Bull Environ Contam Toxicol (2009) 82:601–604
DOI 10.1007/s00128-008-9624-1

Levels of Heavy Metals in Some Commercial Fish Species Captured from the Black Sea and Mediterranean Coast of Turkey

Cemal Turan · Meltem Dural · Abdullah Oksuz · Bayram Öztürk

Received: 26 March 2008 / Accepted: 26 November 2008 / Published online: 11 December 2008

Abstract The distribution of some heavy metals in the muscle tissue of *Merlangius merlangus* (whiting), *Mullus barbatus* (red mullet), *Engraulis encrasicholus* (anchovy) from Black and Mediterranean Seas were studied. The highest Al (95.313 μg/g dw), Mn (1.390 μg/g dw), Zn (25.416 μg/g dw) concentration was detected in *E. encrasicholus* from Black Sea; the highest Li (3.200 μg/g dw) concentration was detected in *E. encrasicholus* from Mediterranean Sea; the highest Cd (1.685 μg/g dw) concentration was detected in *M. merlangus* from Mediterranean Sea; the highest Ni (1.363 μg/g dw) concentration was detected in *M. merlangus* from Black Sea; the highest Pb (0.727 μg/g dw) concentration was detected in *M. barbatus* from Black Sea and the highest Cr (1.893 μg/g dw), Fe (21.901 μg/g dw) concentration was detected in *M. barbatus* from Mediterranean Sea.

Keywords Black Sea · Mediterranean Sea · Demersal and pelagic fish · Bioaccumulation · Metals

In aquatic ecosystems, fish integrate and reflect the effects of numerous interacting biotic and abiotic factors. Anthropogenic stresses such as metal contaminants adversely affect fish, which are typically subjected to numerous stressors, including unfavorable or fluctuating temperature, high water velocities, elevated sediment metal loads, low dissolved oxygen concentrations, limited food availability, and other types of episodic variables. These factors individually or together can impose considerable stress on physiological systems of fish and impair their health or condition (Wedemeyer et al. 1990).

Heavy metals like copper, zinc and iron are essential for fish metabolism while some others such as mercury, cadmium and lead have no known role in biological systems. For the normal metabolism of fish, the essential metals must be taken up from water, food or sediment. However, similar to essential metals, non-essential ones are also taken up by fish and accumulated in their tissues. They are natural trace components of the aquatic environment, but their levels have increased due to industrial, agricultural and mining activities. All heavy metals are potentially harmful to aquatic organisms at some level of exposure and absorption. Their presence in some marine environments has increased to some levels, which threaten the health of aquatic and terrestrial organisms, man included (Kalay and Canli 2000).

Contaminants such as metals are introduced into the Black and Mediterranean Seas through rivers or direct discharge of industrial wastes, agricultural and municipal usages. For example, the metal levels in the Black Sea have increased due to oil pollution and airborne contaminants; about 60% of the petroleum hydrocarbons in the Black Sea coast of Turkey came from spill and discharges related to marine transportation and balast wastes in hundreds barrels that had been dumped irresponsibly by foreign ships during the period of 1980 and 1995 (Topçuoglu et al. 1990).

This study has very important tasks; first compare demersal (red mullet, whiting) and pelagic fish (anchovy) simultaneously for heavy metal accumulation and compare the Mediterranean and Black Sea on the same fish species. The objective of this study was also to determine the differences in concentrations of Al, Pb, Cr, Li, Ni, Cd

C. Turan · M. Dural (✉) · A. Oksuz
Fisheries Faculty, Mustafa Kemal University,
31200 Iskenderun, Hatay, Turkey
e-mail: duralmeltem@yahoo.com

B. Öztürk
Fisheries Faculty, Istanbul University, Istanbul, Turkey

(nonessential metals) and Mn, Zn and Fe (essential metals) in the muscle tissue of the whiting, anchovy and red mullet with respect to site and species. *E. encrasicholus* and *M. merlangus* from Mediterranean Sea were studied for the first time in the present study.

