Bull Environ Contam Toxicol (2013) 90:702–707
DOI 10.1007/s00128-013-0978-7

Assessment of Heavy Metal Contamination in Various Tissues of Six Ray Species from İskenderun Bay, Northeastern Mediterranean Sea

Mustafa Türkmen · Yalçın Tepe · Aysun Türkmen · M. Kemal Sangün · Alpaslan Ateş · Ercüment Genç

Received: 3 October 2011 / Accepted: 7 March 2013 / Published online: 22 March 2013

Abstract This study was performed to investigate the heavy metal concentrations in muscle, liver, gill and intestine of six ray species from İskenderun Bay. The present study is the first for rays in İskenderun Bay, providing valuable preliminary information about heavy metal contents in different tissues of the examined ray species from the bay, and indirectly, indicating the environmental contamination of İskenderun Bay. Heavy metal levels in intestines were generally higher than those in other tissues for all species. Metal levels in ray muscle tissue were below the international maximum allowable levels for fish and fishery products, as well as Turkish national guidelines, with the exception of the highest value for Cd in *Dasyatis pastinaca*.

M. Türkmen (✉) · Y. Tepe
Department of Biology, Faculty of Science and Arts,
Giresun University, 28049 Giresun, Turkey
e-mail: mturkmen65@hotmail.com

A. Türkmen
Department of Chemistry, Faculty of Science and Arts,
Giresun University, 28049 Giresun, Turkey

M. Kemal Sangün
Department of Chemistry, Faculty of Science and Arts,
Mustafa Kemal University, 31000 Antakya, Hatay, Turkey

A. Ateş
Department of Maritime Transportation and Management
Engineering, Maritime School, Rize University,
53900 Derepezarı, Rize, Turkey

E. Genç
Fisheries and Aquaculture Department, Faculty of Agriculture,
Ankara University, Dışkapı, 06110 Ankara, Turkey

Keywords Ray · Heavy metal · Tissues · İskenderun Bay · Mediterranean Sea

İskenderun Bay is located in the eastern-most part of the Mediterranean Sea off southern Turkey (36°37′N 35°53′E). The coastal waters of the northeastern Mediterranean Sea serve as important ray fishing grounds; however, these waters have been significantly impacted by human activities (e.g., agricultural runoff, waste disposal, coastal development, shipping, commercial fishing, oil/gas exploration). Industries in this region of the Mediterranean Sea have been expanding, most of which discharge their sewage directly into river or the sea. This chemical pollution may be adversely affecting aquatic ecosystems, as well as human consumers of aquatic life. Wastewater collection and disposal systems have been planned and constructed in some areas, but these are still not sufficient in other areas due to limited budgets. Consequently, the bay serves as an ultimate sink for many pollutants. Since intense pollution in the bay has inevitably increased the levels of heavy metals in the water, it is important to determine the levels of heavy metals in water in order to evaluate the possible health risk of fish and other organisms.

Ray species inhabit the muddy and sandy bottoms of the bay, feeding on fish, zoobenthos, cephalopods and mollusks. Generally, polychaetes and crustaceans are important prey items of smaller individuals, while bony fishes become more important prey items of larger individuals. Ray species may be especially sensitive to pollution and other types of habitat degradation because they are demersal species and live on or near the bottom of the sea where chemical contaminants may accumulate. Because there is limited information on these ray species, this study is the first on metal levels in tissues of these species in İskenderun Bay.

Materials and Methods

A total 99 specimens of six ray species (Table 1) were collected with trawl by fishermen from December 2005 to December 2007 from İskenderun Bay (Fig. 1). Samples were brought to the laboratory in ice chests on sampling days. After total length and weight of the samples were measured, approximately 1 g sample of muscle, liver, gill and intestine (except *Dasyatis pastinaca*, no adequate intestine sample) from each fish was dissected, washed with distilled water, 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 (Merck, İstanbul, Turkey, analytical grade) in Teflon vessels by microwave oven, using the vessel procedure for fish tissues as previously described (Türkmen et al. 2009a). After cooling, the 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. Calibration standards were prepared from a multi-element standard (Merck, Darmstadt, Germany). A Dorm-2 certified dogfish tissue (Ontario, Canada) was used as the calibration verification standard. Percent recoveries were 109 for Cd and Pb, 105 for Cu, 97 for Cr, Fe and Co, 95 for Mn, 107 for Ni and Zn. All samples were analyzed (as mg kg^{-1} wet weight) three times for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn by ICP-AES (Varian Liberty Series-II, Mulgrave, Victoria, Australia). One way ANOVA and Duncan's multiple range test were performed to test the differences of the metal levels among species ($p < 0.05$).

