A Biomonitoring Study: Heavy Metals in *Monodonta turbinata* (Mollusca: Gastropoda) From Iskenderun Bay, North-Eastern Mediterranean

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Abstract.- Metal (Fe, Zn, Cd, Cu, Co, Ni, Al, Mn, Pb and Cr) levels were investigated in the muscle tissue of *Monodonta turbinata* from seven different stations in Iskenderun Bay. Accumulations of all elements were effected from seasonal changes in all stations. The highest levels of Zn (101.42 μ g/g), Cd (9.01 μ g/g), Cu (334.47 μ g/g) and Pb (90.8 μ g/g) were found in the station Çevlik. However, the highest levels of Fe (3176.85 μ g/g), Co (12.76 μ g/g), Ni (26.93 μ g/g), Al (409.30 μ g/g), Mn (49.40 μ g/g) and Cr (45.06 μ g/g) were observed in the station Kaleköy. Mean concentrations except Zn that was lower in the station Dörtyol were generally lower in the station Yumurtalik. Fe showed the highest levels in all stations compared to the rest of the elements. The high concentration of heavy metals was observed during spring. The data indicate that *M. turbinata* is very efficient heavy metal accumulator and, therefore, may be used successfully to monitor heavy metal presence in Iskenderun Bay.

Keywords: Gastropoda, Monodonta turbinata, heavy metals.

INTRODUCTION

Heavy metals in aquatic system can accumulate in low levels naturally by the slow leaching from soil/rock to water causing no serious deleterious effects on human health. The development of industry and agriculture promotes the rapid increase of environmental metal pollution. Aquatic heavy metal pollution usually represents high levels of Hg, Cr, Pb, Cd, Cu, Zn, Ni etc. in water system. The anthropogenic activities such as discharge of heavy metal waste into water contribute to the predominant causation (Yousafzai and Shakoori, 2008; Zhou *et al.*, 2008).

The use of molluscs as biomonitors of heavy metals in coastal zones is well established (Rainbow and Philips, 1993). Although bivalve molluscs have been widely utilised as biomonitors (Goldberg *et al.*, 1983), gastropod molluscs like patellid limpets or top-shell snails are increasingly employed in a similar role (Nicolaidou and Nott, 1998; Cubadda *et al.*, 2001; Hamed and Emara, 2006). Gastropods are dominant group of molluscs in Iskenderun Bay (Bakir *et al.*, 2012). Therefore, it was chosen one of the most abundant specimens of gastropod,

M. turbinata.

In recent years, researchers have focused their attention on the identification of possible bioindicators for trace metal pollution, such as the gastropod molluscs. This is because it is necessary to identify a wider range of bioindicators and thus expand current understanding of different bioaccumulation strategies for trace metals.

This research was conducted in Iskenderun Bay, which is situated on the Eastern Mediterranean coast of Turkey. This region is not only highly industrialized are but also have a huge bad. Due to heavy agricultural and industrial activities in the region, the bay receives large quantities waste from both sources and has one of the most polluted coastal waters of Turkey (Kargin, 1996).

Some studies have been published on determination of trace metals and contaminants in gastropod molluscs *Patella caerulea* from Iskenderun Bay (Türkmen *et al.*, 2005; Yüzereroğlu *et al.*, 2010).

Altough the elemental composition of *Monodonta turbinata* has been studied (Axiak and Schembri, 1982; Nicolaidou and Nott, 1998; Conti and Cecchetti, 2003), there hasn't been any research carried out in Iskenderun Bay, Turkey, Northeastern Mediterranean Sea. The studies on the identification of biomonitor of afore mentioned area are scare and incomplete.

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The primary aim of this work was to quantify levels of Fe, Zn, Cd, Cu, Co, Ni, Al, Mn, Pb and Cr in *M. turbinata* from seven stations of Iskenderun Bay. Besides, possible relationships between concentrations, seasons and stations were also investigated.

MATERIALS AND METHODS

Sample site

Iskenderun Bay is located at the North east part of Mediterranean Turkey. Due to industrial and agricultural activities carried in the region, this Gulf receives large quantities of untreated or partially treated industrial waste and domestic sewage. Previous studies indicated that agricultural and industrial effluents and harbor operations were the main sources of marine pollution problems in this area (Yilmaz *et al.*, 2002; Yilmaz, 2003; Cogun *et al.*, 2005; Türkmen *et al.*, 2005; Firat *et al.*, 2008).

The stations are Yumurtalik, Dörtyol, Payas, Iskenderun, Arsuz, Kale and Çevlik Coasts of Iskenderun Bay and 10 specimens of *M. turbinata* from each station were collected in Spring and Autumn seasons, because of this specimens are more abundant in coastal area of Iskenderun Bay (Fig. 1). Specimens collected during the sampling period were immediately transport to the laboratory on ice. Shell height, weight, shell width, body whorl and aperture width of the samples were measured and the mean average value calculated to centimeter and gram (Table I).



