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Metal Concentrations in Blue Crab (*Callinectes sapidus*) and Mullet (*Mugil cephalus*) in İskenderun Bay, Northern East Mediterranean, Turkey

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Aquatic environmental quality, and how humans may be affecting this, is an area which has received increasing attention in recent years. Marine organisms, among them fish and crab accumulate contaminants from the environment and therefore have been extensively used in marine pollution monitoring programs (Uthe et al. 1991, Unep 1993). Determination of contaminant concentrations in fish muscles in order to assess the health risk for humans, and use fish as environmental indicators of aquatic ecosystems quality are two main objectives being pursued in these programs (Adams 2002). The substantial development of urban and industrial activities results in increasing inputs of chemical contaminants which leads to the loss or alteration of marine habitats. As their spawning and nursery grounds are mainly located in estuarine and coastal areas, many marine organisms, including many commercially valuable shrimps and fish, are directly affected by human activities (Gibson 1994, Amara et al. 2000).

Having an economic importance for fisheries, İskenderun Bay is situated in the northern east part of the Mediterranean Sea off southern Turkey (Figure 1). Sewage wastes and ship maintenance works are dumped directly into the sea without any treatment. Industries, in this region of the Mediterranean Sea, are also expanding; most of these industries such as cement factory, textiles, tin, iron and rubbish treatment, food conserves, oil refinery, phosphate loading activities etc. use sea or river systems to dump their effluent. In addition, the predominant current system indicates that pollution from external source is highly possible and consequently, local practices are not the only potential source of pollution. Wastewater collection and disposal systems have been planned and constructed in some areas, but these are still not sufficient in some other areas due to primarily limited budget. There is lack of information about the history and current situation of pollution along the İskenderun Bay. Intense pollution in the bay has inevitably increased the levels of metals in the water. Therefore, it became important to determine the levels of metals in commercial species in order to evaluate the possible risk of sea food consumption for human health. Two evaluated species chosen were *Callinectes sapidus* and *Mugil cephalus*. These species, both being the most favorite species by consumers, have different biological needs and show different feeding habit than each other. Crab may be especially sensitive to

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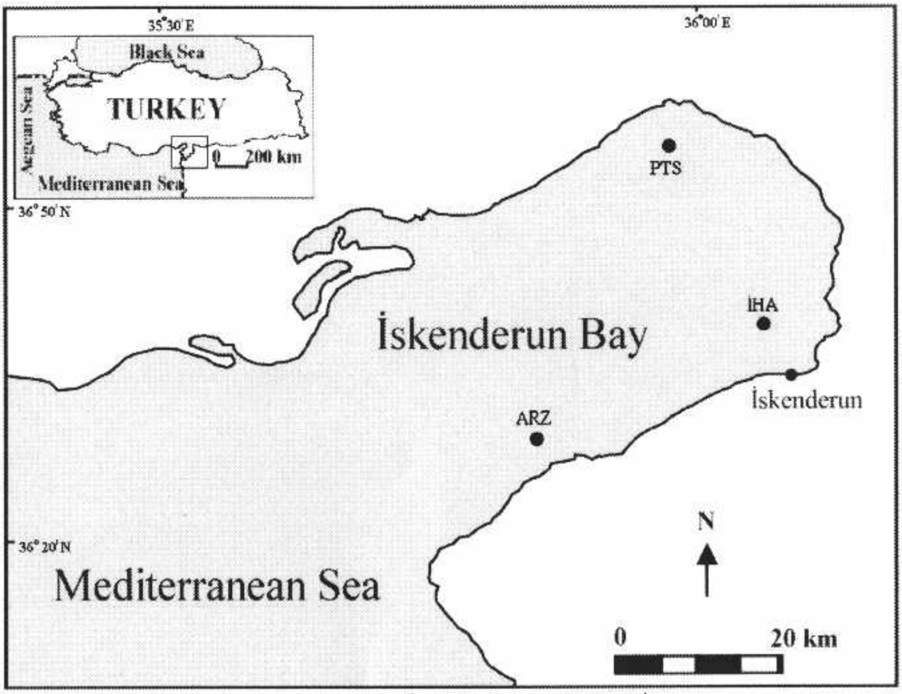

Figure 1. Sampling locations (ARZ, İHA, PTS) along the İskenderun Bay.

pollution and other types of habitat degradation because they reside in bottom sediments where chemical contaminants accumulate. Mullet utilize nearshore habitats, where environmental degradation is likely to be the greatest, as nursery grounds. The aim of this study is to determine the levels of metals (Cd, Cu, Cr, Pb, Co, Zn, Fe, Ni, Al and Mn) in the muscle tissue of two commercially valuable species from the coastal areas of İskenderun Bay in order to assess spatial trends of the fish habitat quality.

