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Seasonal and Spatial Variations of Heavy Metals in the Spiny Rock Oyster, *Spondylus spinosus,* from Coastal Waters of Iskenderun Bay, Northern East Mediterranean Sea, Turkey

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The İskenderun Bay is located in the eastern-most part of the Mediterranean Sea off southern Turkey (36°C20′N-35°C30′E;36°C50′N-35°C00′E). There is lack of information about the history of pollution along the eastern part of the Mediterranean Sea (Turkish coast). Along the coast of the bay, there are many towns including İskenderun, with an approximate population of 700.000 to 800.000. The bay has an economic importance for aquaculture and fisheries. Sewage wastes from these cities and ship maintenance works are dumped directly into the sea without any treatment. Industries in this region of the Mediterranean Sea have been expanding. Most of these industries, such as a cement factory, textiles, tin, iron and steel factories, aluminum works, battery factory, wood processing, power station, rubbish treatment, food conserves, oil refinery, phosphate loading activities etc., use sea or river systems to dump their sewage. In addition, local practices are not the only potential source of pollution. The predominant current pattern indicates that pollution from outside the Mediterranean Sea is highly possible. Consequently, industrial and urban development in coastal areas exacerbates the marine pollution problem. Wastewater collection and disposal systems have been planned and constructed in some areas, but these are still not sufficient in some other primarily areas due to limited budgets.

One of the most important threats to the Mediterranean ecosystem is metal pollution. Raised levels of several trace metals, released into the marine ecosystem by natural and anthropogenic sources, have been reported in different areas of the Mediterranean basin (Cubadda et al. 2001). Intense pollution in the bay has inevitably increased the levels of heavy metals in the water. Therefore, it became important to determine the levels of heavy metals in water in order to evaluate the possible health risk of fish and other organisms consumed by humans. This paper indicates preliminary results on the levels of cadmium, iron, copper, chromium, cobalt, zinc, lead, nickel, aluminum and manganese in spiny rock oyster, *Spondylus spinosus*, from the İskenderun Bay.

MATERIAL AND METHODS

Oysters were collected in October 2001 and January, April and July 2002 in three

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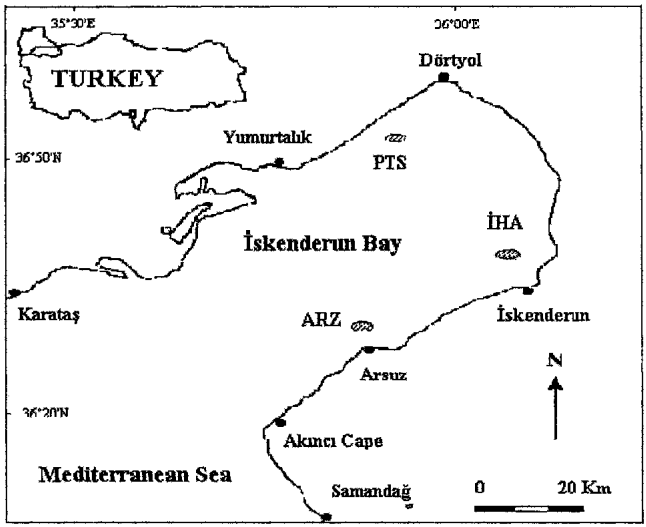

Figure 1. Location map of sampling stations in İskenderun Bay.

stations in İskenderun Bay. Figure 1 shows these stations as Arsuz (ARZ), İskenderun Harbour Area (IHA) and Petrotrans (PTS). During the study, about 300 oysters, *Spondylus spinosus*, were manually collected in depths of 5-15 m by snorkeling and scuba diving, and transferred to the laboratory. About 25-35 oysters at each station were pooled monthly, producing 7 subsamples to analyze. Edible body parts were rinsed with distilled water and dried at 105 °C to a constant dry weight (Mo and Neilsen 1994). Samples were digested with concentrated ultrapure nitric acid in a microwave oven (Cem Mars-5 Closed Vessel Microwave Digestion System), and stored until analysis (Blust et al., 1998). Analysis of metals (Cd, Fe, Cu, Pb, Zn, Co, Cr, Al, Mn, Ni) were carried out by using Varian SpectrAA 220 Fast Sequential Flame-AAS. Analytical blanks were run in the same way as the samples and concentrations were determined using standard solutions prepared in the same acid matrix. Suspensions were duplicated with results as mean values. Results were expressed in mg kg^{-1} dry weight. The absorption wavelength and detection limits were 228.8 nm and 0.02 ppm for Cd; 324.7 nm and 0.03 ppm for Cu; 425.4 nm and 0.4 ppm for Cr; 232.0 nm and 0.1 ppm for Ni; 217.0 nm and 0.1 ppm for Pb; 213.9 nm and 0.01 ppm for Zn; 240.7 nm and 0.05 ppm for Co; 396.1 nm and 0.5 ppm for Al; 279.5 nm and 0.02 ppm for Mn; 248.3 nm and 0.06 ppm for Fe, respectively. The accuracy and precision of present results were checked by analyzing standard reference material. The results indicated good agreement between the certified and analytical values, the recovery of elements being practically complete for most of them.

