9. HEAVY METALS

9.1. INTRODUCTION

As for as environmental pollutants are concerned heavy metals and their appearance in waters and biota evidence the presence of natural or anthropogenic sources associated with industrial and domestic sewage discharge (Biney et al., 1994; Zarazua et al., 2006). The initial bio accumulation has been done by the primary consumer (algae) and their transmission value by the food chain across the higher levels leads to bio magnification (Page et al., 1987). The most toxic heavy metals pollutant are lead, copper, cadmium, chromium, arsenic were reported by Hutton (1987). The enactment of an efficient controlling program to identify the contaminant in a given ecosystem became an important priority (Abd-Allah and Bream, 2001). Due to industrialization Tuticorin waters have been affected for the past few years. The discharges of effluents from various anthropogenic activities such as industries, fertilizers, chemical plants and untreated sewages are the main source for the heavy metal pollution in Tuticorin coastal zone. (Easterson, 1998; Murugan and Edward, 2000). Senthilnathan et al. (1998) reported that seasonal variation with an elevated metal load during monsoon period in the mussel and oysters from the southeast coast of India. Ganesan and Kannan (1995) recorded higher concentration of Fe and Mn in the sea water, sediment and algae in the vicinity of Tuticorin Port. Palanichamy and Rajendran (2000) reported high concentration of Cd and Pb in the bottom waters than the surface waters off Tuticorin. Satyanarayanan and Murty (1990) observed nearly excessive concentrations. Baskaran et al. (2002) recorded relatively higher concentration of Fe, Cu, Zn and Al in the fly ash discarding area than in the deeper waters off Tuticorin.
Ganesan et al. (1991) revealed higher concentration of heavy metals like Mn, Fe, Cu and Zn in the seaweeds off Tuticorin. Along the coasts of the Mediterranean Sea, despite a large amount of domestic and industrial sewage discharge into the sea (USEPA, 2003), few presented account survives concerning the effects of sewage effluents on gastropods dwelling on rocky shores. On rocky shores, sewage releases can modify natural occurrence patterns of sessile organisms. The strike of sewage on shallow hard substrate assemblages has been determined along south west Apulian coast, Italy, (Terlizzi et al., 2002). Marine fauna and flora i.e., sea grass, fish and bivalves have the tendency to absorb heavy metals and nutrients from both sediments and sea water (Nicolaidou and Nott, 1988; Stapel et al., 1996).

Though aquatic pollution started long back, rapid development occurred during the last few decades and now the situation has become alarming particularly in India (Girija et al., 2007). The availability of heavy metals in solution has widely been realized as a major factor in the geochemical behaviour, transport and biological effects in natural waters (Ananthan et al., 1992; Karthikeyan et al., 2004, 2007). The littorinid gastropods have been used by several researchers to assess heavy metal contamination in estuaries and coastal areas (Nickless et al., 1972; Bryan and Hummerstone, 1977; Portmann, 1979). Winkles may consume metals from the surrounding water or from the diet, as evident from the experimental studies on Littorina sp, which feeds on fucoid seaweeds, suggests that the diet is the most important source (Young, 1975; Klumpp, 1980). It is commonly known that molluscs are able to accumulate heavy metals which may impose health hazard to consumers (Gregori, 1992). Heavy metal levels available in sea foods of Hong Kong are arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), antimony (Sb) and tin (Sn). They are regulated by the Food Adulteration (Metallic Contamination)
Regulations of the Public Health and Municipal Services Ordinance (PHMSO) (Fang et al., 2001).

