INT. J. BIOL. BIOTECH., 7 (1-2): 121-126, 2010.

SEASONAL VARIATION IN HEAVY METALS OF TWO SPECIES OF MOLLUSCS, *PERNA VIRIDIS* (BIVALVIA) AND *TURBO CORONATUS* (GASTROPOD) FROM MANORA, KARACHI, PAKISTAN

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ABSTRACT

The concentration of Fe, Pb, Zn, Cd, Cu and Ni in the soft tissues of two molluscs, *Perna viridis* (Bivalve) and *Turbo coronatus* (Gastropod), from Manora rocky beach, Karachi, Pakistan was determined. The concentration of iron was highest among the metals. The other metals were present in following decreasing order of concentration: lead, zinc, copper, cadmium and nickel in both the species. The concentration of all metals except Cu was higher in *T. coronatus* than *P. viridis*.

Keywords: Heavy metals, bivalve, gastropod, Karachi.

INTRODUCTION

Majority of molluscan species either exhibit extremely limited mobility or are completely sessile as adults. These species, therefore, are ideal to study contamination state of their habitat. Bioaccumulation of contaminants by shellfish is a human health issue and is indicative of deteriorating water quality of the ecosystem. Bivalves were widely used for bioindication and biomonitoring purposes (Larsen, 1979; O'Leary and Breen, 1997; Szefer *et al.*, 1997; Goksu *et al.*, 2005; Metian *et al*., 2009). The use of marine gastropods as biomonitors of trace metals is also documented in the literature (Szefer, *et al*., 1999; Campanella *et al*., 2001; Gharuko and Friday, 2007; Wolf and Rashid, 2008).

The BOD load discharged into the marine environment of Karachi was reported to be approximately 3750 tons per day or 1.368 million tons per year consisting of 12 per cent domestic sewage and 84 per cent industrial waste (Beg, 1998). Ahmed (1979) pointed out the extent of industrial and domestic pollution damaging the flora and fauna of the area. He also performed the baseline chemical and biological survey of the Gharo-Phitti creek system to monitor pollution. Numerous publications appeared quantifying the heavy metal concentration in various species of fish, shellfish and mangrove leaves from the coastal area of Karachi (Rizvi *et al.*, 1986; Siddiqui *et al*., 1988; Fatima and Temuri, 1991; Jaleel *et al.*, 1993; Aftab and Qasim, 1994; Fatima, 1996; Saleem *et al.*, 1999; Saleem *et al.*, 2005- to mention a few).The heavy metals in seawater and sludge from various localities of Karachi coast were analyzed by Khan and Saleem (1986) and Beg *et al.* (1992).

This study examines the state of pollution due to heavy metals in two species of molluscs, namely, *Perna viridis* (bivalve) and *Turbo coronatus* (gastropod) from Manora Rocky Shore of Karachi.

MATERIAL AND METHODS

The studies were made on quarterly basis during the ebb tide from March 2008 to December 2008. Forty five to 60 individuals of green mussel (*Perna viridis*) and snail (*Turbo coronatus*) were randomly handpicked from intertidal area of Manora rocky ledge along the coast of Karachi.

The samples were then brought to the laboratory, placed in a deep freezer in order to contain their metabolic activity and to prevent from deterioration. The collected mussels and snails were then washed with tap water to remove sand, silt and barnacles from the exterior.

The mussels were then opened with the help of a stainless steel knife and the shells of snails were broken down with the hammer and their tissues excised on an absorbent paper. The tissues were weighed after drying at 70^0 in a vacuum oven (Memmert) for dry weight.

The dry tissues were grounded using mortar pestle; 0.5 g of powdered samples of a species was digested in PTFE beaker. Digestion was carried out by adding 8 ml. of nitric acid and 1 ml of per-chloric acid on a hot plate placed under a fuming hood following the practice of Qasim *et al*., 1985. After digestion, the sample was diluted with deionised water and distillate was filtered through Whatman No.1 paper. The volume was adjusted to 25 ml with distilled water, and kept in plastic vials. Fe, Pb, Zn, Cd, Cu and Ni were determined using Perkin Elmer A

Analyst-700 Atomic Absorption Spectrophotometer. The metal content was represented as mg/100g dry weight. Three replicates were employed for each treatment.