MATERIALS AND METHODS

Samples were collected from the three stations along İskenderun Bay in August 2003. Three sampling stations were Arsuz (ARZ), relatively clean area, İskenderun Harbor Area (IHA) and Petrotrans (PTS), intensively polluted areas by both industrial and domestic sources (Figure 1). Mullet (*M. cephalus*) were sampled alive by a 22 mm mesh size nylon monofilament gillnets from the sampling stations. Blue crabs (*C. sapidus*) were trawled from the same stations during the same period. Fifteen fish and crab samples were obtained from each station. Samples were washed with clean sea water at the point of collection, separated to species, placed on ice, brought to laboratory on the same day. Samples were then frozen at −20 °C until dissection. Total size and weight of the samples were measured to the nearest millimeter and gram before dissected with clean equipment. The mean length and weights of the samples were 25.6 ± 2.35 cm and 175.4 ± 36.3 g for *M. cephalus* and 6.2 ± 0.4 cm carapax length and 123.1

± 19.7 g for *C. sapidus*, respectively. The muscle samples from fish and crab were removed with a plastic knife for metal analysis, homogenized and weighed, and then individual samples were dried to constant weight at 60 °C in acid-washed Petri dishes. The digestion was performed in a microwave digester (CEM MARS-5 Closed Vessel Microwave Digestion System) to prepare the samples for analysis. The completely digested samples were allowed to cool to room temperature, filtered and diluted to 50 ml in volumetric flasks with double distilled water. All digested samples were analyzed three times for the metals Cd, Cu, Cr, Pb, Co, Zn, Fe, Ni, Al and Mn using AAS (Varian Spectraa 220 Fast Sequential Flame Atomic Absorption Spectrometry). The accuracy and precision of our results were checked by analyzing certified reference material (CRM, Dorm-2, dogfish muscle obtained from the National Research Council, Canada). The results indicated good agreement between the certified and the analytical values (Table 1), the recovery of elements being partially complete for most of them. The absorption wavelengths as nm and detection limits as mg kg^{-1} were 228.8 and 0.02 for Cd; 324.7 and 0.03 for Cu; 425.4 and 0.4 for Cr; 232.0 and 0.1 for Ni; 217.0 and 0.1 for Pb; 213.9 and 0.01 for Zn; 240.7 and 0.05 for Co; 396.1 and 0.5 for Al; 279.5 and 0.02 for Mn; 248.3 and 0.06 for Fe, respectively. All chemicals and standard solutions used in the study were obtained from Merck, and were of analytical grade. Doubled distilled water was used throughout the study. All glassware and other containers were thoroughly cleaned and finally rinsed with double distilled water several times and air dried prior to use. All metal concentrations were quoted as mg kg^{-1} dry weight unless otherwise stated. A logarithmic transformation was done on the data to improve normality. One-way analysis of variance (ANOVA) and Duncan's test were used to access whether metal concentrations varied significantly between sites and species, possibilities less than 0.05 ($p<0.05$) were considered statistically significant. All statistical calculations were performed with SPSS 9.0 for Windows.

RESULTS AND DISCUSSION

This study examined the concentrations of aluminum, chrome, cobalt, copper, manganese, nickel, cadmium, lead, zinc and iron in *M. cephalus* and *C. sapidus* from three sites in İskenderun Bay. A total of 45 fish and 45 crabs were analyzed in this study. The average metal concentrations and comparison in mixed sites of examined species are reported in Table 2. Iron has the highest levels in both species. Following iron, zinc was the second highest metal found in the muscles of examined species. The differences between mean metal concentrations of species were statistically significant ($p<0.05$) for most of the measured metals. *C. sapidus* showed the highest values of aluminum, chromium, copper, manganese, cobalt, nickel, lead, and zinc. Cadmium and iron concentrations were fairly constant and not significantly different between the species. Since, one of the purposes of this study is to compare metal levels at several sampling sites, levels of metal concentrations (mg kg^{-1} dry weight) and their comparisons in *C. sapidus* from different sites were done and shown in Table 2.