Fig. 1. Sampling areas in Iskenderun Bay.

Digestion procedures

Ten samples from each sampling station were analyzed in spring and autumn in order to determine metals in their muscle tissues. Their muscle tissues were dried at 110°C for 48 h. Average 1g sample was transferred into a digestion flask containing 2 ml nitric acid and 1 ml perchloric acid (Merck) and digested at 120°C for 3 h (Liang *et al.*, 1999). The digest was diluted with distilled water appropriately in the range of standards which were prepared from stock standard solution of the metals (Merck). A blank digest was carried out in the same way. All metals were determined against aqueous standards. Three replicates of digested samples were analyzed each metal.

Table I.-The weight (g), shell width (cm), body whorl
(cm), shell height (cm) and aperture width
(cm) of Monodonta turbinata.

Season	n	Spring	Autumn
Weight (g)	10	0.48 ± 0.03	3.29±0.16
Shell width (cm)	10	2.20 ± 0.05	2.07±0.03
Body whorl (cm)	10	2.34 ± 0.07	2.33±0.02
Shell height (cm)	10	2.62 ± 0.08	2.62 ± 0.06
Aperture width (cm)	10	1.70 ± 0.04	1.20 ± 0.03

Mean±SEM

Analytical procedures

After dilution, metal contents of tissue measured on a inductively coupled plasma atomic emission spectrometry (ICP-AES) (Varian model, Liberty Series II; Palo Alto, USA) and metal concentration in the tissue was presented as $\mu g/g$. For calibration ICP-AES was used as a High Purity Multi Standard.

Metal concentrations were calculated $\mu g/g$ dry weight. The quality of data was checked against the analysis of standard reference material DORM-2 (National Research Council of Canada; dogfish muscle and liver MA-A-2/TM Fish Flesh). Replicate analyses of reference materials showed good accuracy with recovery rates for metals between 96% and 106%. The results showed good agreement between the certified and the analytical values.

Statistical analysis

To test the differences between the element concentrations in stations and seasons, two way analysis was performed. The posthoc test (Tukey) was applied to determine statistically significant differences (SPSS 17.0).

RESULTS AND DISCUSSION

Metal levels in *M. turbinata* samples collected from the seven sites in Iskenderun Bay are given in Table II. The results of statistical comparisons of metal levels between seven stations are also given in this table.

The comparison between metal levels in the samples from the seven stations showed that all metal concentrations differed significantly in Spring and Autumn. The maximum levels in all metals except Cu and Ni were observed in spring. It could be owing to heavy rainfall during spring which increases the metal content of water by washing down the agricultural wastes (Ersoy and Çelik, 2010).

The concentrations of heavy metals showed location-dependent variation. The heavy metal concentrations were significantly different between stations (p<0.05).

The highest levels of Zn (101.42 μ g/g), Cd (9.01 µg/g), Cu (334.47 µg/g) and Pb (90.8 µg/g) were found in the station Çevlik. However, the highest levels of Fe (3176.85 µg/g), Co (20.03 μg/g), Ni (26.93 μg/g), Al (409.30 μg/g), Mn (49.40 $\mu g/g$) and Cr (45.06 $\mu g/g$) were determinated in the station Kaleköy. Cevlik is a fishing port but Kaleköy is a busy area in terms of residential quarters which discharges high quantity of household wastes. This situaiton may explain why the stations Kaleköy and Çevlik are more polluted than other the stations. On the other hand, mean concentrations except Zn, that was lower in the station Dörtyol, were generally lower in the station Yumurtalik. Fe showed the highest accumulation in all stations, and Cu accumulated at the second highest levels in all stations except Kaleköy and Arsuz which Al concentrations were second.

Gastropod molluscs and bivalve molluscs are good indicators for the long-term monitoring of metal pollution in the marine environment. These species are easy to identify and to sample, and are available all year around and in almost all coastal areas of Mediterranean Sea (Conti and Cecchetti, 2003). The ability of molluscs to accumulate heavy metals in their tissues in well known. Molluscs are filter-feeding organisms characterized by low biotransformation capacities. They accumulate the bio-available fraction of the contaminants present in the water and the metal content of their tissues reflect generally the profile of the pollution (Storelli and Marcotrigiano, 2001).

In *M. turbinata* collected from seven stations, the levels of Fe, Zn, and Cu have been found quite high. Zn, Fe, and Cu are essential elements and play important roles in growth, cell metabolism, and survival of most animals including molluscs. Hence, the relatively high levels of these metals can be attributed to their essentiality (Pourang *et al.*, 2005). A capacity to regulate the internal concentrations of these essential elements has been reported for some mollusks (Amiard-Triquet *et al.*, 1986).

