Comparison of Metals in Tissues of Fish From Paradeniz Lagoon in the Coastal Area of Northern East Mediterranean

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Abstract Present study was performed to examined the metal concentrations in muscle, liver, gonad and gill of gilthead seabream, European seabass, Leaping mullet and Flathead grey mullet from Paradeniz Lagoon, Mediterranean coastal area. The metal concentrations found in muscle tissue varied for Fe: 2.3-51.4, Zn: 6.63-14.8, Cu: 0.38-1.10, Mn: 0.38-1.06, Cr: 0.34-1.13, Ni: 0.58-.074, Pb: 0.32-1.02, Cd: 0.20-0.67 and Co: 0.30-0.61 mg/kg wet weight. Iron showed the highest levels in all tissues, and generally followed by zinc. On the other hand, cadmium, cobalt and lead showed lower levels than other metals. Statistically significant differences were observed in the mean metal values obtained from investigated fish species and their tissues. The levels of metals in the examined fish were well below the regulatory values of various govermental agencies.

Because economically important sea foods such as fish, crabs, oysters and mussels accumulate contaminants from the aquatic environments, they have been extensively used in the assessment of aquatic pollution and monitoring studies (Türkmen et al. 2005, 2008; Tepe et al. 2008; Tuzen and Soylak 2009; Carneiro et al. 2011; Mutlu et al.

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2011). The coastal areas such as lagoon and bay in seas are important grounds for vital activities of valuable aquatic organisms such as crabs, fish, oysters and muscles. Because human activities directly affect these areas, contamination studies frequently should be made in these areas. Having economic importance for fisheries, Paradeniz Lagoon (36°17′24.02″N, 33°59′45.26″E) is situated in Silifke town of Mersin city on the coast of the northern east Mediterranean Sea where close by Mersin Bay. Approximate surface area of the lagoon is 492 ha with an average depth of 1.5 m. Heavy metals within coastal lagoons are an increasing concern because they have high phytotoxic effect and ability to change the primary productivity of the coastal environment (Lacerda 1994). Therefore, it is imperative to analyze metals within commercial species in assessing potential toxic levels from the human-nutritional standpoint (Vazquez et al. 1995). In general, metal accumulations in different tissues of the fishes show significant differences. For example, fish liver showed higher enrichment coefficients than gill and muscle (Türkmen et al. 2009, 2010; Kandemir et al. 2010). The aim of the study was to investigate the metal levels in different tissues of Mugil cephalus, Liza saliens, Sparus aurata and Dicentrarchus labrax collected from Paradeniz Lagoon and to assess whether these fish are acceptable for human

Materials and Methods

consumption.

Specimens were collected with various fishing methods by fishermen in autumn 2006 and spring 2007 from Paradeniz Lagoon, Mediterranean coastal area of Turkey (Fig. 1). Totally 101 fish specimens captured from the lagoon in sampling times were brought to the laboratory in ice chests.





Fig. 1 Paradeniz Lagoon (36°17'24.02"N, 33°59'45.26"E)

The measured mean lengths of the samples were 348 ± 7.0 mm for *Mugil cephalus* (25 samples), 292 ± 4.0 mm for *Liza saliens* (29 samples), 279 ± 5.0 mm for *Dicentrarchus labrax* (29 samples) and 179 ± 2.0 mm for *Sparus aurata* (18 samples).