The level of Mn concentrations varied significantly among the stations ($p<0.05$) in *C. sapidus*. Mn concentration was the highest in PTS station and the lowest in

Table 1. Concentrations of metals found in Standard Reference Material, Dorm-2 (dogfish muscle, means ± standard errors (SE), m=10, in mg kg^{-1} dry wt).

Value	Cd	Cu	Cr	Pb	Zn	Ni	Mn	Al	Fe	Co
Certified	0.043	2.34	34.7	0.065	26.6	19.4	3.66	10.9	142	0.182
SE	0.008	0.16	5.5	0.007	2.3	3.1	0.34	1.7	10	0.031
Observed	0.047	2.39	33.8	0.067	24.8	18.3	3.88	10.4	136	0.186
SE	0.009	0.19	1.53	0.008	1.82	0.94	0.41	0.52	11.7	0.018
Recovery (%)	109	102	97	103	93	94	106	95	96	102

ARZ station. Similarly, iron concentration also showed significant differences between the stations in *C. sapidus.* The highest iron concentrations in *C. sapidus* were found in PTS station while lowest concentration was found in ARZ station. The levels of cadmium, cobalt and lead in *C. sapidus* were not significantly different from station to station. ARZ station showed the lowest metal concentrations in overall.

Levels of metal concentrations (mg kg^{-1} dry weight) and their comparisons in *M. cephalus* from different sites were also done and summarized in Table 2. The level of zinc concentrations varied significantly among the stations ($p<0.05$) in *M. cephalus*. Zinc concentrations were the highest in PTS station and the lowest in ARZ station. The levels of lead in *M. cephalus* were not significantly different from station to station. PTS station showed the highest metal concentrations in overall. In general, the pattern of metal concentrations followed our expectations based on land uses in the watersheds, with high levels of metals in PTS and IHA and lower levels of metals in ARZ. The elevated metal levels at PTS, in particular, are not surprising given the prevalence of industrial activities, domestic sewage and urban runoff in the area. Boating and domestic activities might probably be the main reasons for high levels of metals in IHA.

Canli and Atli (2003) measured the heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) concentrations in the muscle, gill and liver of six different fish species from İskenderun Bay in 2000. Present results generally were lower for Fe, Pb and Zn than their findings. On the other hand, Cd, Cu and Cr concentrations were relatively similar with the present results (Table 3). This situation indicated that the metal concentrations in İskenderun Bay were relatively decreased from 2000 to 2003. The greatest decrease was observed in zinc concentrations. The decrease in regional mercantile marine, and consequently, gradual decrease in industrial business by the start of Gulf War in early 1990s, might be the reason for this slight decrease in metal concentrations.

Table 3 shows the comparison the data of the present study with that from elsewhere. Concentrations of Cu, Fe, Mn, Ni and Zn measured in the muscles of blue crab, *C. sapidus*, in our study were lower than those reported for Australian waters by Mortimer (2000). Concentrations of other metals, however, agreed well with our findings. Cu and Zn concentrations reported by Al-Mohanna and Subrahmanyam (2001) for blue crab from Kuwait waters were greater, while Cr, Fe and Pb concentrations were lower than those found the present study. Jewett

Table 2. The comparison of the mean metal concentrations of species and stations (the parenthesis are indicated minimum and maximum values)*.