Materials and Methods

Anchovy (*Engraulis encrasicholus*), red mullet (*Mullus barbatus*) and whiting (*Merlangius merlangus*) samples were caught by fishermen's nets in 2005 from Black and Mediterranean Seas (Fig. 1). The sampling sites are selected near the industrial areas (Near to Istanbul city and Iskenderun Bay). Ten fish of each species from each location were used for the analysis. Fish samples were transported to the laboratory in a thermos flask with ice. Total size and weight of fishes were measured and given in Table 1. Approximately 2 g of the epaxial muscle on the dorsal surface of fish from each sample were dissected, washed with distilled water, dried in filter paper, weighed, packed in polyethylene bags and kept at −22°C until analysis. The sample preparation and analysis were carried out according to the procedure described by UNEP reference methods (1984). The tissues digested with concentrated nitric acid and percholoric acid (2:1, v/v) at 60°C for 3 days. All samples were diluted with bidistilled water and assayed using ICP-AES (Varian model-Liberty Series II). All digested samples were analyzed three times for each metal. The standard addition method was used to correct for matrix effects. Instrument was calibrated with standard solutions prepared from commercial materials. Analytical blanks were run in the same way as the samples and determined using standard solutions prepared in the same acid matrix. Standard solution was prepared from stock standard solution of metals. All chemicals and standard solutions used in this study were of analytical grade. The metal concentration in tissue was recorded as μg metal/g dry weight. The accuracy of analytical procedure was checked by analyzing the standard reference materials (National Research Council of Canada; dogfish muscle and liver) DORM2 and DOLT2 in three replicates for each batch of fish samples digested. Recovery rates ranged from 93% to 100% for all investigated elements. The detection limits were as follows: 0.001 ppm for Cd, 0.0046 ppm for Fe, 0.0014 ppm for Mn, 0.0042 ppm for Pb, 0.0059 ppm for Zn, 0.001 ppm for Cr, 0.008 ppm for Ni.

Table 1 Average wet weights and total length of fishes used in this study

Species	Locations	n	$L \pm SD$	$W \pm SD$
Merlangius merlangus	Mediterranean Sea	10	23.5	180.5
	Black Sea	10	22.8	175.6
Mullus barbatus	Mediterranean Sea	10	12.3	35.5
	Black Sea	10	11.5	30.3
Engraulis encrasicholus	Mediterranean Sea	10	10.6	15.6
	Black Sea	10	11.7	17.6

L: mean length; *W*: mean weight; SD: standard deviation

Statistical analysis of data was carried out using SPSS statistical package programs. One-way analysis of variance tests was conducted on each metal to test for significant differences between sites. Data showed normal distribution or close to normal distribution, and therefore no transformation were done for statistical analyses.

Results and Discussion

The highest Al (95.313 μg/g dw), Mn (1.390 μg/g dw), Zn (25.416 μg/g dw) concentration were detected in *E.*