Table 1 Mean length and weight of the species examined in the study (Mean ± SE)

Species	Station	Number	Length (cm)	Weight (g)
Dasyatis pastinaca (*R.c.*)	A	17	36.4 ± 1.06	270 ± 27.8
Raja miraletus (*R.m.*)	Y	15	32.9 ± 0.75	207 ± 13.6
Raja radula (*R.r.*)	Y	22	32.6 ± 0.77	202 ± 17.7
Gymnura altavela (*G.a.*)	Y	15	41.4 ± 1.09	1785 ± 130
Raja clavata (*R.c.*)	D	15	37.8 ± 1.31	287 ± 38.5
Pteromylaeus bovinus (*P.b.*)	K	15	65.9 ± 2.89	778 ± 115

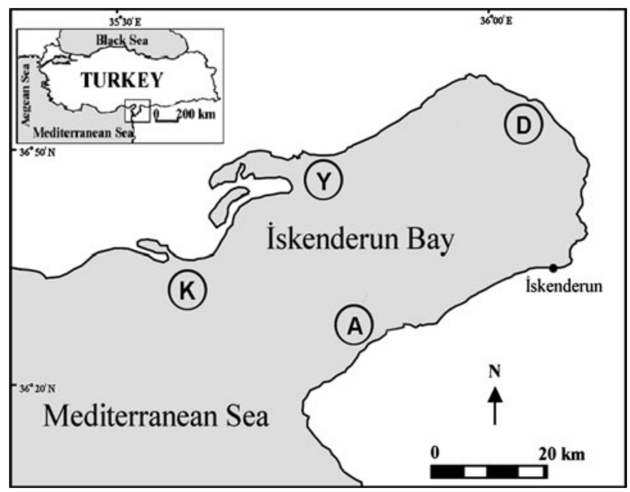

Fig. 1 İskenderun Bay (Sampling sites; K: Karataş offshore, Y: Yumurtalık Bay, D: Dörtyol offshore, A: Arsuz offshore)

Results and Discussion

Iron showed the highest concentrations in all tissues of the examined ray species, followed by Zn (Table 2). Metal concentrations in different tissues of the same species were significantly different ($p < 0.05$) for Cd, Co and Cr in *D.p.*, for Cu and Fe in all species, for Mn in other species except *P.b.*, and for Ni in *R.r., G.a.,* and *D.p*. On the other hand, when the same tissue was compared in different species, the differences were statistically significant for Cr, Fe and Ni in muscles, for Cr, Cu, Fe and Zn in livers, and for Cr, Cu and Mn in gills ($p < 0.05$). Heavy metal levels in intestines were generally higher than those in other tissues for all species. It was reported that levels in gut and intestine were higher than muscles (Huang 2003; Türkmen et al. 2008b; Ali et al. 2011). In addition, as reported by many researchers, liver metal levels in this study also were higher than muscle metal levels (Zauke et al. 1999; Endo et al. 2008; Türkmen et al. 2008a, b; Tepe et al. 2008; Tepe 2009; Türkmen et al. 2010).

In livers, minimum metal levels in mg kg^{-1} were 0.10 (Cd) in *R.c.*, 0.12 (Co), 1.11 (Cu), 8.58 (Zn) in *D.p.*, 0.44 (Cr), 0.85 (Mn) in *P.b.*, 71.6 (Fe), 0.64 (Pb) in *R.m.*, and 0.47 (Ni) in *G.a.* On the other hand, maximum metal levels in mg kg^{-1} were 0.25 (Cd), 1.70 (Mn) in *R.r.*, 0.48 (Co), 3.66 (Cu), 20.8 (Zn) in *R.m.*, 1.40 (Cr), 157 (Fe), 7.59 (Ni) in *D.p.*, and 1.20 (Pb) in *G.a.* Metal concentrations in mg kg^{-1} for livers in literature were reported as 0.509 (Cd), 1.98 (Cu), 0.026 (Pb) and 0.083 (Zn) for *Raja fyllae* (Mormede and Davies, 2001); <0.10–8.1 (Cd), 11–51 (Cu), <0.10 (Ni), <0.3 (Pb) and 13–58 (Zn) for three ray species (Zauke et al. 1999); 0.05–0.71 (Cd), 0.13–0.75 (Co), 0.56–1.84 (Cr), 3.35–51.1 (Cu), 82.6–270 (Fe), 0.47–2.38 (Mn), 1.07–3.06 (Ni), 0.71–2.88 (Pb) and 13.2–42.1 (Zn) for eight marine fish species from İskenderun Bay and 0.11–0.86 (Cd), 0.10–0.96 (Co), 0.65–2.71 (Cr), 1.56–19.9 (Cu), 54.2–279 (Fe), 0.80–2.94 (Mn), 1.55–6.09 (Ni), 0.69–1.18 (Pb) and 13.3–30.3 (Zn) for four marine fish