The heavy metal concentrations were determined gastropod molluscs from other areas of Eastern Mediterranean Sea. Nicolaidou and Nott (1998) reported that Cd, Cu, Fe, Mn, Ni and Zn levels in M. mutabilis were 3.6, 43.15, 158.9, 9.4, 2.2. 109.0 µg/g, respectively. Heavy metal concentrations of M. turbinata were similar to those reported for the east costs of Greece in the Mediterranean. It was reported that Cd, Cr, Cu, Pb and Zn concentrations of M. turbinate collected at six coastal stations in the area of the Gulf of Gaeta (Tyrrhenian Sea, central Italy) were 0.86-1.41, 0.26-50.5-83.0, 0.44-0.67, 77.7-129.3 0.72. $\mu g/g$, respectively (Conti and Cecchetti, 2003). Cr, Cu and Zn values are similar to our results; however Pb and Cd values were lower than our values. Similarly, Cd, Cr, Cu and Zn levels were reported as 0.68-2.93, 0.12-0.41, 5-18.5, 13.8-53.7 µg/g, respectively in M. turbinata collected from four stations in Mediterranean Sea (Cubadda et al., 2001).

Other studies carried out Iskenderun Bay obtained similar results (Türkmen *et al.*, 2005; Yüzereroğlu *et al.*, 2010). Yüzereroğlu *et al.* (2010) measured the concentrations of Cd, Cu, Zn, Fe, Pb, Ni, and Co in gastropod molluscs *Patella caerulea* in the Iskenderun Bay and concluded that, generally, high concentrations of heavy metals occurred during