Concentrations of Cd, Zn, Cu, Pb, Fe, Mn, Ni, Cr and Co in *Mytilus edulis* in the Indian Ocean have been calculated in muscle tissue. The maximum concentration of each of the metals present in the fish was well below the values given in the National Health and Medical Research Council Standards. The low concentrations occurred in fish flesh are lower than in invertebrates such as the mussel (Plaskett et al., 2005). Heavy metal concentrations in samples collected from Japanese coastal waters were high in the hepatopancreas, gill and eggs. Residual concentrations of heavy metals were comparable to those recorded in most benthic organisms (Kannan et al., 1995). The concentrations of heavy metals in two tropical fish species from Ogba River, Nigeria showed changing concentration of Cu, Mn, Zn, Pb, Cr, Ni, and Cd in fish tissues. Concentrations of Cu, Mn, Cr and Ni in both fish were higher than the acceptable reports by WHO and FEPA, while those of Zn, Pb and Cr were lower than permissible concentrations.

Marine gastropods are known to be great accumulator of heavy metals in their various body parts. *Trochus* is a genus of small sea snails, known as top snails or top shells, marine gastropod molluscs in the family Trochidae inhabiting the upper intertidal zone on rocky shores, graze on algal films or macroscopic algae. The present chapter is to elaborate the concentrations of various heavy metals present in *Trochus radiatus*, sediment and water.
Figure 9.1. Coal is importing from a ship at Tuticorin port

Figure 9.2. Coal is transporting via conveyor belt to Tuticorin Thermal Power Station (TTPS)
9.2. MATERIALS AND METHODS

Water, sediment and radite top shell samples for heavy metal analysis were collected at regular monthly interval. The study area is closer to Tuticorin Port and Tuticorin Thermal Power Station’s effluent dumping point (08° 47’ 10.36” N; 78° 11’ 56.76” E). The sediment samples collected by Van Veen grab were brought to the laboratory in polythene bags. The collected radite top shells were washed and kept in filtered sea water to empty the gut. Whole body tissue of animals were removed and washed in distilled water. The tissue samples were digested using microwave digestion system (Milestone model 1200) using 10 ml of Nitric acid HNO₃ (69%) for 10 minutes, 1 ml of Perchloric acid HClO₄ (70%) for 5 minutes and 5 ml of Hydrogen peroxide H₂O₂ (30%) for 10 minutes at 250W power settings. The digested solutions were made up of 25ml and stored in well cleaned polythene vials in refrigerator till the time of analysis.

**Figure 9.3. A view of Tuticorin Thermal Power Station (TTPS)**
The metals Fe, Mn, Zn, Cu, Cd and Ni were extracted from dried and finely ground sediment samples (5 g) by following acid digestion procedure (Dalziel and Baker, 1984) and were detected on a Perkin Elmer AAS (Model 2380) in an air acetylene flame. Surface water samples from 1 m depth were collected from the same locality. The heavy metals Zn, Cu, Pb and Cd 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. (2007). The mean values of each metal concentration were analyzed to test one way analysis of variance (ANOVA).