Table 2 Mean metal concentrations in tissues of six ray species

St.	Sp./Tis.	Mean metal concentrations with ± SE (mg kg^{-1} wet wt)*								
		Cadmium	Cobalt	Chromium	Copper	Iron	Manganese	Nickel	Lead	Zinc
Y	R.m									
	Ms.	0.06 ± 0.01^{ax}	0.10 ± 0.02^{ax}	0.24 ± 0.06^{bx}	1.36 ± 0.05^{ax}	44.4 ± 2.99^{bx}	0.50 ± 0.20^{ax}	0.22 ± 0.05^{bx}	0.41 ± 0.09^{ax}	12.5 ± 0.32^{ax}
	Lv.	0.14 ± 0.02^{ax}	0.48 ± 0.18^{ax}	0.64 ± 0.07^{bx}	3.66 ± 0.53^{bxy}	71.6 ± 8.95^{bxy}	0.96 ± 0.38^{ax}	0.62 ± 0.08^{bx}	0.64 ± 0.09^{ax}	20.8 ± 2.87^{bx}
	Gl.	0.07 ± 0.01^{ax}	0.18 ± 0.02^{ax}	0.35 ± 0.06^{bx}	1.81 ± 0.42^{abx}	61.9 ± 9.62^{ax}	1.57 ± 0.29^{abxy}	0.71 ± 0.14^{ax}	0.73 ± 0.21^{ax}	10.2 ± 0.44^{ax}
	In.	0.20 ± 0.03^{ax}	0.17 ± 0.02^{ax}	0.50 ± 0.07^{ax}	7.96 ± 1.49^{ay}	199 ± 33.6^{ay}	4.80 ± 0.75^{ay}	2.33 ± 0.58^{ax}	0.67 ± 0.12^{ax}	18.3 ± 1.78^{ax}
Y	R.r.									
	Ms.	0.09 ± 0.02^{ax}	0.12 ± 0.02^{ax}	0.37 ± 0.06^{bx}	1.39 ± 0.18^{ax}	48.7 ± 5.34^{bx}	0.66 ± 0.27^{ax}	0.57 ± 0.08^{bx}	0.52 ± 0.08^{ax}	10.2 ± 2.12^{ax}
	Lv.	0.25 ± 0.11^{ax}	0.18 ± 0.03^{ax}	0.56 ± 0.09^{bx}	2.43 ± 0.29^{abx}	96.3 ± 15.8^{abx}	1.70 ± 0.42^{ax}	0.71 ± 0.16^{bx}	0.88 ± 0.14^{ax}	10.8 ± 1.33^{abx}
	Gl.	0.19 ± 0.05^{ax}	0.14 ± 0.03^{ax}	0.46 ± 0.07^{abx}	1.08 ± 0.26^{abx}	66.1 ± 7.04^{ax}	1.75 ± 0.32^{abx}	0.82 ± 0.12^{ax}	0.54 ± 0.11^{ax}	11.5 ± 2.15^{ax}
	In.	0.45 ± 0.12^{ax}	0.24 ± 0.03^{ax}	0.55 ± 0.08^{ax}	8.73 ± 1.56^{ay}	247 ± 40.0^{ay}	6.75 ± 1.24^{ay}	2.15 ± 0.50^{ay}	0.72 ± 0.11^{ax}	17.9 ± 2.41^{ax}
D	R.c.									
	Ms.	0.07 ± 0.02^{ax}	0.12 ± 0.02^{ax}	0.36 ± 0.09^{bx}	0.97 ± 0.10^{ax}	35.1 ± 1.08^{bx}	0.19 ± 0.03^{ax}	0.37 ± 0.05^{bx}	0.58 ± 0.14^{ax}	9.31 ± 0.44^{ax}
	Lv.	0.10 ± 0.02^{ax}	0.19 ± 0.03^{ax}	0.53 ± 0.12^{bx}	2.29 ± 0.38^{abxy}	101 ± 5.12^{abx}	1.56 ± 0.23^{axy}	1.80 ± 0.72^{bx}	0.97 ± 0.18^{ax}	12.5 ± 0.87^{abx}
	Gl.	0.16 ± 0.02^{ax}	0.13 ± 0.03^{ax}	0.33 ± 0.06^{bx}	1.68 ± 0.16^{abx}	53.0 ± 2.94^{ax}	3.05 ± 0.33^{axy}	0.48 ± 0.02^{ax}	1.38 ± 0.23^{ax}	9.70 ± 0.53^{ax}
	In.	0.43 ± 0.11^{ax}	0.27 ± 0.04^{ax}	0.56 ± 0.11^{ax}	7.27 ± 1.23^{ay}	262 ± 31.8^{ay}	5.09 ± 0.95^{ay}	3.78 ± 0.85^{ax}	0.90 ± 0.18^{ax}	17.5 ± 2.05^{ax}
K	P.b.									
	Ms.	0.05 ± 0.01^{ax}	0.14 ± 0.02^{ax}	0.24 ± 0.02^{bx}	0.98 ± 0.10^{ax}	28.5 ± 2.63^{bx}	0.21 ± 0.02^{ax}	0.39 ± 0.06^{bx}	0.49 ± 0.07^{ax}	9.61 ± 1.24^{ax}
	Lv.	0.13 ± 0.02^{ax}	0.21 ± 0.03^{ax}	0.44 ± 0.05^{bx}	2.87 ± 0.47^{abxy}	96.6 ± 8.92^{abxy}	0.85 ± 0.26^{ax}	0.86 ± 0.02^{bx}	0.73 ± 0.19^{ax}	16.2 ± 0.95^{abx}
	Gl.	0.10 ± 0.02^{ax}	0.05 ± 0.01^{ax}	0.30 ± 0.03^{bx}	2.75 ± 0.23^{axy}	68.8 ± 2.63^{axy}	1.64 ± 0.35^{abx}	0.50 ± 0.08^{ax}	0.92 ± 0.13^{ax}	12.3 ± 0.96^{ax}
	In.	3.17 ± 1.44^{ax}	0.23 ± 0.06^{ax}	0.58 ± 0.15^{ax}	4.06 ± 0.58^{ay}	229 ± 49.3^{ay}	2.63 ± 0.70^{ax}	3.69 ± 1.38^{ax}	0.85 ± 0.12^{ax}	22.7 ± 2.95^{ax}
Y	G.a.									
	Ms.	0.07 ± 0.01^{ax}	0.11 ± 0.01^{ax}	0.22 ± 0.05^{bx}	1.09 ± 0.07^{axy}	36.4 ± 1.13^{bx}	0.11 ± 0.03^{ax}	0.35 ± 0.08^{bx}	0.65 ± 0.17^{ax}	6.04 ± 1.07^{ax}
	Lv.	0.15 ± 0.02^{ax}	0.14 ± 0.01^{ax}	0.51 ± 0.05^{bx}	1.99 ± 0.36^{abxy}	74.0 ± 2.28^{bx}	1.57 ± 0.39^{ax}	0.47 ± 0.04^{bx}	1.20 ± 0.17^{ax}	15.1 ± 1.35^{abx}
	Gl.	0.08 ± 0.02^{ax}	0.14 ± 0.02^{ax}	0.27 ± 0.04^{bx}	0.96 ± 0.17^{bx}	43.5 ± 1.99^{ax}	0.59 ± 0.18^{bx}	0.32 ± 0.04^{ax}	0.55 ± 0.03^{ax}	19.8 ± 4.92^{ax}
	In.	0.10 ± 0.02^{ax}	0.19 ± 0.04^{ax}	1.01 ± 0.27^{ax}	3.25 ± 0.52^{ay}	242 ± 11.4^{ay}	3.96 ± 0.15^{ay}	3.10 ± 0.57^{ay}	0.78 ± 0.04^{ax}	16.5 ± 2.14^{ax}
A	D.p.**									
	Ms.	0.12 ± 0.01^{ax}	0.05 ± 0.01^{ax}	0.88 ± 0.08^{ax}	0.60 ± 0.08^{ax}	58.2 ± 1.99^{ax}	0.69 ± 0.03^{ax}	1.56 ± 0.23^{ax}	0.45 ± 0.08^{ax}	6.54 ± 0.71^{ax}
	Lv.	0.20 ± 0.01^{ay}	0.12 ± 0.01^{ay}	1.40 ± 0.07^{ay}	1.11 ± 0.07^{ay}	157 ± 7.59^{ay}	1.22 ± 0.05^{ay}	7.59 ± 0.97^{ay}	0.78 ± 0.09^{ax}	8.58 ± 0.68^{ax}
	Gl.	0.10 ± 0.01^{ax}	0.07 ± 0.01^{axy}	0.90 ± 0.08^{ax}	0.98 ± 0.09^{abxy}	67.6 ± 2.52^{ax}	1.38 ± 0.06^{aby}	3.20 ± 1.10^{ax}	0.65 ± 0.12^{ax}	8.90 ± 0.47^{ax}

