this study, bluefish are migratory, pelagic species, feed voraciously on their prey, eating almost anything they can catch and swallow. Garfish is a pelagic, oceanodromous needlefish found in brackish and marine waters and feed on very small prey like, e.g. polyps. These species-specific characteristics may result in the variation of trace element accumulation between the species from Turkish coastal waters. Turkish acceptable limits for fish muscles are reported as Cd: 0.1, Cu: 20, Pb: 1.0 and Zn: 50 $\mu g\ g^{-1}$ (TKB 2002). Comparison of our data with the Turkish acceptable limits showed that our values for selected metals are lower than the guidelines (except Cd and Cr levels in bluefish from AB and IB). Therefore, except the levels of Cd and Cr in bluefish from AB and IB it can be concluded that these metals have posed no threat for consumption of garfish and bluefish for time span of these.

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