Open Journal of Marine Science, 2021, 11, 92-102
https://www.scirp.org/journal/ojms
ISSN Online: 2161-7392
ISSN Print: 2161-7384

Seasonal Variation of Heavy Metals in the Intertidal Gastropod *Trochus radiatus* of Gulf of Mannar

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How to cite this paper: Mohanraj, T., Sheeba, M., Cross, S.R.T.S. and Rajathy, T.J. (2021) Seasonal Variation of Heavy Metals in the Intertidal Gastropod *Trochus radiatus* of Gulf of Mannar. *Open Journal of Marine Science*, **11**, 92-102.
https://doi.org/10.4236/ojms.2021.112007

Received: October 11, 2020
Accepted: April 27, 2021
Published: April 30, 2021

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Abstract

Heavy metals are considered to be the most common environmental pollutants in waters and biota; that indicate presence of effluents associated with industrial and domestic sources. The present study aimed to evaluate the trace metal accumulation (Fe, Mn, Zn, Cu, Cd, Pd and Ni) in the tissue of radiate top shell, the sediment and water samples collected from the Hare Island, Tuticorin, during May 2015 to April 2016. During the study, the metal accumulation in the Water, Sediment and Tissue were in the order of Zn > Pb > Cu > Cd; Fe > Mn > Zn > Cu > Cd; Fe > Zn > Mn > Cu > Cd > Pb > Ni respectively. The concentration of Fe dominated in the sediment and tissue sample throughout the study period. Elevated levels of trace metals especially Fe, Mn, Cu, Pb and Zn was observed during October to December, *i.e.*, during the northeast monsoon in all the samples. One way ANOVA indicated statistically no significant difference ($p > 0.01$) in the variation of Fe, Mn and Ni within the samples.

Keywords

Heavy Metal, *Trochus radiatus*, Accumulation, Sediment, Tissue

1. Introduction

The Ocean and coastal waters constitute a variety of human activities that primarily includes fisheries, agriculture, navigation, oil and mineral exploration and waste disposal [1]. Due to easy accessibility and subsequently high human intrusion, rivers, estuaries and coastal waters are found to be more susceptible to pollution [2]. Among the pollutants, trace metals are a serious threat as most of them have detrimental effect on living organisms [3] [4]. The heavy metal pollution chiefly results from the effluents that are discharged untreated into the sea and river mainly from the industrial and municipal sources [5] [6] [7]. These heavy metals are easily accumulated by the primary consumers especially the algae, and are further biomagnified through their transmission across the higher levels of the food chain thus resulting in a direct impact on the human health [8]. Hutton [9] reported Lead, copper, cadmium, Chromium and arsenic to be the most toxic heavy metal pollutants.

Marine pollution especially in India started long back, but has exaggerated during the last few decades and now the situation is turning out to be more dreadful at alarming rate [10]. The distribution of heavy metals in natural waters has widely been recognised as a major aspect in the geochemical behaviour, transport and biological effects of these elements [11] [12] [13]. The evidence from experimental studies on heavy metal contamination in estuaries and coastal waters on *Littorina* sp. that feeds on fucoid seaweeds, suggests that the diet is the most important source of these heavy metal intake [14] [15].

Tuticorin is one of the significant and foremost port hubs that handle several hundreds of ships in a year. It is integrated with several major chemical industries like SPIC, Copper smelting plant, Thermal power station and small scale industrial units of SIPCOT complex. The main source of heavy metal pollution along Tuticorin coastal waters is the effluent discharges especially from the Thermal power station that has a direct effluent (ash) dumping point into the open sea; besides, the fishing operation by mechanized boats also to an extent liberates effluents and petrochemical products into the sea. Earlier investigations by Easterson [16] and Murugan and Edward [17] reveal that in the past few years Tuticorin waters have been adversely affected by industrialization.

A study by Ganesan and Kannan [18] evidenced a higher concentration of Fe and Mn in the sea water, sediment and algae in the vicinity of Tuticorin Port. Palanichamy and Rajendran [7] noticed elevated levels of Cd and Pb in the bottom waters than the surface waters off Tuticorin. Similar surveillance of heavy metals by Baskaran *et al.*, [19] observed a relatively higher concentration of Fe, Cu, Zn and Al in the fly ash dumping area than in the deeper waters off Tuticorin. The intensity of trace metals and nutrients are relatively higher in low saline inshore waters, but lowers with increased salinity [20].