* Vertically, letters *a* and *b* show differences among the same tissues of different species, *x* and *y* differences among different tissues of the same species, and samples sharing the same letters were not significantly different from one another. *St.* Stations, *Sp.* Species, *Tis.* Tissues, *Ms.* Muscle, *Lv.* Liver, *Gl.* Gill, *In.* Intestine, *D.p. Dasyatis pastinaca*, *R.m. Raja miraletus*, *R.r. Raja radula*, *R.c. Raja clavata*, *P.b. Pteromylaeus bovinus*, *G.a. Gymnura altavela*

** No adequate intestine sample

species from Antalya Bay, Mediterranean Sea (Türkmen et al. 2009a). Metal levels in liver of eight fish species from Iskenderun Bay were 0.12–0.86 (Cd), 0.27–1.24 (Co), 0.75–4.40 (Cr), 1.22–8.03 (Cu), 47.31–516.86 (Fe), 0.87–4.88 (Mn), 1.31–9.99 (Ni), 1.46–6.05 (Pb) and 16.43–74.39 (Zn) (Tepe 2009); 0.406–1.829 (Cd), 0.85–5.21 (Cr), 0.233–9.525 (Cu), 13.87–80.55 (Fe), 0.06–0.720 (Mn) and 0.106–2.252 (Ni) for two shark species (Company et al. 2010); 2.638–3.913 (Cd), 0.018–0.027 (Co), 0.833–1.754 (Cu), 0.179–0.427 (Mn) and 6.898–10.39 (Zn) for two shark species (McMeans et al. 2007); 0.02–2.97 (Cd), 0.71–4.09 (Cu), 6.87–102 (Fe) and 1.58–6.16 (Zn) for four shark species (Endo et al. 2008); and 1.31 (Cd), 0.73 (Co), 2.36 (Cr), 4.91 (Cu), 77.6 (Fe), 2.51 (Mn), 1.91 (Ni), 3.42 (Pb) and 24.1 (Zn) for seven ray species from Mersin Bay, Mediterranean Sea (Türkmen et al. 2008b).