Metals	Seasons	Çevlik	Konacık	Kaleköy	Arsuz	İskenderun	Dörtyol	Yumurtalık
Fe	Spring [*]	391.49±52.93 ^{a.x}	52.56±10.37 ^{b.x}	3176.85±1232.55 ^{cx}	513.14±31.03 ^{a.x}	196.18±45.54 ^{a.b.x}	36.43±13.54 ^{d.x}	7.95±1.42 ^{d.x}
	Fall [*]	232.31±86.54 ^{a.x}	275.07±65.70 ^{a.x}	361.26±139.49 ^{ay}	265.03±50.18 ^{a.x}	156.75±10.74 ^{a.x}	450.12±106.84 ^{a.y}	197.22±47.96 ^{a.x}
Zn	Spring*	$101.42\pm11.41^{a.x}$	$30.17\pm7.93^{\rm b.x}$	32.56±4.39 ^{b.x}	54.00±18.54 ^{b.x}	$43.81\pm20.79^{b.x}$	15.87±6.15 ^{c.x}	27.32±8.56b ^{b.x}
	Fall*	79.98 $\pm10.97^{a.y}$	$85.97\pm18.07^{\rm a.y}$	79.33±9.73 ^{a.y}	60.66±6.15 ^{b.x}	$80.37\pm16.67^{a.y}$	89.30±28.64 ^{a.y}	76.66±8.81 ^{a.y}
Cd	Spring*	9.01±3.02 ^{a.x}	3.24±0.66 ^{b.x}	2.51±0.43 ^{b.x}	5.42±1.35 ^{c.x}	3.50±1.15 ^{d.x}	$4.95\pm1.01^{c.x}$	2.15±0.08 ^{d.x}
	Fall*	7.63±0.29 ^{a.y}	6.50±1.28 ^{b.y}	8.58±0.95 ^{c.y}	6.48±1.05 ^{a.x}	7.69±1.57 ^{a.y}	$6.63\pm2.70^{b.y}$	8.15±1.23 ^{c.y}
Cu	Spring [*]	$29.30\pm 9.81^{a.x}$	25.17±7.39 ^{a.x}	$20.03\pm3.07^{a.x}$	40.61±14.78 ^{a.x}	$30.57\pm9.15^{a.x}$	39.38±10.94 ^{ª.x}	11.05±2.29 ^{a.x}
	Fall [*]	$334.47\pm 83.27^{a.y}$	181.76±35.38 ^{b.y}	$156.25\pm52.79^{c.y}$	157.98±27.13 ^{c.y}	$177.13\pm38.40^{b.y}$	140.35±54.89 ^{d.y}	139.04±69.56 ^{d.y}
Co	Spring [*]	$6.63\pm1.14^{a.x}$	1.73±0.20 ^{b.x}	14.21±4.63 ^{c.x}	$1.97\pm0.59^{b.x}$	1.56±0.56 ^{b.x}	$5.40\pm1.56^{a.x}$	2.62±0.34 ^{b.x}
	Fall [*]	12.76±1.03 ^{a.y}	10.66±1.32 ^{b.y}	8.47±1.42 ^{c.y}	5.21±0.80 ^{d.y}	4.21±0.16 ^{d.y}	$4.92\pm1.44^{d.x}$	2.74±0.76 ^{e.x}
Ņ	Spring [*]	4.91±1.97 ^{a.x}	5.81±1.84 ^{a.x}	$3.22\pm1.51^{a.x}$	16.89±1.11 ^{b.x}	$2.93\pm1.46^{a.x}$	$12.04\pm4.20^{b.x}$	$5.33\pm2.63^{a.x}$
	Fall [*]	2.67±0.82 ^{a.x}	4.86±1.13 ^{a.x}	$26.93\pm14.10^{b.y}$	17.16±4.80 ^{b.x}	$2.55\pm0.37^{a.x}$	9.08 $\pm4.57^{b.x}$	$2.38\pm0.62^{a.x}$
W	Spring [*]	$11.86\pm 2.44^{a.x}$	57.57±10.76 ^{b.x}	409.30±37.94°. ^x	329.41±46.69 ^{d.x}	21.58±9.50 ^{a.x}	$70.33\pm23.78^{b.x}$	$3.49\pm1.02^{a.x}$
	Fall [*]	37.02 $\pm 12.78^{a.y}$	34.64±8.28 ^{a.y}	41.82±26.53 ^{a.y}	38.25±7.12 ^{a.y}	3.059±5.60 ^{a.x}	$100.75\pm27.60^{b.y}$	26.29 $\pm8.68^{a.y}$
Mn	Spring [*]	$15.50\pm5.11^{a.x}$	5.56±2.11 ^{b.x}	49.40±7.66 ^{°.x}	15.64±2.69 ^{a.x}	3.09±1.86 ^{b.x}	3.26±1.29 ^{b.x}	$1.67\pm0.96^{b.x}$
	Fall [*]	4.91±0.70 ^{a.y}	3.14±0.75 ^{a.x}	12.85±2.89 ^{b.y}	3.56±0.71 ^{a.y}	4.23±0.16 ^{a.x}	12.19±4.52 ^{b.y}	5.12±1.07 ^{a.y}
Pb	Spring [*]	90.8±2.61 ^{a.x}	2.97±0.61 ^{b.x}	$3.25\pm0.19^{b.x}$	1.44±0.32 ^{b.x}	$3.34\pm1.82^{b.x}$	5.36±2.11 ^{c.x}	2.64±0.89 ^{b.x}
	Fall [*]	13.34±0.44 ^{a.y}	15.68±1.55 ^{b.y}	$13.02\pm1.40^{a.y}$	13.29±3.17 ^{a.y}	$13.54\pm0.91^{a.y}$	12.47±1.63 ^{a.y}	14.30±1.19 ^{a.b.y}
Cr	Spring [*]	$3.67\pm1.68^{a.x}$	32.24±6.40 ^{b.x}	45.06±13.43°.×	2.91±1.65 ^{a.x}	1.43±0.49 ^{a.x}	$2.20\pm0.72^{a.x}$	$0.46\pm0.39^{a.x}$
	Fall [*]	$3.02\pm0.91^{a.x}$	1.74±0.32 ^{b.y}	6.46±2.42°. ^y	3.53±0.72 ^{a.x}	1.76±0.19 ^{b.x}	$3.31\pm1.50^{a.x}$	4.37±1.04 ^{a.y}
Letters x an Data shown	d y show diff with differen	erences among sease it letters are statistic	ons; a,b,c and d amc ally significant at th	ng stations. e differences p<0.05 lev	vel.			

Mean heavy metal concentrations (±standard deviation) (µg/g dry weight) in muscle of *M. turbinata*. Table II.-

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the winter and spring months. Finally, researchers suggested that *P. caerulea* may be used successfully to monitor heavy metal presence in Iskenderun Bay.

CONCLUSIONS

M. turbinata has considerable potential as biomonitor of heavy metals and this species is available in every season all over the Mediterranean coastal area and is easy to sample and identify. The maximum metal levels except Cu and Ni were found in Spring season. The differences between stations were statistically significant. The highest levels of heavy metals were found in the stations Cevlik and Kaleköy. The cause for such pollution in the station Cevlik and Kaleköy is due to considerable industrial activity and domestic discharges into the sea in recent years. Among the metals analyzed Cu and Fe were the most abundant in M. turbinata. Seasonal variation in the concentrations of Fe, Zn, Cd, Cu, Co, Ni, Al, Mn, Pb and Cr was found in all samples collected at seven separate locations.

This study is the first on gastropod molluscs *M. turbinata* in this area and data are important as a background for the estimation of the future impact of metal concentrations in this region. The data indicate that this species is very efficient heavy metal accumulator and can be used as a valuable bioindicator.

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