Approximately 0.5 g sample of muscle, liver, gonad and gill each (the tissues of 2-5 samples were pooled when liver and gonad tissues were lesser than 0.5 g) from each fish were dissected, washed with distilled water, weighed, packed in polyethylene bags and stored at -18° C until the performance of chemical analysis. Dissected tissues were homogenized and digested with 10 mL of nitric acid (analytical grade) by using microwave oven as previously described (Türkmen et al. 2010). Then, residue was transferred to 25 mL volumetric flasks and diluted to level with deionized water. Before analysis, the samples were filtered through a 0.45 µm filter. Sample blanks were prepared in the laboratory in a similar manner to the field samples. All samples were analyzed three times for Fe, Mn, Ni, Cd, Co, Cr, Cu, Zn and Pb by ICP-OES, VARIAN VISTA-MPX OES. Detection limits were 0.001 for Cd and Pb, 0.002 for Cr and Mn, 0.02 for Cu and Ni, 0.3 for Fe and 0.2 for Zn. All metal concentrations were determined on wet weight basis as mg kg⁻¹. Standard solutions were prepared from stock solutions (Merck, multi element standard). A Dorm-2 certified dogfish tissue was used as the calibration verification standard. Recoveries are 111 for Cd, 104 for Cu and Ni, 95 for Cr, 98 for Fe, 97 for Mn and Zn, 106 for Pb and 93 for Co in percent. Extractions and analyses of tissues were performed in the Food Quality Control Laboratory of Hatay. One way ANOVA and Tukey multiple range test were performed to test the differences of the metal levels between species. All statistical calculations were performed with SPSS 13.0 for windows to Özdamar (1999).

Results and Discussion

The comparisons of the metal levels in tissues of the examined species from Paradeniz Lagoon are presented in Table 1. Iron had the highest concentrations in all tissues of examined species (except Zn in gonads of D. labrax). Second highest metal was zinc after iron (except Cu in livers of L. saliens and D. labrax, and Mn in gills of M. cephalus). Although cobalt levels in all tissues of L. saliens and S. aurata (except gonad) were higher than Cd, Co levels in all tissues of D. labrax and M. cephalus were lower than Cd. The differences between accumulations in species were statistically significant for cadmium, cobalt, chromium and manganese in muscles, for cadmium, cobalt, chromium copper and zinc in livers, for cadmium, cobalt, chromium, iron, manganese and zinc in gills, and for cobalt, chromium and copper in gonads (p < 0.05). In general, levels in livers were higher than those in muscles (except chromium for L. saliens, chromium, nickel and lead in D. labrax), especially for copper, iron and zinc were very high. Also, levels in gills and gonads were generally higher than those in muscles. Similar situations were reported many researchers (Kalay et al. 1999; Çoğun et al. 2005; Türkmen and Ciminli 2007; Tepe et al. 2008; Türkmen et al. 2010).

While the lowest metal levels were generally observed in *S. aurata* for muscles, livers and gills, and in *M. cephalus* for gonads, the highest metal levels were generally observed in *D. labrax* for muscles, gills and gonads, and in



Table 1 Mean metal levels (mg kg $^{-1}$ wet weight \pm SE) in tissues of fish from Paradeniz Lagoon and comparison of the species