In muscles, the lowest metal levels in mg kg^{-1} were 0.05 (Cd), 28.5 (Fe) in *P.b.*, 0.05 (Co), 0.60 (Cu) in *D.p.*, 0.22 (Cr), 0.11 (Mn), 6.04 (Zn) in *G.a.*, 0.22 (Ni), and 0.41 (Pb) in *R.m.*. On the other hand, the highest metal levels in mg kg^{-1} were 0.12 (Cd), 0.88 (Cr), 58.2 (Fe), 0.69 (Mn), 1.56 (Ni) in *D.p.*, 0.14 (Co) in *P.b.*, 1.39 (Cu) in *R.r.*, 0.65 (Pb) in *G.a.*, and 12.5 (Zn) in *R.m.* Metal levels in mg kg^{-1} for fish muscles in literature were reported as <0.30–8.33 (Cd), <0.01–0.54 (Cr), <0.05–5.30 (Cu), 1.0–89.8 (Fe), <0.02–1.04 (Mn), <0.03–20.0 (Ni), <0.05–2.77 (Pb) and 11.8–24.5 (Zn) for nine ray species (Carvalho et al. 2000); <0.10 (Cd), 1.8–3.3 (Cu), <0.3 (Ni), <0.3 (Pb) and 15–21 (Zn) for three ray species (Zauke et al. 1999); 0.03–0.12 (Cd), 0.26–0.82 (Cu), 7.15–16.5 (Fe), 0.40–2.44 (Pb) and 8.27–76.98 (Zn) for three marine fish from Tuzla Lagoon, Mediterranean (Dural et al. 2007); 0.002–0.029 (Cd), 3.30–16.6 (Cr), 0.125–7.049 (Cu), 5.67–54.49 (Fe), 0.273–0.986 (Mn) and 1.158–6.174 (Ni) for two shark species (Company et al. 2010); 0.21 (Cd), 0.26 (Co), 1.19 (Cr), 1.05 (Cu), 19.9 (Fe), 0.85 (Mn), 2.78 (Ni), 0.54 (Pb) and 6.17 (Zn) for three marine fish from İskenderun Bay and 0.10 (Cd), 0.07 (Co), 0.59 (Cr), 0.80 (Cu), 72.3 (Fe), 0.93 (Mn), 0.81 (Ni), 0.38 (Pb) and 8.34 (Zn) for three marine fish from Antalya Bay, Mediterranean Sea (Türkmen et al. 2008a); 0.34 (Cd), 0.32 (Co), 0.46 (Cr), 1.1 (Cu), 21.5 (Fe), 0.89 (Mn), 1.13 (Ni), 0.93 (Pb) and 5.37 (Zn) for seven ray species from Mersin Bay, Mediterranean Sea (Türkmen et al. 2008b); and 0.07–0.38 (Cd), 0.05–0.42 (Co), 0.42–1.87 (Cr), 0.22–1.15 (Cu), 13.4–23.7 (Fe), 0.44–0.85 (Mn), 0.12–4.7 (Ni), 0.62–0.81 (Pb) and 4.78–8.17 (Zn) for two marine fish from İskenderun Bay (Türkmen et al. 2009b). In another study from Iskenderun Bay, metal levels in muscles of eight fish had similar ranges of 0.03–0.39 (Cd), 0.02–0.44 (Co), 0.14–1.90 (Cr), 0.10–2.06 (Cu), 10.29–53.45 (Fe), 0.38–1.34 (Mn), 0.22–4.72 (Ni), 0.32–1.15 (Pb) and 4.71–8.61 (Zn) (Table 4).

In gills, minimum metal levels in mg kg^{-1} were 0.07 (Cd) in *R.m.*, 0.05 (Co) in *P.b.*, 0.27 (Cr), 0.96 (Cu), 43.5 (Fe), 0.59 (Mn), 0.32 (Ni) in *G.a.*, 0.54 (Pb) in *R.r.*, and 8.90 (Zn) *D.p.* On the other hand, maximum metal levels in mg kg^{-1} were 0.19 (Cd) in *R.r.*, 0.18 (Co) in *R.m.*, 0.90 (Cr), 3.20 (Ni) in *D.p.*, 2.75 (Cu), 68.8 (Fe) in *P.b.*, 3.05 (Mn), 1.38 (Pb) in *R.c.*, and 19.8 (Zn) in *G.a.* Metal concentrations in mg kg^{-1} for gills in literature were reported as 0.094 (Cd), 0.47 (Cu), 0.012 (Pb) and 0.101 (Zn) for *Raja fyllae* (Mormede and Davies 2001); 0.04–1.59 (Cd), 0.83–7.82 (Cu), 60.5–344.8 (Fe), 2.67–6.75 (Pb) and 12.2–60.5 (Zn) for three marine fish from Tuzla Lagoon, Mediterranean (Dural et al. 2007); 1.75 (Cd), 0.47 (Co), 2.15 (Cr), 3.36 (Cu), 51.4 (Fe), 2.13 (Mn), 3.16 (Ni), 1.73 (Pb) and 17.4 (Zn) for seven ray species from Mersin Bay, Mediterranean Sea (Türkmen et al. 2008b); 0.045–0.446 (Cd), 1.43–15.54 (Cr), 0.490–1.839 (Cu), 18.32–104.7 (Fe), 0.513–2.947 (Mn) and 0.573–12.51 (Ni) for two shark species (Company 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) for three marine fish from Yelkoma Lagoon, Mediterranean (Türkmen et al. 2010); and 0.26–0.75 (Cd), 0.34–0.69 (Co), 0.41–1.34 (Cr), 1.12–2.25 (Cu), 60.4–107 (Fe), 3.11–13.0 (Mn), 0.75–1.35 (Ni), 0.45–0.73 (Pb) and 12.0–22.4 (Zn) for three marine fish from Paradeniz Lagoon, Mediterranean (Türkmen et al. 2011).