Metals	Stations	N	*M. cephalus*	*C. sapidus*
Aluminum	ARZ	15	0.614^{a} (0.04-1.75)	4.797^{a} (1.23-10.65)
	IHA	15	1.492^{ab} (0.07-3.53)	6.682^{ab} (2.12-13.59)
	PTS	15	1.713^{b} (0.49-3.66)	10.53^{b} (4.66-17.56)
	Overall	45	1.273^{x} (0.04-3.53)	7.347^{y} (1.23-17.56)
Chrome	ARZ	15	1.686^{a} (0.25-4.26)	2.823^{a} (0.57-6.59)
	IHA	15	1.017^{ab} (0.07-3.37)	6.555^{b} (1.56-11.59)
	PTS	15	0.589^{b} (0.02-2.01)	4.197^{ab} (1.29-6.30)
	Overall	45	1.097^{x} (0.13-4.26)	4.527^{y} (0.57-11.59)
Copper	ARZ	15	0.738^{a} (0.06-2.46)	3.881^{a} (1.26-7.36)
	IHA	15	1.640^{b} (0.43-3.44)	9.388^{b} (4.32-14.29)
	PTS	15	2.243^{b} (0.84-4.64)	7.783^{b} (3.65-12.65)
	Overall	45	1.540^{x} (0.06-4.64)	7.018^{y} (1.26-14.36)
Manganese	ARZ	15	1.296^{a} (0.48-3.43)	1.828^{a} (0.10-3.69)
	IHA	15	1.841^{a} (0.70-3.83)	8.475^{b} (3.79-15.43)
	PTS	15	3.092^{b} (1.46-6.01)	4.154^{c} (1.94-7.19)
	Overall	45	2.076^{x} (0.48-6.01)	4.819^{y} (0.10-15.43)
Cobalt	ARZ	15	1.183^{ab} (0.08-4.74)	2.534^{a} (0.53-5.59)
	IHA	15	0.726^{a} (0.02-1.76)	3.172^{a} (0.77-7.65)
	PTS	15	1.912^{b} (0.42-4.35)	2.951^{a} (0.65-5.65)
	Overall	45	1.274^{x} (0.02-4.74)	2.951^{y} (0.65-5.65)
Nickel	ARZ	15	0.661^{a} (0.05-1.83)	1.627^{a} (0.32-3.15)
	IHA	15	1.274^{b} (0.09-3.54)	4.195^{b} (1.34-7.28)
	PTS	15	1.587^{b} (0.21-3.43)	2.669^{b} (1.52-4.58)
	Overall	45	1.174^{x} (0.05-3.54)	2.830^{y} (0.32-7.28)
Cadmium	ARZ	15	0.234^{a} (0.03-1.21)	1.055^{a} (0.09-2.26)
	IHA	15	0.195^{a} (0.02-1.14)	2.509^{a} (0.36-5.65)
	PTS	15	0.551^{b} (0.04-1.84)	1.741^{a} (0.14-3.65)
	Overall	45	0.327^{x} (0.01-1.84)	1.768^{y} (0.09-5.65)
Lead	ARZ	15	1.263^{a} (0.09-3.44)	3.529^{a} (1.25-6.65)
	IHA	15	1.690^{a} (0.14-3.85)	4.304^{a} (1.29-7.36)
	PTS	15	2.088^{a} (0.64-4.26)	2.667^{a} (0.32-6.23)
	Overall	45	1.681^{x} (0.09-4.26)	3.513^{y} (0.43-6.92)
Zinc	ARZ	15	3.202^{a} (1.28-5.68)	6.760^{a} (3.56-11.24)
	IHA	15	5.109^{b} (2.31-7.86)	11.52^{b} (5.49-18.27)
	PTS	15	8.032^{c} (3.76-12.25)	8.947^{ab} (4.26-16.54)
	Overall	45	5.448^{x} (1.28-12.26)	9.074^{y} (3.56-18.27)
Iron	ARZ	15	8.869^{a} (4.35-13.24)	7.251^{a} (2.13-11.32)
	IHA	15	13.29^{b} (7.28-21.50)	12.56^{b} (6.35-22.42)
	PTS	15	18.75^{b} (8.15-38.21)	23.27^{c} (8.25-45.25)
	Overall	45	13.64^{x} (4.35-38.24)	14.36^{x} (2.13-45.25)

* Letters a, b and c show differences among stations of same species; x and y between species at same station. Within columns, means with the same letter are not significant, p>0.05.

Table 3. Comparison of the mean metal concentrations in *C. sapidus* and *M. cephalus* with results taken from the other studies.*

Species	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	R
A.b., E.e., D.l., M.e.	<0.02-0.24	<0.05-0.40	0.06-0.84	1.01-4.54	30-60	0.69-3.56	<0.01-2.04	<0.05-0.06	25.7-44.2	1
S.a., A.h., M.c., T.c., S.p., S.s.	0.37-0.79	--	1.24-2.42	2.19-4.4	19.6-78.4	--	--	2.98-6.12	16.5-37.4	2
F.p., L.a., A.a.	0.1-0.3	--	1.9-24	1.9-7.5	--	--	0.61-12	0.8-4.1	36-150	3
P.p.	--	--	0.15-0.66	110-143	--	0.72-2.01	--	1.72-2.08	188-221	4
P.c.	0.19-0.25	--	0.75-1.63	56.9-90.9	--	--	0.85-4.90	0.26-0.70	159-189	5
L.h., P.b.	0.016-0.15	--	0.05-0.65	3.7-43	--	--	--	0.032-0.88	13-69	6
A.t., S.serrata	0.03-0.89	0.068-14.2	0.22-18.3	16.4-194	7.48-7580	6.7-544	2.82-12.7	0.028-26.7	55.6-249	7
M.c.	0.19-0.55	0.73-1.91	0.59-1.69	0.74-2.24	8.87-18.8	1.30-3.09	0.66-1.59	1.26-2.09	3.20-8.03	8
C.s.	1.06-2.51	2.53-3.17	2.82-6.56	3.88-9.39	7.25-23.27	1.83-8.48	1.63-4.19	2.67-4.30	6.76-11.5	8