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Tis./sp.*	Iron	Zinc	Copper	Manganese	Chromium	Nickel	Lead	Cadmium	Cobalt
Muscle									
L. saliens	51.4 ± 6.96	14.8 ± 5.89	1.10 ± 0.16	$1.00\pm0.15^{\rm a}$	$0.95\pm0.15^{\rm b}$	0.60 ± 0.07	0.52 ± 0.10	0.48 ± 0.06^{a}	$0.50\pm0.05^{\rm ab}$
D. labrax	42.2 ± 5.20	8.53 ± 1.35	0.83 ± 0.05	$1.06\pm0.07^{\rm a}$	$1.13 \pm 0.07^{\rm b}$	0.74 ± 0.02	1.02 ± 0.27	$0.67 \pm 0.01^{\rm a}$	$0.61 \pm 0.01^{\rm b}$
M. cephalus	34.8 ± 3.42	6.63 ± 0.70	1.08 ± 0.20	$0.86\pm0.05^{\mathrm{ab}}$	$0.71\pm0.05^{\mathrm{ab}}$	0.61 ± 0.04	0.63 ± 0.17	$0.49 \pm 0.05^{\rm b}$	0.41 ± 0.06^{ab}
S. aurata	23.4 ± 1.13	7.24 ± 0.39	0.38 ± 0.06	$0.38 \pm 0.07^{\rm b}$	$0.34\pm0.10^{\mathrm{a}}$	0.58 ± 0.12	0.32 ± 0.03	$0.20\pm0.05^{\rm b}$	$0.30 \pm 0.04^{\rm a}$
Liver									
L. saliens	205 ± 26.3	$28.2\pm2.35^{\rm a}$	$69.9 \pm 12.8^{\rm a}$	2.23 ± 0.44	0.94 ± 0.09^{a}	0.87 ± 0.09	0.82 ± 0.18	$0.63 \pm 0.08^{\rm a}$	0.91 ± 0.12^{a}
D. labrax	139 ± 14.6	25.3 ± 1.81^{ab}	$46.0\pm9.52^{\rm ab}$	1.46 ± 0.09	$1.02 \pm 0.04^{\rm a}$	0.73 ± 0.02	0.42 ± 0.06	$0.74 \pm 0.03^{\rm a}$	0.62 ± 0.01^{ab}
M. cephalus	112 ± 22.6	17.8 ± 1.20^{b}	$13.1 \pm 3.85^{\mathrm{b}}$	1.50 ± 0.19	$0.84\pm0.08^{\rm a}$	0.86 ± 0.06	0.88 ± 0.22	0.62 ± 0.07^{ab}	0.53 ± 0.08^{ab}
S. aurata	102 ± 14.1	$17.5\pm0.97^{\rm b}$	$6.59 \pm 2.12^{\mathrm{b}}$	1.36 ± 0.37	$0.35\pm0.08^{\mathrm{b}}$	1.59 ± 0.43	0.68 ± 0.10	$0.27\pm0.06^{\mathrm{b}}$	$0.45 \pm 0.03^{\rm b}$
Gill									
L. saliens	$107 \pm 9.07^{\rm a}$	$13.6\pm1.30^{\rm a}$	2.25 ± 0.37	$3.22 \pm 0.43^{\rm a}$	1.09 ± 0.13^{a}	0.75 ± 0.06	0.73 ± 0.10	$0.48\pm0.06^{\rm ab}$	0.64 ± 0.07^{ab}
D. labrax	66.0 ± 3.78^{ab}	22.4 ± 0.99^{b}	1.68 ± 0.11	$3.11\pm0.15^{\rm a}$	1.34 ± 0.08^{a}	0.90 ± 0.03	0.49 ± 0.07	$0.75\pm0.02^{\rm a}$	$0.69 \pm 0.03^{\rm a}$
M. cephalus	$80.3 \pm 9.45^{\mathrm{ab}}$	$12.0\pm0.80^{\rm a}$	1.14 ± 0.11	$13.0 \pm 2.23^{\rm b}$	$0.88 \pm 0.07^{\mathrm{ab}}$	0.87 ± 0.09	0.54 ± 0.06	$0.52\pm0.05^{\rm ab}$	0.46 ± 0.07^{ab}
S. aurata	60.4 ± 7.22^{b}	$16.3 \pm 1.31^{\rm b}$	1.12 ± 0.08	$4.76 \pm 0.43^{\rm a}$	$0.41 \pm 0.10^{\mathrm{b}}$	1.35 ± 0.31	0.45 ± 0.05	$0.26 \pm 0.07^{\rm b}$	$0.34 \pm 0.05^{\rm b}$
Gonad**									
L. saliens	88.2 ± 10.6	15.9 ± 1.70	1.52 ± 0.19^{ab}	2.81 ± 0.57	$0.93\pm0.10^{\rm ab}$	0.71 ± 0.06	0.51 ± 0.08	0.49 ± 0.06	$0.58\pm0.07^{\rm a}$
D. $labrax$	72.0 ± 10.1	93.2 ± 7.38	$2.17\pm0.23^{\rm a}$	1.79 ± 0.25	$2.46 \pm 0.64^{\rm b}$	1.29 ± 0.14	0.70 ± 0.16	1.25 ± 0.17	$1.11\pm0.15^{\rm b}$
M. cephalus	61.7 ± 20.3	16.5 ± 1.92	$0.91\pm0.10^{\rm b}$	0.99 ± 0.11	$0.78\pm0.06^{\rm a}$	0.67 ± 0.04	0.57 ± 0.05	0.50 ± 0.05	$0.41\pm0.06^{\rm a}$

Vertically, letters a and b show differences among species for the same tissues (p < 0.05)