In intestines, the lowest metal levels in mg kg^{-1} were 0.10 (Cd), 3.25 (Cu), 16.5 (Zn) in *G.a.*, 0.17 (Co), 0.50 (Cr), 199 (Fe), 0.67 (Pb) in *R.m.*, 2.63 (Mn) in *P.b.*, and 2.15 (Ni) in *R.r.* On the other hand, the highest metal levels in mg kg^{-1} were 3.17 (Cd), 22.7 (Zn) in *P.b.*, 0.27 (Co), 262 (Fe), 3.78 (Ni), 0.90 (Pb) in *R.c.*, 1.01 (Cr) in *G.a.*, 8.73 (Cu), and 6.75 (Mn) in *R.r.* Metal concentrations in mg kg^{-1} for intestines in literature were reported as 26.37 (Zn), 3.33 (Cu), 0.33 (Cd) and 0.14 (Pb) for intestines of twenty fish species from coastal waters of eastern Taiwan (Huang 2003); 2.95–4.92 (Cd), 16–24.01 (Co), 9.06–17.98 (Cr), 6.41–11.43 (Cu), 1431–5150 (Fe), 27.87–48.75 (Mn), 13.75–16.64 (Ni), 14.41–41.32 (Pb) and 91.76–105 (Zn) for stomach contents of three marine fish species from the Jordan Gulf of Aqaba (Ismail and Abu–Hilal 2008); 0.02–2.96 (Cd), 0.01–0.03 (Co), 0.56–1.75 (Cu), 5.51–16.7 (Fe), 0.18–2.24 (Mn), 13.5–49.1 (Zn) for stomach of two marine fish from Fujian province (Onsanit et al. 2010); 2.12 (Cd), 0.43 (Co), 2.86 (Cr), 13.5 (Cu), 97.6 (Fe), 3.98 (Mn), 1.77 (Ni), 2.99 (Pb) and 47.1 (Zn) for seven ray species from Mersin Bay, Mediterranean Sea (Türkmen et al. 2008b); and 6.09 (Cu), 25.42 (Zn), 6.80 (Pb) and 1.87 (Cd) for gut contents of four fish species from the Jeddah coast (Ali et al. 2011).

Table 3 Comparison of metal concentrations among different stations for the same tissues

Tis./St.	Mean metal concentrations with ± SE (mg kg^{-1} wet wt)*								
	Cadmium	Cobalt	Chromium	Copper	Iron	Manganese	Nickel	Lead	Zinc
Ms.									
Y	0.08 ± 0.01^{ab}	0.11 ± 0.01^{ab}	0.30 ± 0.04^{a}	1.30 ± 0.08^{a}	44.4 ± 2.57^{ab}	0.47 ± 0.13^{a}	0.43 ± 0.05^{a}	0.53 ± 0.07^{a}	9.59 ± 1.03^{a}
D	0.07 ± 0.02^{ab}	0.12 ± 0.02^{ab}	0.36 ± 0.09^{a}	0.97 ± 0.10^{ab}	35.1 ± 1.08^{a}	0.19 ± 0.03^{a}	0.37 ± 0.05^{a}	0.58 ± 0.14^{a}	9.31 ± 0.44^{a}
K	0.05 ± 0.01^{a}	0.14 ± 0.02^{a}	0.24 ± 0.02^{a}	0.98 ± 0.10^{ab}	28.5 ± 2.63^{a}	0.21 ± 0.02^{a}	0.39 ± 0.06^{a}	0.49 ± 0.07^{a}	9.61 ± 1.24^{a}
A	0.12 ± 0.01^{b}	0.05 ± 0.01^{b}	0.88 ± 0.08^{b}	0.60 ± 0.08^{b}	58.2 ± 1.99^{b}	0.69 ± 0.03^{a}	1.56 ± 0.23^{b}	0.45 ± 0.08^{a}	6.54 ± 0.71^{a}
Lv.									
Y	0.20 ± 0.05^{a}	0.27 ± 0.06^{a}	0.57 ± 0.04^{a}	2.67 ± 0.24^{a}	83.9 ± 6.98^{a}	1.46 ± 0.22^{a}	0.63 ± 0.07^{a}	0.89 ± 0.08^{a}	14.7 ± 1.21^{a}
D	0.10 ± 0.02^{a}	0.19 ± 0.03^{a}	0.53 ± 0.12^{a}	2.29 ± 0.38^{a}	101 ± 5.12^{a}	1.56 ± 0.23^{a}	1.80 ± 0.72^{a}	0.97 ± 0.18^{a}	12.5 ± 0.87^{a}
K	0.13 ± 0.02^{a}	0.21 ± 0.03^{a}	0.44 ± 0.05^{a}	2.87 ± 0.47^{a}	96.6 ± 8.92^{a}	0.85 ± 0.26^{a}	0.86 ± 0.02^{a}	0.73 ± 0.19^{a}	16.2 ± 0.95^{a}
A	0.20 ± 0.01^{a}	0.12 ± 0.01^{a}	1.40 ± 0.07^{b}	1.11 ± 0.07^{a}	157 ± 7.59^{b}	1.22 ± 0.05^{a}	7.59 ± 0.97^{b}	0.78 ± 0.09^{a}	8.58 ± 0.68^{a}
Gl.									
Y	0.13 ± 0.02^{a}	0.15 ± 0.01^{a}	0.39 ± 0.04^{a}	1.62 ± 0.17^{ab}	60.3 ± 4.13^{a}	1.46 ± 0.17^{a}	0.68 ± 0.07^{a}	0.59 ± 0.07^{a}	13.0 ± 1.63^{a}
D	0.16 ± 0.02^{a}	0.13 ± 0.03^{a}	0.33 ± 0.06^{a}	1.68 ± 0.16^{ab}	53.0 ± 2.94^{a}	3.05 ± 0.33^{b}	0.48 ± 0.02^{a}	1.38 ± 0.23^{b}	9.70 ± 0.53^{a}
K	0.10 ± 0.02^{a}	0.05 ± 0.01^{a}	0.30 ± 0.03^{a}	2.75 ± 0.23^{a}	68.8 ± 2.63^{a}	1.64 ± 0.35^{a}	0.50 ± 0.08^{a}	0.92 ± 0.13^{ab}	12.3 ± 0.96^{a}
A	0.10 ± 0.01^{a}	0.07 ± 0.01^{a}	0.90 ± 0.08^{b}	0.98 ± 0.09^{b}	67.6 ± 2.52^{a}	1.38 ± 0.06^{a}	3.20 ± 1.10^{a}	0.65 ± 0.12^{a}	8.90 ± 0.47^{a}
In.**									
Y	0.31 ± 0.06^{a}	0.18 ± 0.01^{a}	0.62 ± 0.07^{a}	7.57 ± 0.85^{a}	234 ± 20.1^{a}	5.75 ± 0.60^{a}	2.36 ± 0.30^{a}	0.69 ± 0.06^{a}	17.8 ± 1.25^{a}
D	0.43 ± 0.11^{a}	0.27 ± 0.04^{a}	0.56 ± 0.11^{a}	7.27 ± 1.23^{a}	262 ± 31.8^{a}	5.09 ± 0.95^{a}	3.78 ± 0.85^{a}	0.90 ± 0.18^{a}	17.5 ± 2.05^{a}
K	3.17 ± 1.44^{b}	0.23 ± 0.06^{a}	0.58 ± 0.15^{a}	4.06 ± 0.58^{a}	229 ± 49.3^{a}	2.63 ± 0.70^{a}	3.69 ± 1.38^{a}	0.85 ± 0.12^{a}	22.7 ± 2.95^{a}