A logarithmic transformation was done on the data to improve normality. One-way analysis of variance (ANOVA) and Duncan's test ($p=0.05$) were used to access whether heavy metal concentrations varied significantly between stations and seasons. Statistical analysis were considered significant at $p<0.05$. Data were analyzed with SPSS 9.0 for Windows.

RESULTS AND DISCUSSION

Seasonal and spatial variations of the heavy metal concentrations (HMCs) in *Spondylus spinosus* from İskenderun Bay were reported in Table 1 and shown in Figure 2. The HMCs in *S. spinosus* varied seasonally, and differences among seasons were significant ($p<0.05$) except Cu in all stations, Zn in stations İHA and PTS, Cr in station ARZ, and Al in station PTS. Generally, Cd, Pb, Co, Ni and Al (October in PTS) in January, Fe, Cr and Mn (July in PTS) in April, Zn (April in İHA) in July were higher when compared other months (Table 1). On the other hand, HMC differences among the stations were significant except Cu, Mn and Zn. The levels of Cr in *S. spinosus* were also higher in station ARZ than those in the other stations. The levels of Cu, Zn, Co, Al and Mn in station İHA, Cd, Fe and Pb in station PTS were higher than those in other stations. It is reported that HMCs may vary by season and can be due to changes in growth, reproduction, etc. (Morley et al. 1997; Akçay et al. 2003; Türkmen et al. 2005a).

Table 1. Seasonal and spatial variations of mean HMCs in the spiny rock oyster from İskenderun Bay (seven samples in each month for each station).

	Mean HMCs (mg kg^{-1} dry weight)*									
	Cd	Fe	Cu	Pb	Zn	Co	Cr	Al	Mn	Ni
ARZ										
Oct	4.71^{b}	67.1^{a}	17.2^{a}	4.63^{c}	79.2^{a}	2.54^{b}	16.5^{a}	70.8^{bc}	9.05^{a}	9.85^{b}
Jan	13.5^{a}	52.7^{a}	10.5^{a}	151^{a}	63.4^{a}	10.5^{a}	13.7^{a}	124^{a}	19.5^{ab}	38.5^{a}
April	0.52^{b}	75.4^{a}	16.7^{a}	54.8^{b}	20.8^{b}	0.38^{b}	24.6^{a}	33.2^{c}	41.7^{c}	33.8^{a}
July	1.63^{b}	62.2^{a}	13.6^{a}	29.2^{bc}	95.8^{a}	0.52^{b}	17.7^{a}	87.5^{ab}	29.2^{bc}	8.91^{b}
Total	*4.96^{x}*	*64.4^{x}*	*14.5^{x}*	*59.9^{x}*	*64.8^{x}*	*3.47^{x}*	*18.1^{x}*	*78.8^{x}*	*24.8^{x}*	*22.8^{x}*
İHA										
Oct	9.21^{b}	205^{ab}	18.9^{a}	12.9^{b}	71.6^{a}	12.6^{a}	9.47^{a}	109^{ab}	12.1^{a}	29.4^{bc}
Jan	29.8^{a}	147^{a}	13.1^{a}	266^{a}	67.3^{a}	14.7^{a}	8.26^{a}	155^{a}	18.5^{ab}	72.6^{a}
April	3.74^{b}	315^{b}	23.3^{a}	79.3^{b}	104^{a}	3.17^{b}	4.54^{a}	54.2^{b}	54.2^{c}	50.5^{ab}
July	1.78^{b}	203^{ab}	26.1^{a}	63.5^{b}	88.2^{a}	8.96^{ab}	16.8^{b}	134^{a}	37.5^{bc}	4.79^{c}
Total	*11.1^{y}*	*218^{y}*	*20.4^{x}*	*105^{y}*	*82.8^{x}*	*9.85^{y}*	*9.78^{y}*	*113^{y}*	*30.6^{x}*	*39.3^{xy}*
PTS										
Oct	11.2^{b}	188^{a}	16.1^{a}	67.1^{b}	75.7^{a}	11.7^{ab}	8.38^{a}	84.6^{a}	9.38^{a}	36.5^{bc}
Jan	40.3^{a}	171^{a}	18.1^{a}	352^{a}	59.4^{a}	16.4^{a}	10.5^{a}	49.3^{a}	26.4^{ab}	101^{a}
April	4.71^{b}	358^{b}	13.2^{a}	70.7^{b}	75.8^{a}	2.04^{c}	25.5^{b}	63.0^{a}	38.0^{b}	42.2^{b}
July	4.08^{b}	288^{ab}	10.9^{a}	41.7^{b}	91.7^{a}	8.33^{c}	13.7^{a}	67.1^{a}	41.7^{b}	5.21^{c}
Total	*15.1^{y}*	*251^{y}*	*14.6^{x}*	*132^{y}*	*75.7^{x}*	*9.61^{y}*	*14.5^{x}*	*66.0^{x}*	*28.9^{x}*	*46.3^{y}*