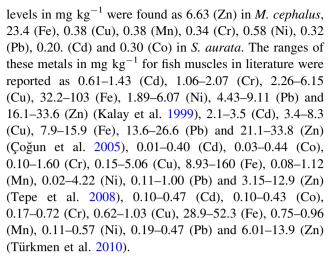
* Tis. tissues, Sp. species, ** insufficient gonad samples for S. aurata



L. saliens for livers. In gills, the highest levels in mg kg^{-1} were 107 (Fe), 2.25 (Cu) and 0.73 (Pb) in L. saliens, 22.4 (Zn), 1.34 (Cr), 0.69 (Co) and 0.75 (Cd) in D. labrax, 13.0 (Mn) in M. cephalus, 1.35 (Ni) in S. aurata. On the other hand, the lowest levels in mg kg⁻¹ were 0.75 (Ni) in L. saliens, 3.11 (Mn) in D. labrax, 12.0 (Zn) in M. cephalus, 60.4 (Fe), 1.12 (Cu), 0.41 (Cr), 0.45 (Pb), 0.26 (Cd) and 0.34 (Co) in S. aurata. The ranges of these metals in mg kg⁻¹ for fish gills in literature were reported as 2.19-3.70 (Cd), 3.20-8.82 (Cr), 7.1-17 (Cu), 173-299 (Fe), 8.1–15.8 (Ni), 15.6–22.4 (Pb) and 30.5–67.7 (Zn) (Kalay et al. 1999), 0.01-0.87 (Cd), 0.12-5.94 (Cu), 52.1-236 (Fe), 2.22-8.66 (Pb) and 15.1-53.9 (Zn) (Frias-Espericueta et al. 2010), 0.13-0.62 (Cd), 0.16-0.62 (Co), 0.35-1.01 (Cr), 1.68-5.08 (Cu), 69.3-119 (Fe), 1.61-4.56 (Mn), 0.18-0.68 (Ni), 0.42-0.68 (Pb) and 11.7-14.8 (Zn) (Türkmen et al. 2010). In gonads, the highest levels in mg kg $^{-1}$ were 88.2 (Fe) and 2.81 (Mn) in *L. saliens*, 93.2 (Zn), 2.17 (Cu), 2.46 (Cr), 1.29 (Ni), 0.70 (Pb), 1.25 (Cd) and 1.11 (Co) in D. labrax. On the other hand, the lowest levels in mg kg^{-1} were 15.9 (Zn), 0.51 (Pb) and 0.49 (Cd) in L. saliens, 61.7 (Fe), 0.91 (Cu), 0.99 (Mn), 0.78 (Cr), 0.67 (Ni) and 0.41 (Co) in M. cephalus. The ranges of these metals in mg kg⁻¹ for fish gonads in literature were reported as 0.094 (Cd), 0.197 (Co), 0.054 (Cr), 0.62 (Cu), 3.894 (Fe), 0.062 (Ni) and 101.8 (Zn) (Kandemir et al. 2010), 0.14-0.62 (Cd), 0.11-0.60 (Co), 0.38-1.12 (Cr), 1.79-3.72 (Cu), 45.4-114 (Fe), 1.37-6.29 (Mn), 0.12-0.95 (Ni), 0.41-0.54 (Pb) and 11.9-20.9 (Zn) (Türkmen et al. 2010), 0.79 (Cr), 0.85 (Cu), 41.5 (Fe), 0.52 (Mn), 0.22 (Ni) and 110 (Zn) (Carneiro et al. 2011).

In livers, maximum metal levels in mg kg $^{-1}$ were found as 205 (Fe), 28.2 (Zn), 69.9 (Cu), 2.23 (Mn) and 0.91 (Co) in *L. saliens*, 1.02 (Cr) and 0.74 (Cd) in *D. labrax*, 0.88 (Pb) in *M. cephalus*, 1.59 (Ni) in *S. aurata*. Minimum levels in mg kg $^{-1}$ were found as 102 (Fe), 17.5 (Zn), 6.59 (Cu), 1.36 (Mn), 0.35 (Cr), 0.27 (Cd) and 0.45 (Co) in *S. aurata*, 0.73 (Ni) and 0.42 (Pb) in *D. labrax*.