* Vertically letters *a* and *b* show differences among different stations in the same tissues ($p < 0.05$). *St.* Stations, *K* Karataş offshore, *Y* Yumurtalık Bay, *D* Dörtyol offshore, *A* Arsuz offshore, *Tis.* Tissues, *Ms.* Muscle. *Lv.* Liver. *Gl.* Gill. *In.* Intestine

** No adequate intestine sample in station A

Table 4 Comparison of heavy metal concentration ranges in edible muscle tissue of rays from this study with other studies and guidelines for maximum allowable concentrations

Studies/ Guidelines	Metals and concentrations (mg kg^{-1})								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
This study	0.05–0.12	0.05–0.14	0.22–0.88	0.60–1.39	28.5–58.2	0.11–0.69	0.22–1.56	0.41–0.65	6.04–12.5
Carvalho et al. (2000)	<0.30–8.33	–	<0.01–0.54	<0.05–5.30	1.0–89.8	<0.02–1.04	<0.03–20.0	<0.05–2.77	11.8–24.5
Zauke et al. (1999)	<0.10	–	–	1.8–3.3	–	–	<0.3	<0.3	15–21
Dural et al. (2007)	0.03–0.12	–	–	0.26–0.82	7.15–16.5	–	–	0.40–2.44	8.27–76.98
Company et al. (2010)	0.002–0.029	–	3.3–16.6	0.13–7.05	5.67–54.5	0.27–0.99	1.16–6.17	–	–
Türkmen et al. (2008a)	0.21	0.26	1.19	1.05	19.9	0.85	2.78	0.54	6.17
Türkmen et al. (2008b)	0.34	0.32	0.46	1.1	21.5	0.89	1.13	0.93	5.37
Türkmen et al. (2009b)	0.07–0.38	0.05–0.42	0.42–1.87	0.22–1.15	13.4–23.7	0.44–0.85	0.12–4.70	0.62–0.81	4.78–8.17
TKB (2002)	0.1	–	–	20	–	–	–	1.0	50
Nauen (1983)	0.05–5.5	–	1.0	10–100	–	–	–	0.5–6.0	30–100

Metal concentrations in a given tissue type for all species together collected from each station were examined to determine the effect of sampling site on the results (Table 3). According to Table 3, the differences among stations were statistically significant for Cd, Co, Cr, Cu, Fe and Ni in muscles, for Cr, Fe and Ni in livers, for Cr, Cu, Mn and Pb in gills, for Cd in intestines ($p < 0.05$). Rays from station A had significantly higher Cr and Ni levels in muscles, Cr, Fe and Ni levels in livers, and Cr levels in gills. Manganese levels in gills had the highest overall concentration at station D. Cadmium levels in intestines were significantly higher at station K than other stations.