RESULTS

A. Metal Concentration

i. *Perna viridis*

The concentration of iron ranged from 22.41 mg/100 g (March) to 70.95 mg/100g (June). Next in order of amount was Pb which was minimum (16.18 mg/100g) in March and maximum in December (17.36 mg/100g). The concentration of Zn ranged from 8.49 mg/100 g (June & September) to 9.09 mg/100g (March). Cadmium was minimum (0.26 mg/100g) in March and maximum in September (0.59 mg/100g). The concentration of Cu ranged from 0.24 mg/100 g (June) to 0.58 mg/100g (December). The lowest of all the metals was nickel (Table 1). Values of Fe varied significantly between different months. The values of Pb and Zn did not change with the season.

Table 1. Concentration of heavy metals (mg/100 g dry weight) in soft tissue of *Perna viridis* from Manora rocky shore during 2008. Figures in parentheses denote SD.

Months	Fe	Pb	Zn	Cd	Cu	Ni
March	22.41 (0.02)	16.18 (0.047)	9.09 (0.009)	0.26 (0.005)	0.34 (0.002)	0.15 (0.004)
June	70.95 (0.007)	17.23 (0.032)	8.49 (0.005)	0.36 (0.0008)	0.24 (0.003)	0.03 (0.009)
September	55.25 (0.132)	17.26 (0.037)	8.49 (0.005)	0.59 (0.004)	0.53 (0.005)	0.001 (0.024)
December	44.90 (0.045)	17.36 (0.025)	8.69 (0.008)	0.35 (0.002)	0.58 (0.004)	0.12 (0.012)
Mean	48.38 (20.36)	17.01 (0.56)	8.69 (0.28)	0.39 (0.14)	0.42 (0.16)	0.07 (0.07)

Table 2. Concentration of heavy metals (mg/100 g dry weight) in soft tissue of *Turbo coronatus* from Manora rocky shore during 2008. Figures in parentheses denotes SD.

Months	Fe	Pb	Zn	Cd	Cu	Ni
March	150.20 (0.1)	8.45 (0.085)	11.92 (0.0024)	1.93 (0.0007)	5.99 (0.009)	1.34 (0.033)
June	151.65 (0.132)	13.50 (0.035)	8.46 (0.026)	1.64 (0.003)	5.10 (0.005)	0.68 (0.013)
September	153.20 (0.349)	16.09 (0.049)	8.69 (0.8)	0.78 (0.0039)	2.39 (0.007)	0.78 (0.013)
December	156.20 (0.245)	17.14 (0.035)	8.42 (0.065)	1.23 (0.004)	4.15 (0.022)	0.93 (0.012)
Mean	152.81 (2.57)	13.79 (3.88)	9.37 (1.70)	1.39 (0.50)	4.40 (1.54)	0.93 (0.29)

ii. *Turbo coronatus*

The concentration of iron was extremely high compared to other metals (Table 2), ranging from 150.20 mg/100g (March) to 156.20 mg/100g (December). Next in order of amount was Pb which was minimum (8.45 mg/100g) in March and maximum in December (17.14 mg/100g). The concentration of Zn ranged from 8.42 mg/100

g (December) to 11.92 mg/100g (March). Cadmium was minimum (0.78 mg/100g) in September and maximum in March (1.93 mg/100g). The concentration of Cu ranged from 2.39 mg/100 g (September) to 5.99 mg/100g (March). The lowest of all the metals was nickel which ranged from 0.68 mg/100 gm (June) to 1.34 mg/100 g in (March).

Table 3. Comparative account of concentrations of metals reported in gastropod and bivalve molluscs (mg/100 g dry weight).