The ranges of these metals in mg kg⁻¹ for fish livers in literature were reported as 0.84–5.93 (Cd), 1.22–3.11 (Cr), 9.45–242 (Cu), 135–522 (Fe), 1.70–11.2 (Ni), 4.73–15.7 (Pb) and 27.3–76.2 (Zn) (Kalay et al. 1999), 5.9–13.7 (Cd), 20.8–260 (Cu), 236–363 (Fe), 33–62 (Pb) and 111–160 (Zn) (Çoğun et al. 2005), 0.06–0.69 (Cd), 0.06–0.53 (Co), 0.33–2.97 (Cr), 0.99–30.7 (Cu), 51.2–316 (Fe), 0.32–9.67 (Mn), 0.20–11.6 (Ni), 0.26–3.38 (Pb) and 12.5–145 (Zn) (Türkmen et al. 2008), 0.03–1.13 (Cd), 0.09–0.88 (Co), 0.14–5.01 (Cr), 0.59–34.3 (Cu), 43.3–238 (Fe), 0.38–9.18 (Mn), 0.12–9.56 (Ni), 0.35–4.70 (Pb) and 12.2–136 (Zn) (Türkmen et al. 2009). In muscles, maximum metal levels in mg kg⁻¹ were found as 51.4 (Fe), 14.8 (Zn) and 1.10 (Cu) in *L. saliens*, 1.06 (Mn), 1.13 (Cr), 0.74 (Ni), 1.02 (Pb), 0.67 (Cd) and 0.61 (Co) in *D. labrax*. Minimum



The daily and weekly intakes were estimated for fish species examined in this study (Table 2). The average daily fish consumption in Turkey is 20 g per person (FAO 2008). This is also equivalent to 140 g per person per week. The EWI (estimated weekly intake) and EDI (estimated daily intake) values presented in Table 2 were estimated as previously described (Türkmen et al. 2010). The EWI and EDI in this study are agreement with values reported for

Table 2 The comparison with recommended values and the estimated daily and weekly intakes of metal in muscles of fish species examined in this study

Metal	PTWI*	PTWI ^b	PTDI ^c	EWI ^d (EDI) ^e
Cd	7 ^a	490	70	93.8 (13.4)
Co	-	_	-	85.4 (12.2)
Cr	-	_	-	158.2 (22.6)
Cu	3500 ^a	245,000	35,000	154 (22)
Fe	5600 ^a	392,000	56,000	7,196 (1,028)
Ni	35 ^g	2,450	$350^{\rm f}$	103.6 (14.8)
Mn	980 ⁱ	68,600	$9,800^{h}$	148.4 (21.2)
Pb	25 ^a	1,750	250	142.8 (20.4)
Zn	7000 ^a	490,000	70,000	2,072 (296)

^{*} Provisional Tolerable Weekly Intake (PTWI) in $\mu g/\text{week/kg}$ body weight



^a (FAO/WHO 2004)

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

 $^{^{\}rm c}$ 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

f WHO recommends a TDI (Tolerable Daily Intake) of 5 μg/day/kg body weight, i.e. 350 μg/day for a 70-kg person (WHO 1993)

g Calculated for a week (µg/week/kg body weight)

 $^{^{\}rm h}$ EPA recommends a RfD (Reference Dose) of 0.14 mg/day/kg body weight, i.e. 9,800 μ g/day for a 70-kg person (EPA 2008)

ⁱ Calculated for a week (µg/week/kg body weight)

fish by Ikem and Egiebor (2005), Ikem and Egilla (2008), Türkmen et al. (2010). As can be seen in Table 2, the EWI and EDI values calculated for fish examined in present study were far below the recommended values (FAO/WHO 2004; WHO 1993; EPA 2008). The results of the this study supply valuable information about metal contents in tissues of the examined species from Paradeniz Lagoon and indirectly indicate the environmental contamination of the lagoon. Moreover, these results can also be used to understand the chemical quality of fish and to evaluate the possible risk associated with their consumption. Because PTWI and PTDI values estimated for examined fish and metals were far below the established values by FAO/ WHO (2004), WHO (1993), EPA (2008), it may be concluded that consumption of these species from this lagoon is not a problem on human health.

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