The present study is the first for rays in the bay. It provides valuable preliminary information on metal contents in different tissues of the ray species from the study sites, and indirectly indicates the environmental contamination of the bay. Moreover, the results showed that muscle tissue of rays was not heavily burdened with metals, as concentrations were below the legal values for fish and fishery products proposed by Nauen (1983). Comparison of our data with the Turkish acceptable limits (TKB 2002) showed that our values were also lower than national guidelines (except for the highest value of Cd in *D.p.*) (Table 4). However, these results should be confirmed occasionally by running more detailed studies in the bay to update our knowledge of heavy metal contaminants in fish.

Acknowledgments Thanks to TÜBİTAK for its financial support (Project No: 106Y210) and Kamil Yerdoğan and Esra Aslan for microwave oven digestion.

References

Ali AA, Elazein EM, Alian MA (2011) Determination of heavy metals in four common fish, water and sediment collected from red sea at Jeddah Isalmic port coast. J Appl Environ Biol Sci 1:453–459

Carvalho CEV, Rezende CE, Ferreira AG, FariaVV, Gomes MP, Cavalcante MPO (2000). Trace metals in muscle tissue from southern Brazilian coast fish. http://www.cprm.gov.br/pgagem/Manuscripts/carvalhoctrace.htm

Company R, Felicia H, Serafim A, Almeida AJ, Biscoito M, Bebianno MJ (2010) Metal concentrations and metallothionein-like protein levels in deep-sea fishes captured near hydrothermal vents in the Mid-Atlantic ridge off azores. Deep Sea Res I 57:893–908

Dural M, Göksu MZL, Özak AA (2007) Investigation of heavy metal levels in economically important fish species captured from the Tuzla lagoon. Food Chem 102:415–421

Endo T, Hisamichi Y, Haraguchi K, Kato Y, Ohta C, Koga N (2008) Hg, Zn and Cu levels in the muscle and liver of tiger sharks (*Galeocerdo cuvier*) from the coast of Ishigaki Island, Japan: relationship between metal concentrations and body length. Mar Pollut Bull 56:1774–1780

Huang WB (2003) Heavy metal concentrations in the common benthic fishes caught from the coastal waters of eastern Taiwan. J Food Drug Anal 11:324–330

Ismail NS, Abu-Hilal AH (2008) Heavy metals in three commonly available coral reef fish species from the Jordan Gulf of Aqaba, red sea. Jordan J Biol Sci 1:61–66

McMeans BC, Borga K, Bechtol WR, Higginbotham D, Fisk AT (2007) Essential and non-essential element concentrations in two sleeper shark species collected in arctic waters. Environ Pollut 148:281–290

Mormede S, Davies IM (2001) Trace elements in deep-water fish species from the Rockall Trough. Fish Res 51:197–206

Nauen CE (1983). Compilation of legal limits for hazardous substances in fish and fishery products. FAO Fish Circular, FAO (764): pp. 102

Onsanit S, Ke C, Wang X, Wang KJ, Wang WX (2010) Trace elements in two marine fish cultured in fish cages in Fujian province, China. Environ Pollut 158:1334–1342

Tepe Y (2009) Metal concentrations in eight fish species from Aegean and mediterranean seas. Environ Monit Assess 159:501–509

Tepe Y, Türkmen M, Türkmen A (2008) Assessment of heavy metals in two commercial fish species of four Turkish seas. Environ Monit Assess 146:77–284

TKB (2002). Fisheries laws and regulations. Ministry of Agriculture and Rural Affairs, Conservation and Control General Management. Ankara, Turkey

Türkmen M, Türkmen A, Tepe Y (2008a) Metal contaminations in five fish species from black, marmara, aegean and mediterranean seas, Turkey. J Chil Chem Soc 52:1435–1439

Türkmen M, Tepe Y, Genç E, Sangün MK, Türkmen A, Ateş A, Gökkuş K, Erol C (2008b). Assessment of heavy metal accumulations in ray species from İskenderun, Mersin and Antalya bays. Project Result Report (Tübitak 106Y210), pp. 39

Türkmen M, Türkmen A, Tepe Y, Töre Y, Ateş A (2009a) Determination of metals in fish species from Aegean and Mediterranean seas. Food Chem 113:233–237

Türkmen A, Tepe Y, Türkmen M, Mutlu E (2009b) Heavy metal contaminants in tissues of the Garfish, *Belone belone* L., 1761, and the Bluefish, *Pomatomus saltatrix* L., 1766, from Turkey waters. Bull Environ Contam Toxicol 82:70–74

Türkmen A, Türkmen M, Tepe Y, Çekiç M (2010) Metals in tissues of fish from Yelkoma Lagoon, northeastern Mediterranean. Environ Monit Assess 168:223–230

Türkmen M, Türkmen A, Tepe Y (2011) Comparison of metals in tissues of fish from Paradeniz Lagoon in the coastal area of northern east mediterranean. Bull Environ Contam Toxicol 87:381–385

Zauke GP, Savinov VM, Ritterhoff J, Savinova T (1999) Heavy metals in fish from the Barents Sea (summer 1994). Sci Total Environ 227:161–173