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Gastropod shells used as a Biomonitor

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Abstract

Level of trace metals (Fe, Mg, Zn and Cu) in four species of gastropod (*Turbo bruneus, Littorina scabra, Nodilittorina pyramidalis* and *Morula funiculata*) shells from Kanniyakumari, southeast coast of India was studied. The accumulation of trace metals was in the order of Mg > Fe > Zn > Cu. The accumulation of Mg and Fe in *T. bruneus* shell was higher than that of in other species. But in the case of Zn and Cu, the concentration was more in *Morula funiculata;* whereas the minimum accumulation of all the metals studied was recorded in the shells of *L. scabra*. In the present study Mg content was found to be varying from 65.35 ± 0.1 (*T. bruneus*) to 13.10 ± 0.284312 ppm (*L. scabra*). The Fe content was higher in *T. bruneus* (3.247 ± 0.005 ppm) and lower in *L. scabra* (1.171± 0.0070 ppm); whereas the Zn content was reported maximum in *Morula funiculata* (2.262 ± 0.005 ppm) and minimum in *L. scabra* (0.655 ± 0.0333 ppm). The Cu concentration was ranging between 0.450 ± 0.05ppm and 0.122 ± 0.007 ppm in *Morula funiculata* and *L. scabra* respectively. So as to understand the background concentration of these trace metals when the level of these metals were studied in the sediment Mg recorded the maximum value of 70.23 ± 0.153 ppm and Cu, the minimum value of 0.7 ± 0.2 ppm.

Key words*:* Trace metals, Turbo bruneus, Littorina scabra, Nodilittorina pyramidalis Morula funiculata and Kanniyakumari.

Introduction

The accumulation of heavy metals in molluscs has been mainly studied from the content of soft tissues [1]. Although heavy metals could be accumulated in soft tissue and calcareous shells of molluscs, yet the biokinetic characteristics of the shell is poorly known [2-3]. The mollusc shell is a microlaminate composite of mineral and biopolymers with exceptional regularity, and with a strength far exceeding that of the crystals themselves in that the calcium carbonate inorganic phase of the shell contributes 98% of the shell mass. The use of gastropod shells as a bioindicator may be useful for determining the extent of biotransformation in aquatic food webs, as an essential component of risk assessment of heavy metals [4].

Although [5] suggested 40 years ago that bivalve shells may act as receptacles for unwanted chemical species, shell trace-metal analyses have rarely been reported in monitoring programs. This is likely related to earlier studies suggesting that metal levels in shells were due to passive adsorption processes and hence, were not indicative of their bioavailability [6-7].

Most metals are generally concentrated many times over within an organism's soft tissue, rather than the shell, and so the vast majority of studies concentrate on the soft tissue. However, some studies of the shell material have also been conducted, and many authors suggest that shells can provide a more accurate indication of environmental change and pollution; they exhibit less variability than the living organism's tissue, and they provide a historical record of metal content throughout the organism's life time, with this record still preserved after death [8-11]. Few studies addressing the heterogeneity in chemical composition amongst shells within the population of an individual species collected from a single location exist. Those that have been reported relate to Patellidae species [12]. The present study mainly focuses on the heavy metal content in the shell of four different species of gastropods commonly found in the rocky shore of Kanniyakumari coast and seeks to determine whether these gastropods can be used as a "biomonitor / bioindicator" of pollution.

Materials and Methods

Metals such as Mg, Fe, Zn and Cu were analysed in the shells of four different species of gastropods such as *Turbo bruneus, Littorina scabra, Nodilittorina pyramidalis* and *Morula funiculata* collected from Kalvilai, (Lat. 08º04'N; Long. 77º36'E) Kanniyakumari, Southeast coast of India. The area was situated in the vicinity of Chinnamuttam landing centre where the untreated domestic sewage is dumping into the sea and also lot of agricultural activities going on near to the study area. The gastropods were collected using hand picking. Then the gastropod shell was broken and the soft tissues were removed. Then the shells were washed with distilled water and dried at 60°C (constant temperature) for 24 hours in a hot air oven then the shells were ground using pestle and mortor. The resulting powder was selected, using a plastic sieve with 0.2mm opening size and was stored in dessicator for further analysis. To estimate the trace metal content (Mg, Fe, Zn and Cu) samples were digested (1g) with conc. HNO_3 and conc. $HClO_4$ (4:1) and analysed in optical emission spectrophotometer (optima 2100DV) [13]. The metal content in sediment was determined by following the method of [14]. The values were expressed in ppm. The standard deviation was calculated and the Analysis of covariance (ANOVA) was performed between the different metals and animals.