Species	Zn	Cu	Pb	Cd	Ni	Fe	Locality/References
Gastropods							
Turbo coronatus	9.37	4.4	13.7	1.39	0.92	152.8	Present Studies
Cellana radiata	6.66	2.46	-	0.90	-	26.93	Pakistan (Fatima & Temuri, 1991)
Litorina littorea	1.08	0.25	0.17	-	0.11	-	Nigeria (Gharuko & Friday, 2007)
Monodonta lineata	8.70	0.56	-	-	0.003	4.92	Ireland (O'Leary & Breen, 1997)
Patella vulgata	21.37	4.45	-	-	0.51	2.12	Ireland (O'Leary & Breen, 1997)
Nucella lapillus	5.0	5.2	-	-	0.3	34.1	Ireland (O'Leary & Breen, 1997)
L. littorina	1.45	1.88	-	-	2.66	21.14	Ireland (O'Leary & Breen, 1997)
Patella caerulea (5 places)	0.35-1.46	0.12-0.2	0.14-1.5	3.3-6.3	-	-	Italy (Campanella *et al.* , 2001)
Monodonta turbinata (4 places)	1.4-5.5	0.57-2.1	0.15-0.6	0.58-0.6	-	-	Italy (Campanella *et al.* , 2001)
Patella rustica	0.884	0.177	1.27	0.37	-	-	Spain (Collado *et al.*, 2006)
P. candei crenata	3.374	0.294	0.09	0.71	-	-	Spain (Collado *et al.*, 2006)
Bivalves							
Mytilus edulis	8.78	0.69	-	-	0.30	23.77	Ireland (O'Leary & Breen, 1997)
Oyster	26.5	1.74	-	-	-	4.1	Pakistan (Kher-un-Nisa *et al.*, 1995)
Crassostrea rivularis	43.3	33.7	-	-	-	57.8	Pakistan (Qasim *et al.*, 1985)
C. madrasensis	55.2	21.3	-	-	-	50.2	Pakistan (Qasim *et al.*, 1985)
C. tuberculata	49.7	44.8	-	-	-	126.1	Pakistan (Qasim *et al.*, 1985)
C. glomerata	39.15	49.6	-	-	-	107.9	Pakistan (Qasim *et al.*, 1985)
Perna viridis	8.6	0.42	17.0	0.38	0.07	48.3	Present Studies
Perna viridis	5.3-18.8	1.1-2.0	-	-	-	27.7-88.3	Pakistan (Rizvi *et al*., 1986)
Perna viridis	6.5-18	1.24-2.1	-	0.287-0.79	-	40.7-60.3	Pakistan (Fatima, 1996)

B. Comparison of Metal Concentration in Two Species of Molluscs

Values of iron in snail (*Turbo coronatus*) are about three times higher than values of mussel (*Perna viridis*). On the contrary, amount of Pb is higher in *P. viridis*. Moreover, the Pb concentration remained almost same throughout the year in *P. viridis* whereas in *T. coronatus* the values gradually increase from a minimum of 8.45 mg/100 gm in March to almost double (17.14 mg/100 gm) in December. The annual average of Zn values of both the species are almost same. The annual average of Cd (1.39 mg/100 gm), Cu (4.40 mg/100 gm) and Ni (0.93 mg/100 gm) of snail (gastropod) is relatively higher than that of mussel (bivalve): Cd (0.39 mg/100 gm), Cu (0.42 mg/100 gm) and Ni (0.07 mg/100 gm).

The average concentration of all metals except Pb was higher in *T. coronatus* than *P. viridis*. Higher amounts of most of the metals in the tissues of *T. coronatus* may be explained due to its free movement in the environment.

Values of trace metals of a few of the gastropod molluscs are presented in Table 3. Results of the presented study showed that concentrations of most of the metals determined are higher than the reported values. Exceptions are, however, seen in case of *Patella vulgata* from Shannon Estuary, Ireland (O'Leary & Breen, 1997). Zn and Cu values were significantly higher than other gastropod species. Similarly, Ni values are extremely high in *Littorina obtusata* and *L. littorina* from Ireland. The values of Fe in the present study are extraordinary high. Next to the present study values are reported for *Nucella lapillus* (Table 3).

Comparative values of trace metals in the tissues of some bivalve molluscs are presented in Table 3. Trace metal values in the oyster species are much higher than those of mussels. However, values of trace metals in *Perna viridis* in the present study are in agreement with those of earlier studies from the same coast but from a different site.

DISCUSSION

Molluscs (bivalves & gastropods) are established accumulators of trace metals and are considered tolerant to a wide range of environmental contaminants (Goksu *et al.*, 2005; Beldi *et al.*, 2006; Collado *et al*., 2006; Gharuko and Friday, 2007; De Wolf and Rashid, 2008; Metian *et al*., 2009). Of the bivalve molluscs, *Mytilus edulis* is the most studied species. Literature on *M. edulis* as biomonitors is reviewed by Bayne (1976) and recently by Szefer *et al.* (1997). It was described by O'Sullivian (1971) as an indifferent species that is the one whose distribution is not greatly affected by pollution. It is because of these characteristics that reported values of trace metals vary greatly not only between different species but in the same species at different sites (Sidwell *et al*., 1973; Gorden and Roberts, 1977). These variations may be attributed to factors such as size, age, sex and degree of sexual maturity (Kher-un-Nisa *et al*., 1995).