Marine fauna and flora including sea grass, fish and bivalves have the capacity to absorb heavy metals and nutrients from both sediments and sea water [21] [22]. Past studies concerning mussels and oysters from the southeast coast of India show that seasonal variation appear to have an increased metal load, especially during monsoon period [23]. Terlizzi *et al.*, [24] assessed the impact of sewage on rocky shore substrate along the south west Apulian coast, Italy and the results indicated that these effluents could modify the assemblage and natural distribution patterns of sessile organisms. Accordingly in the present study an attempt has been made to determine the levels of seven important trace metals such as Zinc, Iron, Manganese, Copper, Cadmium, Nickel and Lead in the water, sediment as well as the tissue of radiate top shell *Trochus radiatus*, from the Tuticorin waters at different seasons.

2. Materials and Methods

2.1. Study Area

Hare Island (8'47"N and 78'12"E) is located along Tuticorin coast, having sandy substratum, with corals and rocky patches that have luxuriant growth of marine plants, sea grasses and algae (**Figure 1**). The total length of this island is 2.59 Kilometers that is predominantly covered by the trochus bed which is fully exposed during the low tide. Out of the various species of sea weeds inhabiting the study area, *Ulva lactuca* and *Gracillaria* sp. prefer trochus shells as a substratum for its attachment as well as form the primary food source for *Trochus radiatus*. During the rainy season forms a small seasonal stream from east side of the Island that is well connected with the Tuticorin Thermal Power Station's thermal effluent dumping point which leads to mixing of fly ash water with the Island's terrestrial and marine ecosystem. From this study site Water, sediment and radiate top shells were collected manually once every month for heavy metal analysis. The heavy metals namely Fe, Ni, Zn, Mn, Cu, Pb and Cd in the samples were evaluated and the values of each metal were tabulated to check the analysis of variance (ANOVA).

2.2. Tissue Sample

Trochus which is a genus of small sea snails, known as top snails or top shells, inhabit the upper intertidal zone on rocky shores, where they graze on algal films or macroscopic algae. The accumulation of heavy metals was studied over a period of one year *i.e.* from May 2015 to April 2016. The shells were collected manually, washed and kept in filtered sea water to empty the gut. Subsequently

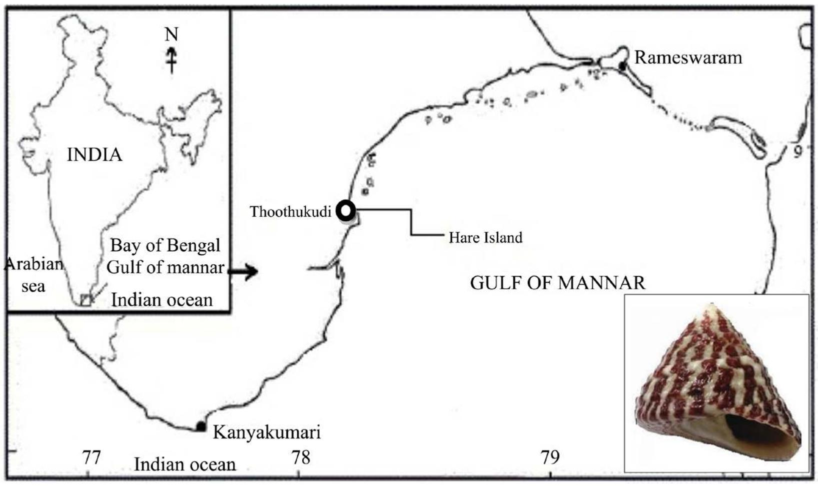

Figure 1. Map showing study area, inset bottom right—photograph of *Trochus radiatus*.

the whole body tissues of animals excluded from the shell were rinsed in distilled water for further drying in the oven at 80˚C ± 2˚C. Trace metals were extracted from finely ground tissue by following acid digestion procedure [25] and were identified using Perkin Elmer AAS (Model 2380) in an air acetylene flame.

2.3. Water Samples

Water samples from the surface up to 1 m depth were collected from the study area. The heavy metals in sea water were analysed using Stripping Voltametry in a 757 VA Computrace attached to 765 Dosimat (Metrohm, Switzerland) following the method outlined by Anoop *et al*., [26].