Results and Discussion

The use of mollusc shells as sentinels for metal pollution monitoring in marine waters has several advantages over that of the soft tissues. The shells are easy to store and handle and appear to be sensitive to environmental heavy metals over the long term. Since shell growth occurs incrementally they can provide a signal over a discrete time period, unlike the tissues which are strong accumulation of metals and integrate the chemical contamination signal over the life of the organism. Refinement of techniques for determining element using bivalves is important if global monitoring is to become a reality [15-17].

Copper is used in antifouling paints on boats and fish farming equipment, electrical equipment and water pipes. Municipal wastewater, mining and processing of nickel and copper ferro sulphide ($CuFeS_2$) are also notable point sources of copper into the water [18]. In sea water copper exist both dissolved in water and bound to particulate matter [19]. Copper is essential in respiration for many organisms and other enzymatic functions. In contrast, some dissolved copper salts are hazardous for many algae, bacteria and fungi, as well as fish and plankton.

Zinc it is a main sources are metallurgic industry, pyrite mines, galvanic industry, incineration plants and anti corrosive products, paints, plastic and rubber. It is an essential element to all organisms, and for humans a daily intake of 9 mg zinc is needed for normal body functions [20].

Iron is another essential metal, generally abundant in any environment, and has several properties similar to those of manganese; for example, its partitioning between water and sediments is largely controlled by the oxygen concentration in water. Magnesium should be maintained at roughly three times the level of calcium. High magnesium levels are encountered by inappropriate supplementation and can be lethal to some reef invertebrates.

Since shell chemistry roughly reflects that of the water in which the mussel's live, important information on past environmental conditions may be acquired by studying the shell [21-22]. For the same purpose, the chemical composition of shells of living mussels was compared to that of shells from museum collections. The results of this comparison were very interesting and involved a variety of topics such as acidification, eutrophication and metal pollution [23]. Sediments are one of the major sinks of trace metals in the aquatic environment. Sediments may be good indicators of long and medium term metal loads. Likewise, molluscan shell and tissues is also good indicator of metal pollution as they are sessile and sedentary and they reflect the heavy metal concentration of that particular area. The trace metal results obtained by sediment analysis, unlike sea water analysis are generally above the detection limit and contamination risks are significantly reduced concentration of heavy metals in sediments usually exceed those of the overlying water by 3 to 5 orders of magnitude [24]. Metals are distributed predominantly among substrata sites on iron oxides, manganese oxides and various types of organic materials in oxidized sediments [25].

The distribution of heavy metals in Vellar estuary for the Iron concentration in sediment was from 285 to 355 $\mu g\ g^{-1}$. Whereas the highest value was recorded during monsoon and lowest during pre monsoon, this value is comparatively lower than that of the present study. The sediments from the present study were screened for the level of Mg, Fe, Zn and Cu. It was found that the levels of Mg and Fe were high 70.23 ± 0.153 and 4.25 ± 0.1 ppm respectively and the contents of Zn were moderate (3.12 ± 0.0608 ppm) while that of Cu were low (0.7 ± 0.2 ppm)[26].

The moderate enrichment in the surface layers (0-5cm) for iron (1607 - 1905$\mu g\ g^{-1}$) and higher enrichment in the middle layers (15 – 20cm) (4582$\mu g\ g^{-1}$). The present study indicates lower concentration than the earlier study[27]. The marine sediment in two stations, Safaga and Quseir harbours revealed high iron value, because of the different shipment activities such as phosphate shipment; bauxite, cement packing and renewing ship operations [28].

The concentration of magnesium in the shell of marine mollusks varies greatly from species to species. This vast range is primarily due to differences in skeletal mineralogy. Magnesium, with an ionic radius less than calcium, forms a hexagonal carbonate isostructural with calcite. On purely steric grounds it is much more difficult for magnesium ions to be incorporated into marine mollusk shells composed of orthorhombic aragonite rather than hexagonal calcite. In general aragonitic shells have low magnesium concentrations within the range 90 to 500 μg g−. The trace metals (Cu and Mn) were both in significantly lower concentrations than iron and zinc. Both elements also displayed high %CV reaching a maximum for manganese [12]. The mean values (SD) of metal concentration calculated for each shell of the gastropod species are reported **(Fig. 1&2)**.

Fig.1 . Mean values of trace metal contents in shells from four species of gastropods