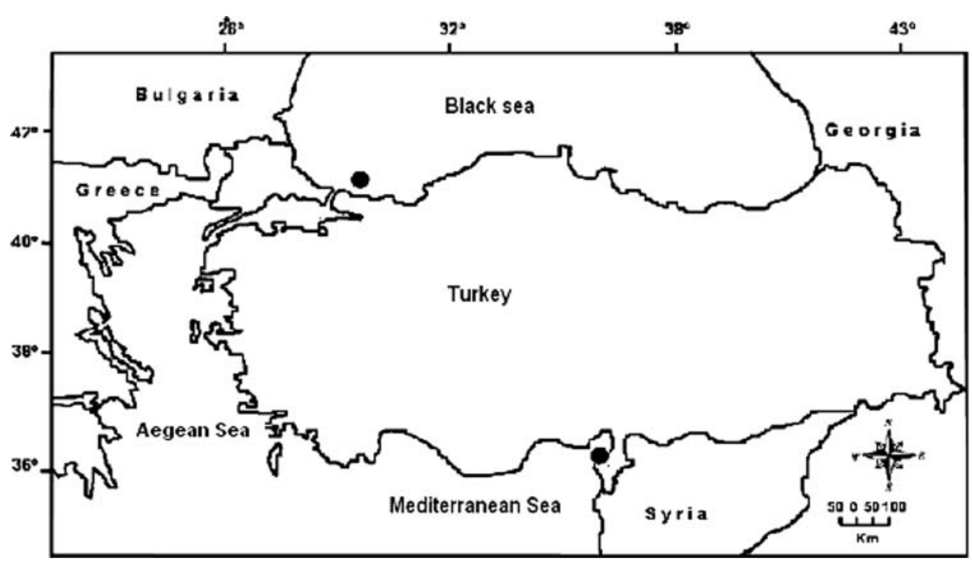

Fig. 1 The map of sampling locations. Black dots indicate sampling locations

encrasicholus from Black Sea; the highest Li (3.200 µg/g dw) concentration was detected in *E. encrasicholus* from Mediterranean Sea; the highest Cd (1.685 µg/g dw) concentration was detected in *M. merlangus* from Mediterranean Sea; the highest Ni (1.363 µg/g dw) concentration was detected in *M. merlangus* from Black Sea; the highest Pb (0.727 µg/g dw) concentration was detected in *M. barbatus* from Black Sea, the highest Cr (1.893 µg/g dw) and Fe (21.901 µg/g dw) concentration were detected in *M. barbatus* from Mediterranean Sea (Table 2). Muscle, generally, accumulated the lowest levels of metals in two regions. The results showed that metal accumulation in the Black Sea was higher than Mediterranean for *M. merlangus* except Cd and Li. Moreover, metal accumulation for *E. encrasicholus* was higher in the Mediterranean part than Black Sea part except Al, Pb, Mn and Zn. On the other hand, Al, Pb, Li, Zn accumulation for *M. barbatus* were higher in the Black Sea than Mediterranean. However Cd, Cr, Fe, Ni, Mn accumulation were higher in the Mediterranean Sea than that in Black Sea.

The concentrations of heavy metals expressed in µg metal/g dry weight in muscle of *M. merlangus*, *M. barbatus*, *E. encrasicholus* are summarized in Table 2. Significant differences ($p < 0.05$) in the accumulation levels of metals for these species were observed between Mediterranean and Black Seas. The detected differences were in *M. merlangus* for Cd, Fe, Li; and in *E. encrasicholus* for Al, Pb, Li, Mn, Zn; and in *M. barbatus* for Zn.

The fish production of Turkey from Black Sea in 1995 was 442,000 tones annually. More than 80% of this catch represent anchovy. The heavy metal concentrations in several fish species in the Black Sea region were given for the period of 1997–1998 (Topçuoğlu 2000). The metal contents ranges in the Black Sea fish are follows: Cd, 0.1–0.2; Cr, 0.2–0.3; Ni, <0.01; Zn, 26–30; Fe, 30–32; Mn, 0.5–0.7 and Pb, 0.3–1.4 µg/g. The ranges of all metal concentrations are generally higher in our study. At the same time, the heavy metal concentrations in red mullet collected from Marmara Sea are higher than the study by Topçuoğlu et al. (2003). The heavy metal levels in anchovy and whiting in the Black Sea have been investigated during the 1997–1998 by Topçuoğlu et al. (2002). The range of metal concentrations were as follows: Cd, 0.10–0.15 for anchovy and <0.02 for whiting; Cr, 0.33–0.76 for anchovy and <0.06 for whiting; Ni, <0.01–2.04 for anchovy and <0.01 for whiting; Zn, 35.7–44.2 for anchovy and 30.2–43.1 for whiting; Fe, 37.0–61.0 for anchovy and 46.0–57.0 for whiting; Mn, 1.81–2.99 for anchovy and 2.22–3.56 for whiting. Much lower concentrations of metals were found of the Turkish Black Sea region in the present study.

The heavy metal concentrations in several fish species from the Mamaia Bay of the Romanian Black Sea sector were determined by Bologa et al. (1988). The ranges of metal concentrations were as follows: Mn, 4.47–5.85; Fe, 52.86–66.18; Cu, 12.24–17.86; Cd, 13.62–16.77 and Pb, 4.01–5.56 mg g^{-1} (dry wt). Fairly lower concentrations of all metals were found at the stations of the Turkish Black Sea region in the present study.

Iskenderun Bay is situated on the eastern Mediterranean coast of Turkey (36°20′N–35°30′ E; 36°50′N–35°00′E). In

Table 2 The mean concentrations and standard deviation of metals in the muscle of *M. merlangus, M. barbatus, E. encrasicholus* captured from Mediterranean Sea and Black Sea

Metal	Locations	Fish species		
		M. merlangus	*E. encrasicholus*	*M. barbatus*
Al	Mediterranean Sea	84.816 ± 7.841	24.753 ± 4.799a	8.384 ± 1.020
	Black Sea	86.301 ± 11.772	95.313 ± 18.270b	9.850 ± 1.439
Pb	Mediterranean Sea	0.426 ± 0.191	0.055 ± 0.019a	0.559 ± 0.164
	Black Sea	0.502 ± 0.104	0.329 ± 0.302b	0.727 ± 0.141
Cd	Mediterranean Sea	1.685 ± 0.124a	0.183 ± 0.026	0.494 ± 0.183
	Black Sea	0.192 ± 0.020b	0.124 ± 0.018	0.208 ± 0.017
Cr	Mediterranean Sea	0.105 ± 0.061	0.241 ± 0.066	1.893 ± 0.470
	Black Sea	0.144 ± 0.050	0.074 ± 0.020	1.055 ± 0.289
Fe	Mediterranean sea	6.749 ± 0.832a	21.369 ± 2.573	21.901 ± 0.420
	Black Sea	4.488 ± 0.441b	18.008 ± 2.697	21.272 ± 1.476
Li	Mediterranean Sea	2.579 ± 0.136a	3.200 ± 0.246a	3.027 ± 0.048
	Black Sea	3.061 ± 0.152b	2.933 ± 0.351b	3.120 ± 0.095
Mn	Mediterranean Sea	0.033 ± 0.016	0.529 ± 0.137a	0.103 ± 0.047
	Black Sea	0.079 ± 0.024	1.390 ± 0.326b	0.005 ± 0.018
Ni	Mediterranean Sea	1.044 ± 0.337	0.559 ± 0.191	0.663 ± 0.354
	Black Sea	1.363 ± 0.500	0.348 ± 0.106	0.658 ± 0.333
Zn	Mediterranean Sea	5.288 ± 0.405	14.062 ± 1.967a	5.870 ± 0.233a
	Black Sea	6.029 ± 0.545	25.416 ± 3.664b	7.573 ± 0.389b