2.4. Sediment Samples

The sediment samples were collected in polythene bags using Van Veen grab and were brought to the laboratory. The samples were dried and finely ground to extract the metals following acid digestion procedure [25] and were detected on a Perkin Elmer AAS (Model 2380) in an air acetylene flame.

3. Results and Discussion

Heavy metal pollutants are often lethal to marine biota. They have been considered as an important group of toxic contaminants because of their high toxicity and persistency in all aquatic systems. Cadmium, Copper and Zinc are the metals with most potential impacts that enter the environment in elevated concentrations through waste water discharges as a result of agriculture and industrial activities [27]. In the present study the trace metals such as Fe, Mn, Cu, Pb and Zn were predominantly higher during the northeast monsoon (October to December) in all the samples, mainly due to the high level input of land based discharges and as a result of surface run off [18]. During the study, the metals accumulated in the Water, Sediment and Tissue are as follows: Zn > Pb > Cu > Cd; Fe > Mn > Zn > Cu > Cd; Fe > Zn > Mn > Cu > Cd > Pb > Ni, which corresponds to the observations made by Ganesan *et al*., [28] in Bay of Bengal, Kaladharan *et al*., [29] in Kochi waters, Senthilnathan *et al*., [23] along selected areas of southeast coast of India and Chandrasekar [30] in Tuticorin waters.

The sediment sample showed the higher trace metal composition for Fe (1928.04 $\mu g \cdot g^{-1}$) and Mn (108.89 $\mu g \cdot g^{-1}$) followed by minimal levels of Zn (23.33 $\mu g \cdot g^{-1}$) and Cu (12.36 $\mu g \cdot g^{-1}$) (**Figure 2**). Meetu *et al*., [31] observed similar results in the tissue samples of plants growing in the fly ash areas of northern India. Copper is an essential element that serves as a cofactor in a number of enzyme systems, but very high intake of Cu can cause adverse health effect problems for most living organisms. The presence of copper in all the samples may be due to the intrusion of domestic and industrial waste. The mean concentration of Fe and Mn in the sediment samples varied between 1365.04 to 1928.04 $\mu g \cdot g^{-1}$ and 78.19 to 108.89 $\mu g \cdot g^{-1}$ respectively; which are higher than those recorded previously by Ganesan and Kannan [18] and Baskaran *et al*., [19], off

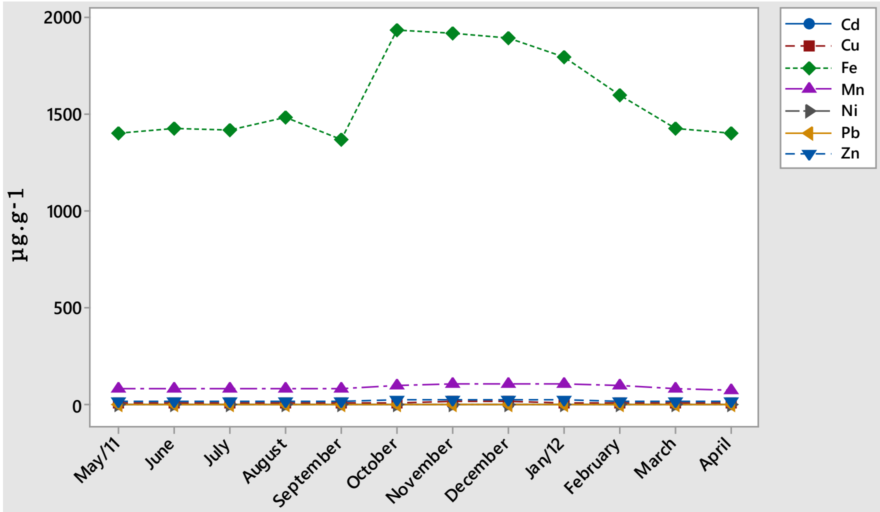

Figure 2. Seasonal variation of heavy metals in sediment sample.

Tuticorin, revealing enhanced industrial pollution especially due to fly ash dumping dyke at Tuticorin Thermal Power Plant. A similar higher value of Fe and Mn was observed by Kupekar and Kulkarni [32] in the sediments collected from the intertidal zone of Uran coast.