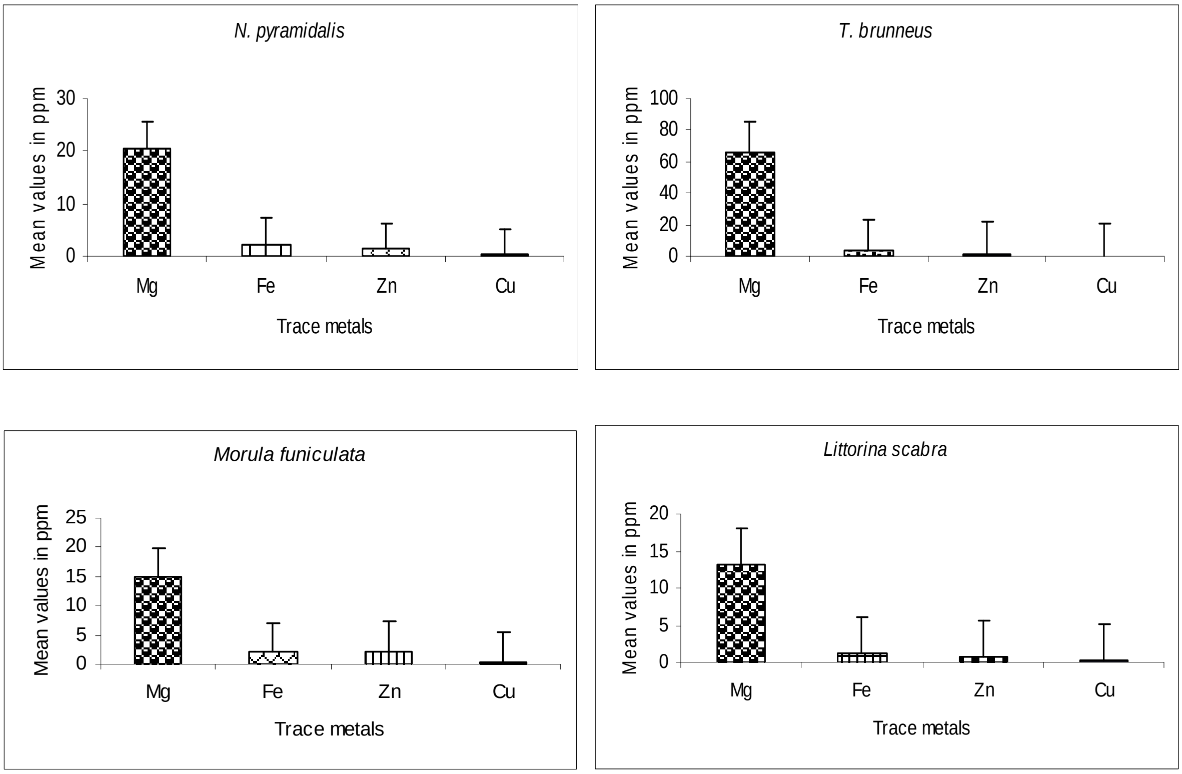
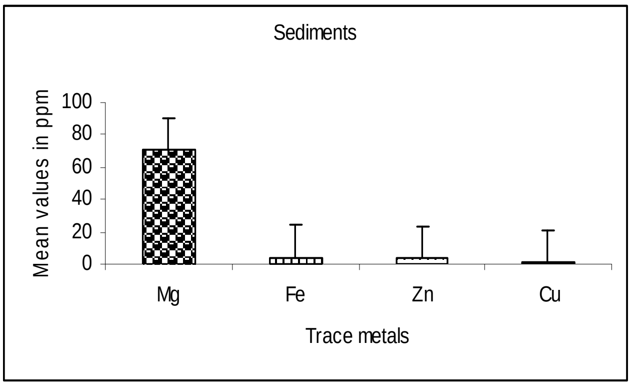


Fig. 2. Mean values of trace metal contents from sediments



These values highlight the fact that the Mg concentration in the 4 species of shells is more than ten times that calculated for the other metals. Accumulation of Mg and Fe found in *T. bruneus* shell were higher than those in other species of shells. But in the case of Zn and Cu concentration was more in *Morula funiculata* and minimum accumulation of all the metal contents was recorded from *L. scabra* because it may be due to the size of the animal which is small compared to other animals taken for analysis and also structure of the shells.

The results obtained from the present study clearly indicate the various levels of accumulation of trace metals in the four different species of gastropod shells. Among the four metals, the degree of accumulation of trace metals in the shells were as follows Mg>Fe>Zn>Cu.

The 'F' value of the analysis of variance between the different metal is significantly varied at $P>0.05$ level (rows) but at the same time the analysis of variance between the animals is not significant at $P<0.05$ level (columns) **Table. 1.**

Table. 1. Analysis of co-variance (ANOVA) between different animals and various metals

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	2225.48	3	741.8266	**4.916401**	**P<0.05**	3.862548
Columns	490.424	3	163.4747	**1.083416**	**P>0.05**	3.862548
Error	1357.993	9	150.8881			
Total	4073.897	15				

The reduced variability associated with nacre - Pb would explain why it provided a better spatial resolution on the degree of Pb contamination among the various sampling sites as compared to the tissue - Pb levels. A total of 5 significantly different ($p < 0.05$) groups were defined based on the tissue - Pb levels, i.e. Groups a to e, whereas 3 additional groups were obtained when using nacre - Pb levels, i.e. Groups g to h from mussel *Mytilus edulis* shell[29].