Results of statistical differences from Mediterranean to Black Sea are indicated and total mean concentrations of metals in muscle tissue for each species are also given. Different online alphabets in columns are significantly different from each other ($p < 0.05$)

this area, there are large quantities of untreated industrial and domestic sewage. This bay has one of the most polluted coastal waters of Turkey, and also has high economic importance for fishery. Two of the most important fish species by consumers, in Turkey, are *Mugil cephalus* and *Trachurus mediterraneus*. The heavy metal concentrations in several fish species from the Iskenderun Bay of the Mediterranean Sea were determined by Yılmaz (2003). The range of metal concentrations were as follows: Fe, 41.84–70.28; Ni, 0.94–1.22; Cr, 1.28–1.46; Pb, 1.03–7.45; Zn, 19.55–38.23 (wet wt). Lower concentrations of all metals (except Ni and Cr) were found in our study. Concentrations of some heavy metals in *Mugil* sp. and *Sparus aurata* have been reported for the Iskenderun Bay (Kargın 1996). The range of metal concentrations were as follows: Fe, 30.7–43.2; Cd, 4.1–7.6; Pb, 14.0–24.6; Zn, 20.8–32.2 for *Sparus aurata*; Fe, 40.4–57.2; Cd, 5.4–10.2; Pb, 19.4–28.5; Zn, 26.6–39.2 for *Mugil sp.* Kargın stated that due to variations in feeding habits and behaviors of species, the levels of metals found in tissues of the benthic *Mullus barbatus* were always higher than those found in pelagic *Sparus aurata* throughout the year. The ranges of all metal concentrations are lower for the studied fish species in our study.

When considering the metal content in marine organisms, suitable for human consumption, the most important aspect is their toxicity to humans. The limit value for cadmium in the edible part of fish, proposed by the European Commission (Commission of the European Communities 2001), is 0.1 µg/g wet weights. In this context, none of the fish samples analyzed presented concentrations exceeding the proposed limits by the European Directive. Furthermore, they were far below the permissible limits for human consumption. Moreover, comparisons with the Canadian food standards (Cu: 100 µg/g; Zn: 100 µg/g), Hungarian standards (Cu: 60 µg/g; Zn: 80 µg/g) and Australian accepted limits (Cu: 10 µg/g; Zn: 150 µg/g) demonstrate that the content of these metals in the edible part of the examined fish is lower than the guidelines above mentioned. Turkish legislation establishes maximum levels for four of the metals studied. The limit is not accepted above 0.1 mg/kg for Cd, 1.0 mg/kg for Pb, 20.0 mg/kg for Cu, 50 mg/kg for Zn for human consumption. Food and Agricultural Organization limits for Cd and Pb is 0.5 mg/kg, and is 30 mg/kg for Cu and Zn. The concentrations of these metals measured in the muscle of the three species studied generally were lower than the levels issued by FAO and Turkish legislations. Consequently, it can be concluded that the levels of heavy metals in muscle are at acceptable levels for all of the studied samples in two regions. Only the Cd levels in all species from both Mediterranean and Black Seas and Pb levels in *M. merlangus* from Mediterranean Sea were higher than the acceptable values for human consumption designated by various health organisations.

Accumulating of heavy metals in fish muscle may be considered as an important warning signal for fish health and human consumption. The present study shows that precautions need to be taken in order to prevent future heavy metal pollution. Otherwise, these pollutions can be dangerous for fish and human health.

This situation may show that Mediterranean and Black Seas have been considerably affected from the sources of pollution. According to these results, detected heavy metal pollution threat these areas should be taking into consideration to protect the biodiversity and human health in this ecosystem.

Acknowledgments Thanks to Turkish Academy of Sciences (TUBA) for financial support.

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