The water sample comprised only Cu, Cd, Pb and Zn metals during the study period (**Figure 3**), with Cadmium being present in lowest concentration (0.49 to 0.89 $\mu g \cdot g^{-1}$). Cadmium is highly toxic non-essential heavy metal which does not have any role in biological process of living organisms. Thus even in meagre concentration, cadmium could be harmful to living organisms [33]. During the study period Pb dominated in the water sample that varied between 6.01 to 9.21 $\mu g \cdot g^{-1}$. Moreover, Lead is one of the toxic metals which can cause musculo-skeletal, renal, ocular, neurological, immunological, reproductive and developmental effects [34] in all life forms. Introduction of Lead in the marine environment could be mainly attributed to the usage of fuels by way of mechanized boats [35].

Gastropod shells are used as bioindicators for determining the extent of biotransformation in aquatic food webs and as a vital component of risk assessment of heavy metals. During the study tissue sample of *Trochus radiatus* accumulated metals such as Cu, Cd, Fe, Zn, Mn, Pb and Ni; of which Fe was recorded to be having the highest concentration (144.54 $\mu g \cdot g^{-1}$) followed by Zn, Mn, Cu, Cd, Pb and finally Ni with lowest concentration of 0.04 $\mu g \cdot g^{-1}$ (**Figure 4**). Heavy metal assessment of gastropods by Kupekar and Kulkarni [32] recorded higher accumulation of Cu in tissue of *Hemifusus pugilinus* than tissues of *Bursa spinosa*. Marine gastropods normally accumulate and store Cu and utilize them for synthesizing the blood pigment hemocyanin [36]. According to Pyatt *et al.*, [37], concentration of metals in the soft tissues of molluscs can be attributed to the measure of metal bioavailability originating from both natural and anthropogenic sources.

The presence of high levels of Fe, Cu, Cd than Ni in the soft tissues of *T. radiatus* could be due to their roles as components of metabolically important

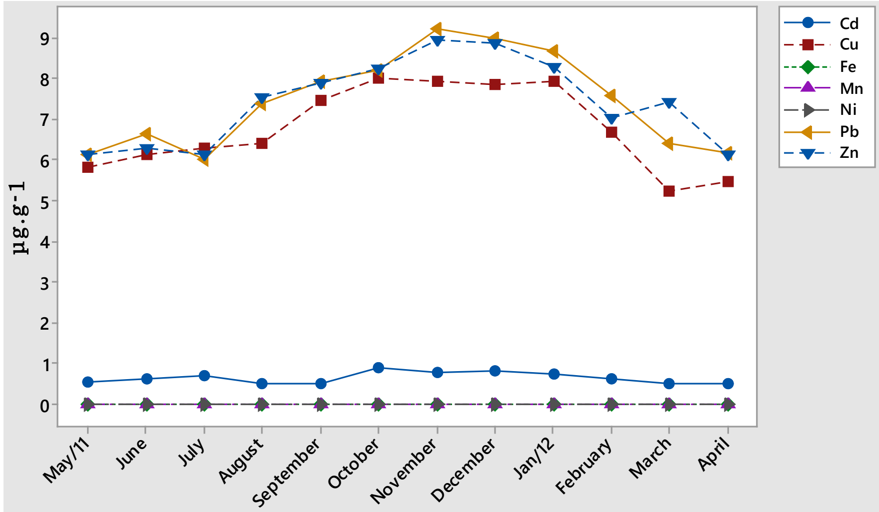

Figure 3. Seasonal variation of heavy metals in water sample.

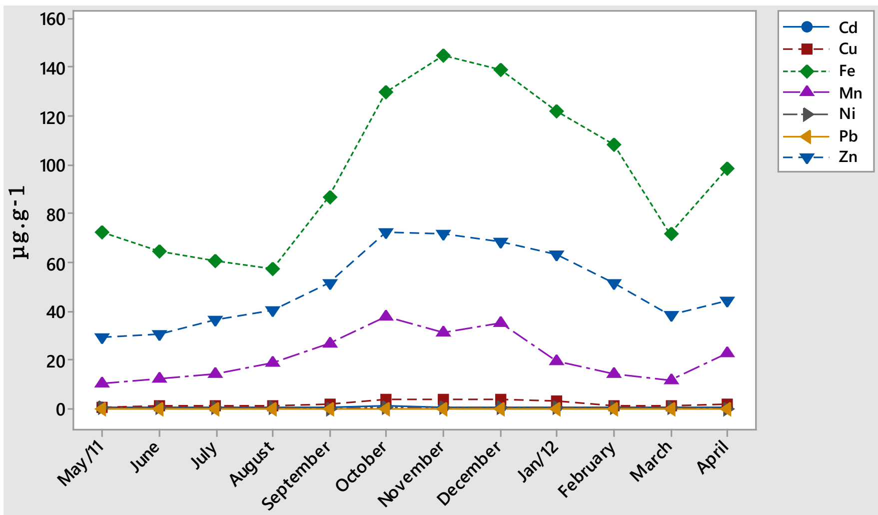

Figure 4. Seasonal variation of heavy metals in tissue samples of *Trochus radiatus*.