* Values represent the ranges expressed as mg kg^{-1} dry wt., *A.b.*: *Alosa bulgarica*, *E.e.*: *Engraulis encrasicolus*, *D.l.*: *Dicentrarchus labrax*, *M.e.*: *Merlangius euxinus*, *S.a.*: *Sparus auratus*, *A.h.*: *Atherina hepsetus*, *M.c.*: *Mugil cephalus*, *T.c.*: *Trigla cuculus*, *S.p.*: *Sardina pilchardus*, *S.s.*: *Scomberesox saurus*, *F.p.*: *Fundulus parvipinnis*, *L.a.*: *Leptocottus armatus*, *A.a.*: *Atherinops affinis*, *P.p.*: *Portunus pelagicus*, *P.c.*: *Paralithodes camtschaticus*, *L.h.*: *Liocarcinus holsatus*, *P.b.*: *Pagurus bernhardus*, *A.t.*: *Australoplax tridentata*, *S.serrata*: *Scylla serrata*, *C.s.*: *Callinectes sapidus*, R: reference, 1: Topcuoğlu et al. 2002, 2: Canli & Atli 2003, 3: Tamira et al. 2001, 4: Al-Mohanna & Subrahmanyam 2001, 5: Jewett & Naidu 2000, 6: Guns et al. 1999, 7: Mortimer 2000, 8: present study.

and Naidu (2000) found lower Cd, Cr and Pb levels, higher Cu and Zn levels for crab in Norton Sound. Guns et al. (1999) investigated heavy metal levels for crab in Belgian coastal waters and results from the present study were higher for Cd, Cr and Pb, lower for Cu and Zn than their findings.

The present study reported the first information on the concentrations of metals in crabs in the bay. The study indicated that crabs may be more suitable biomonitors of metals in the surrounding environment than fish. In general, the highest metal concentrations were found in blue crab, *C. sapidus*, except cadmium and iron. This situation may be explained by that crabs are less active and their feeding habits, ecological needs, other characteristic behaviors and metabolisms are more different than fish. Blue crab lives on sediments on which they bury and from where they mainly feed. Mullet is a demersal fish, whose diet consists of pelagic and benthic organisms and is less exposed to eventually sediment-associated contamination than blue crab. Supporting our findings, Romeo et al. (1999) reported that cadmium, copper, mercury, and zinc concentrations in edible muscles of pelagic fish species are lower than for benthic fish species from the Mauritania coast. Besides, in the another study in the same sampling area, it was reported that the levels in *Balanus* sp. of all metals studied were higher than those in *Patella caerulea* except for chrome, and that *Balanus* sp. proved more successful as a biomonitor of metals than *P. caerulea*, providing a constant picture of metal bioavailability (Türkmen et al. 2005a).

Based on the analyzed samples, metal concentrations found in the muscles of fish were not heavily burdened with metals, and the concentrations were below the legal values for fish and fishery products proposed by Nauen (1983) and EPA (2002). Measured concentrations of Cd (1.06-2.51), Cr (2.82-6.56) and Ni (1.63-4.19) in crab were lower than USFDA (2003) limits for crustacean of 3, 12 and 70 for Cd, Cr and Ni, respectively. However Pb concentration with 2.67-4.30 in the present study was higher than that of USFDA limit (1.5). Similar patterns were reported from İskenderun Bay (Türkmen et al. 2005b, Türkmen and Türkmen 2005). When compared with previous data, present findings indicated that concentrations of metals in fish from the bay slightly decreased. However, these results should be confirmed occasionally by running more detailed studies in the bay to better monitor and understand the current situation.

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