*Vertically, letters a, b and c show differences among months at same stations; x, y and z between stations. Within columns, means with the same letter are not statistically significant, $p>0.05$

The distribution of the HMCs in *S. spinosus* ranges followed as: Cd: 0.52-29.8, Fe: 52.7-358. Cu: 10.5-26.1. Pb: 4.63-352. Zn: 20.8-104. Co: 0.38-16.4. Cr: 4.54-

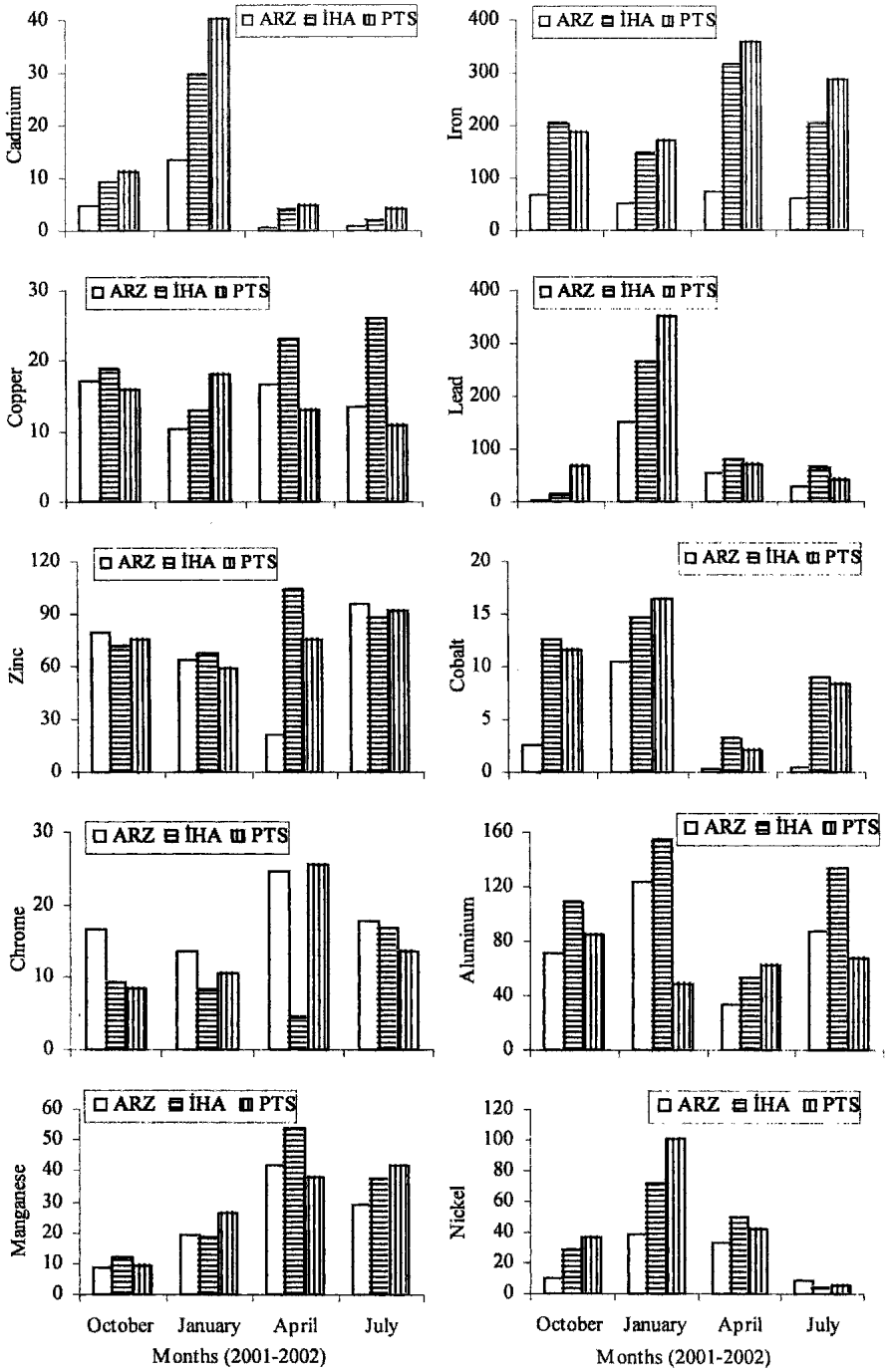

Figure 2. Seasonal and spatial variations of the HMCs as mg kg^{-1} dry weight in the *Spondylus spinosus* from İskenderun Bay (sampling stations; ARZ, İHA and PTS).

Table 2. Comparison of HMCs in the *S. spinosus* from İskenderun Bay with results taken from the other studies.

	Heavy metal concentrations, mg kg^{-1} dry wt.									
Sampling area	Cd	Fe	Cu	Pb	Zn	Co	Cr	Al	Mn	Ni
Florida Bay[1]	0.49-12.9	232-586	63-2013	0.23-13.3	925-9077	-	0.29-11	129-614	11.4-38	0.39-13.4
Mazatlan Bay[2]	2.3	2560	86.9	2.3	1161	-	0.99	-	18.8	5.41
Mexico Bay[3]	4-6	290-370	150-250	0.6	1880-2150	-	-	-	14-18	1.8-2.2
Basque Coast[4]	2.91	102-860	417	3.25	3084	-	2.80	-	-	3.96
Iberian Peninsula[5]	0.3-2.7	28	12-292	2-26.5	190-997	2.3-11.2	3.1-25.8	-	2.3-12.4	5.2-23.8
İskenderun Bay[6]	0.01-4.16	0.82-27.4	0.04-5.43	0.09-6.95	0.60-11.6	0.03-5.61	0.07-6.46	0.02-5.41	0.05-4.64	0.11-12.9
İskenderun Bay[7]	0.52-29.8	52.7-358	10.5-26.1	4.63-352	20.8-104	0.38-16.4	4.54-25.5	33.2-154	12.1-54.2	4.79-101

[1]: Oliver et al. 2001; [2]: Soto-Jiménez et al. 2001; [3]: Presley et al. 1989; [4]: Franco et al. 2002; [5]: Carballeira et al. 2000; [6]: Türkmen et al. 2005a; [7]: This study

25.5, Al: 33.2-154, Mn: 12.1-54.2 and Ni: 4.79-101 mg kg^{-1} dry weight, respectively. Table 2 compares the heavy metal concentrations in the *S. spinosus* from İskenderun Bay with values in oyster species taken from the previous studies. Present results were compared with other oyster species because there were no studies about *S. spinosus*. In this study, concentrations of Pb and Ni measured in *S. spinosus* were higher than those reported for other sampling areas. Cu and Zn levels were lower than those reported for other sampling areas. Cr levels were higher than those reported for Florida Bay (Oliver et al. 2001), Mazatlan Bay (Soto-Jiménez et al. 2001) and Basque Coast (Franco et al. 2002). Generally, Fe levels were lower than other locations except Iberian Peninsula (Carballeira et al. 2000). Cd levels were higher than other locations except Florida Bay. Mn levels were higher than those reported for Iberian Peninsula. This situation indicated that differences between pollution levels of compared areas depend on species and regional properties. On other hand, the results of this study were higher than those determined for fish in the same area (Türkmen et al. 2005a). Thus, it may be said that *S. spinosus* compared to fish in the bay may be useful for monitoring programs of the heavy metal pollution. Besides, in the another study in the same sampling area, it was reported that the levels in *Balanus* sp. of all heavy 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. 2005b).

Heavy metal concentrations in the *S. spinosus* from İskenderun Bay were monitored from October 2001 to July 2002. HMCs showed seasonal and spatial variations during the study. Although the mean concentrations of Cd and Pb in *S. spinosus* from the bay were higher than the legal limits proposed for mollusks by the Republic of Turkish (Anonymous 2002) and Nauen (1983), Cu and Zn levels generally agree with the legal limits. Although the levels of Cd, Pb and Ni were higher than the legal limits proposed by EPA (2002), other metals were lower. According to these results, in future, to prevent this heavy metal pollution threat in İskenderun Bay, taking into consideration the biodiversity in this ecosystem, it is thought that it is inevitable that protective measurements must be started as soon as possible.

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