Relatively less information is available on other classes of molluscs: *Loligo* sp. (Saleem *et al.*, 1999); Squid (Kher-un-Nisa *et al.*, 1995), *Cellana radiata* (Fatima and Temuri, 1991), *Turbo coronatus* (Szefer *et al*., 1999), *Monodonta turbinata* and *Patella caerulea* (Campanella *et al.*, 2001), *Patella rustica* and *P. camdei crenata* (Collado *et al.*, 2006), *Littoraria scabra* (De Wolf and Rashid, 2008).

Trace metal contents of the molluscan tissues are known to vary with changes in salinity (Larsen, 1979; Manuwadi and Yuangthong, 1984), size-classes (Huggett *et al*., 1975; Szefer *et al.*, 1999), spatial distribution (Jung *et al*., 2006; Addison *et al*., 2008), season (Shiber, 1980; Beldi *et al*., 2006), food source (Metian *et al.*, 2009) etc.

In *Turbo coronatus*, relatively high concentrations of iron, lead and zinc were found in December. Whereas in *Perna viridis* relatively high concentration of lead and zinc was found in December and iron in September.

Shiber (1980) recorded that *Brachydontes variabilis* had the highest copper, *Patella coerulea* had the highest iron, and *Pinctada radiata* had the highest zinc values with rather elevated cadmium. The sampling zone influenced the trace element concentrations, and different uptakes were observed between the mollusc species (España *et al*., 2004). They documented that limpets (*Nacella deaurata)* showed higher mean manganese, nickel and cadmium concentrations than mussels (*Mytilus chilensis)*, whilst the mean selenium concentration in mussels was higher from the coastline of the Magellan Strait, Chile. Fatima (1996) found that the level of all the metals was high in herbivorous gastropod (*Cellana*) than filter feeding bivalve species (*Lithophaga* and *Perna*) living at Paradise Point.

Our results also showed that gastropod (*Turbo coronatus*) had higher iron, lead, zinc, cadmium and nickel concentrations than mussels (*Perna viridis*) while the mean copper concentration in mussels was higher than the gastropod.

Szefer *et al.* (1999) found that sewage input at Sira Island, Yemen was the most likely anthropogenic source of Cu and Mn in soft tissues of *Perna perna*. De Wolf and Rashid (2008) revealed that *Littorina scabra* from polluted areas contained higher soft tissue heavy metal levels and were significantly smaller and weighed less compared to the unpolluted areas. The high content of most of the metals in gastropod and mussel tissues from Manora rocky

shore areas reflects the high amount of metals in the environment. Khan and Saleem (1986) had reported the high contents of metals at the Karachi Harbour where Layari river brings heavy amount of industrial waste. It is also evident from the results that the tissues of mussels and snails from the polluted area have high concentrations of iron, lead and zinc.

Szefer *et al.* (1999) recorded significant spatial differences in metal concentrations in both the soft tissue of the molluscs and associated sediments. The metals disproportionally increased in *Acanthopleura haddoni* and *Turbo coronatus* with a degree of enrichment of the sediments in Fe, Cd and Ni, respectively. According to King *et al.* (2005), the net accumulation of metals from the dissolved phase was greater for Cu than Cd as compared to algae and sediment sources in *Tellina deltoidalis* and *Melita plumulosa*.

Working on sea water and sludge of coastal waters of Karachi, Beg *et al.* (1992) mentioned that level of zinc was highest in autumn. Khan and Saleem (1986) worked on the metal contents of Karachi Harbour sea water; they reported zinc values ranging from 0.44 to 0.68 mg/l and iron from 0.50 to 1.25 mg/l. The highest levels of these metals were recorded near Layari outfall. High amount of iron was attributed to heavy shipping traffic, whereas high level of zinc was explained due to the discharge of industrial waste from SITE industrial area. In *T. coronatus*, the concentration of iron and zinc ranged from 150.2 mg/100g to 156.2 mg/100 g and 8.42 to 11.92 mg/100 g, respectively. And the concentration of iron and zinc in mussel tissue ranged from 22.41 mg/100 g to 70.95 mg/100 g and 8.485 to 9.085 mg/100 g, respectively.

ACKNOWLEDGEMENTS

The second author is extremely grateful to the Faculty of Science, University of Karachi for providing research grant.

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(*Accepted for publication January 2010*)