biomolecules including enzymes, metalloenzymes and respiratory pigments [32] [38]. It is usually observed that soft tissues of molluscs accumulate higher concentrations of Cu, Zn and Fe than the shells [39] [40] and their surrounding environment. Further seasonal variation in the amount of heavy metals accumulated by *T.radiatus* could be associated with food supply, changes in runoff particulate material during precipitation and variations related to the reproductive cycle [41]. According to Fang *et al.*, [42] out of the 14 edible molluscs the concentration of Cd, Pb, Ni, Cr, Sb and Sn were observed within the local regulatory limits in only three of the species (*Ruditapes philippinarum*, *Perna viridis* and *Hemifusus tuba*). Most of the samples collected from Hong Kong had significantly higher contents of Pb and Sb. Over 60% of bivalves exceeded maximum permitted level of Cd (2 $\mu g \cdot g^{-1}$) and Cr (1 $\mu g \cdot g^{-1}$), while over 40% of gastropod species exceeded the maximum level of Sb (1 $\mu g \cdot g^{-1}$) and Cr (1 $\mu g \cdot g^{-1}$). In the present study the one way analysis of variance indicated that statistically no significant difference ($p > 0.01$) was noticed in the seasonal variation of heavy metals between the samples except for the Cu, Cd, Zn and Pb metals (**Tables 1-3**).

The determination of heavy metals in seawater and sediment is the area of key interest in the current research scenario, since these trace metals greatly interact with water and sediment and are ultimately ingested by aquatic organisms. Heavy metals such as Cd, Ni, As, Hg, etc. in seawater have been estimated to pose potential threat to the ecosystem [43], which in fact needs continuous effort to assess the impact of these metals on faunal community. In environmental research, owing to their biological non degradability and chronic toxicity of trace metals particularly Cd, Pb, Hg, As, Ni, Cr, etc. are becoming increasingly significant as a result of their accumulation in vital organs of man [44]. Warwick [45] investigated the effects of metal contamination on the intertidal macrobenthic assemblages of the Fal estuary and concluded that of all the environmental factors, heavy metal concentration correlated strongly with composition of biological communities.

In concordance with the present study concentration of heavy metals in the tissue was generally more than that of water and sediment. Nearly all industrial practices concerning water are potential sources of metallic contamination in coastal waters [46]. Dumping industrial wastes in the sea is very common phenomenon in the study area that is toxic and persistent in the sea for a long time finally accumulating in the marine organism in the form of Persistent Organic Pollutants (POPs) which is one of the most serious concerns worldwide. From the environmental perspective, coastal zones are considered as the geographical space of interaction between terrestrial and marine ecosystem which is of great

Table 1. One way analysis of variance for sediment sample.

Source of variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	93,017.74	11	8456.158	0.023655	1	1.924308
Within Groups	25,738,101	72	357,473.6			
Total	25,831,118	83				

Table 2. One way analysis of variance for water sample.

Source of variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	16.41767	11	1.492515	0.102401	0.999881	1.924308
Within Groups	1049.414	72	14.5752			
Total	1065.832	83				

Table 3. One way analysis of variance for tissue sample.

Source of variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4970.212	11	451.8375	0.305708	0.982574	1.924308
Within Groups	106,416.2	72	1478.003			
Total	111,386.5	83				

importance for survival of large variety of plants, animals and marine species [47]. Any adverse anthropogenic effects on the coastal environment including eutrophication, heavy metal, organic and microbial pollution and Oils spills [48] could threaten these marine lives.

4. Conclusion

The results of the findings, give valuable information on the heavy metal level in Water, Sediment and the selected gastropod *Trochus radiatus.* The industrial effluents discharged into the study area are causing an increased level of metal inclusion, which proves that heavy metal concentration will be a bigger problem for this Marine Reserve in the near future. Hence appropriate measures are needed to safeguard our marine system that could possibly be achieved by way of reducing the pollution load into this susceptible environment.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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