The accumulation of metals has been mainly studied from the content of the soft tissues. However, metals can accumulate in the shell, which can act as a receptor for these metals [30]. Cd, Zn, Pb and Ag levels were higher in the tissues of *M. edulis* and *M. californianus* than in the shells, although Cu was greater in the shell than in the tissues[31]. Pb levels in the nacre of *M. edulis* collected from near a lead[29] Smeiter off the coast of Quebec and Dalhousie, Canada, were only a tenth of the levels in the tissues. Cd, Cu, Mn and Zn were found to be most concentrated in the prismatic calcite layer of the shell of the oyster *Crassostrea virginica* [32]. But in the present study Cu concentration was ranging between 0.450 ± 0.05ppm and 0.122 ± 0.007 ppm in *Morula funiculata* and *L. scabra* respectively.

The mean concentrations (µg/g dry weight) of Cd, Cu, Fe, Ni, Pb and Zn in the samples were 3.15, 5.59, 49.78, 24.18, 48.86 and 7.86 in the shells of *Nerita lineate*. The Al, Cu, Zn, Fe and Mn levels in shell of *Unio pictorium mancus* from Italy. They reported that the values were found to be 80.86±100.48, 3.53±3.29, 24.00±14.63, 211.20±273.71 and 461.52±252.67 $\mu g\ g^{-1}$[33]. Iron concentration in *Tridacna maxima* shells varies from 216.4ppm at Abu-Ghusun Lagoon to 1286.4ppm at Safaga Harbor [34]. In the present study the mean Fe content was higher in *T. bruneus* (3.247 ± 0.005 ppm) and lower in *L. scabra* (1.171± 0.0070 ppm); whereas the Zn content was reported maximum in *Morula funiculata* (2.262 ± 0.005 ppm) and minimum in *L. scabra* (0.655 ± 0.0333 ppm).

The concentration of iron in male and female was ranged from 80ppm to 247ppm in 55 to 110mm shell size groups of *T. telescopium*. But in the present study the iron content was maximum in *T. bruneus* (3.247 ± 0.005 ppm) and minimum in *L. scabra* (1.171± 0.007 ppm).The zinc concentration in male and female was varied from 71.5ppm to 200ppm in 55 to 110mm shell size groups of *T. telescopium*. In this study zinc content was ranged from 2.262 ± 0.005 ppm to 0.655 ± 0.0333 ppm**,** it was very low when compare the previous study because the availability of metals in the environment[35].

In the earlier [33] the Mn (59%), Al (12%) and Zn (3%) from the shell of *Unio pictorum*. The levels of Cu, Zn and Pb was significantly higher in the dumpsite shell and also control site shells although Pb and Zn significantly declined from the *Modiolus modiolus* shell[36].

In the present study Mg content was found to be varying from 65.35 ± 0.1 (*T. bruneus*) to 13.10 ± 0.284312 ppm (*L. scabra*). The Cu concentration was ranging from 0.450 ± 0.05ppm and 0.122 ± 0.007ppm in *Morula funiculata* and *L. scabra*. In this study in all the four species of gastropod shell were accumulated maximum in Mg and minimum in copper. The increase in concentration during peak agricultural activities due to release of fresh water from the reservoirs. These drainage waters, which contain high heavy metal concentrations, enter the estuaries and mix up with the seawater and also hundreds of boats are available near to the study area.

Elemental concentration of the shells was attributed to different sources by different authors. The elemental concentration fully depended upon the tissues especially mantle and during the period of shell growth, the levels in the soft parts as well as shell increased appreciably. In the presently studied, rocky intertidal gastropods, the elemental concentration of the shells may be related to that of mantle and also to the overlying water [37]. The Mn concentration closely follow Sr concentration across the transects, it is more likely that the variations are an indication of changes in salinity, possibly relating to times of increased discharge, where a flux of saline waters containing increased metal concentrations enters the system.

It has recently been noted that the progress in monitoring studies may depend on identifying specific pathways and storage sites of metals in molluscs. It is not known as of yet if shell analyses will equally apply to other non-essential metals e.g. Cd, Hg [29] also suggested other trace metals would follow a similar pattern and in this respect the deposition of metals in shells should be given renewed attention.
On such evidence it is easy to conclude that shells are particularly sensitive to environmental levels of exposure and could be valuable for monitoring heavy metal contamination in the marine environment. Conversely, the apparent variability in shell composition can often be traced to non-uniform cleaning and treatment procedures before shell digestion and analysis.

Conclusion

The preliminary results of this study suggest that the shells of *T. bruneus,L. scabra, M. funiculata* and *N. pyramidalis* is likely to be of limited used as a biomonitors of metal contamination in the Kalvilai, Kanniyakumari coast. Further studies on other shells from this area will seek to corroborate and clarify these results and will include analyses of living gastropods compared with the waters of their habitat.

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