9.3. RESULTS

The study area sediment is recorded the highest Cu (12.36 μg.g⁻¹), Zn (23.33 μg.g⁻¹), Fe (1928.04 μg.g⁻¹) and Mn (108.89 μg.g⁻¹) concentrations. High values of Cu, Zn, Fe and Mn in the tissue samples of plants growing in the fly ash areas of northern India was recorded by Meetu et al. (2000). The range of mean concentration of Fe is given in the parenthesis against the samples analyzed in the radiate top shell (57.54 to 144.54 μg.g⁻¹) and sediment (1365.04 to 1928.04 μg.g⁻¹) and Mn in the radiate top shell (10.28 to 37.97 μg.g⁻¹) and sediment (78.19 to 108.89 μg.g⁻¹). These results are higher than those recorded in the previous studies of Ganesan and Kannan (1995) off Tuticorin, revealing enhanced industrial pollution off Tuticorin. In this study the mean concentration of Pb in water varied from 6.01 to 9.21 μg.g⁻¹. Palanichamy and Rajendran (2000) observed high concentration of Pb in the sediment than in water off Tuticorin. Phillips (1976) indicated the importance of fuels as a source of lead in the marine environment. One way ANOVA indicated statistically no significant difference was noticed in the seasonal variation of heavy metals of all samples (Table 9.1 to 9.3). The trace metals concentration particularly Fe, Mn, Cu, Pb
and Zn was higher during the northeast monsoon (October to December) in all the samples. Ganesan and Kannan (1995) reported higher concentration heavy metals during monsoon seasons which might be mainly derived from inputs of land based discharges. The concentration of Cu, Fe and Mn were higher in the sediments. Baskaran et al. (2002) also recorded high concentration of Fe, Cu and Zn in the sediment at fly ash dumping dyke at Tuticorin Thermal Power Plant. Satyanarayanan and Murty (1990) found that accumulation of metals and its stability are more in fine grain sediment. Chandrasekar (2001) also observed higher levels of heavy metals in the sediments of Tuticorin waters. The seawater had only Cu, Cd, Pb and Zn during this study (Figure 9.4). Cadmium is found be the lowest in concentration in water during September (0.49 μg.gl\(^{-1}\)). Iron is the dominant heavy metal in the concentration of sediment than any other metals (Figure 9.5). The lowest concentration of Fe is recorded during in the month of September (1365.04 μg.gl\(^{-1}\)). The tissues samples of *Trochus radiatus* have accumulated the following heavy metals, Cu, Cd, Fe, Mn and Ni (Figure 9.6). Nickel showed the lowest concentration in the tissue of radiate top shell on September (0.04 μg.gl\(^{-1}\)). The Iron was estimated as higher concentration in the *Trochus radiatus* during the month of November (144.54 μg.gl\(^{-1}\)). One way ANOVA indicated statistically insignificant difference (\(p>0.01\)) in the variation of Fe, Mn and Ni among samples.

**9.4. DISCUSSION**

The concentration of various trace metals analyzed in the present study is compared with their concurrence reported in the previous studies conducted along Tuticorin coast (Palanichamy and Rajendran, 2000; Chandrasekhar, 2001; Baskaran et al., 2002). In this study, the metals were accumulated in the Water, Sediment and Tissue as follows, Zn > Pb > Cu > Cd; Fe > Mn > Zn > Cu > Cd; Fe > Zn > Mn > Cu
Cd > Ni, which is in relevance with the observations of Ganesan et al. (1991) in Bay of Bengal and Kaladharan et al. (2005) in Kochi waters, Senthilnathan et al. (1998) along selected areas of southeast coast of India and Chandrasekar (2001) in Tuticorin waters. The concentration of trace metals especially Fe, Mn, Cu, Pb and Zn was higher during October - December, i.e., during the northeast monsoon in all the samples. According to Ergaul et al. (2010) the maximum heavy metal levels were found in autumn in Ulva lactuca. Higher Zn, Mn and Pb levels were found in summer. In P. lividus, Zn and Pb levels were higher in soft parts while Fe and Mn levels were high in shell in lantern parts, respectively. The sediment samples showed higher levels of heavy metals in summer. All metal levels in the sediment samples were higher than those in biota samples. Amongst the 14 edible molluscs, only Cd, Pb, Ni, Cr, Sb and Sn concentrations found in three species (Ruditapes philippinarum, Perna viridis and Hemifusus tuba) were within the local regulatory limits. Over 60% of bivalve species exceeded maximum permitted levels of Cd (2 μg g⁻¹) and Cr (1 μg g⁻¹), while over 40 % of gastropod species exceeded the maximum levels of Sb (1μg g⁻¹) and Cr (1μg g⁻¹). Most of the samples collected from Hong Kong had significantly higher contents of Pb and Sb, but similar levels of Cd, Cu and Zn (Fang et al., 2001).

Sediments act as storage for substances, and if the storage function overtakes its role, that is overloaded, they cause the problems such as pollution affecting preservation. Thus, adequate control is required to manage the accumulation in sediments. There is no marine sediment quality guideline in Korea; therefore our data were compared to US NOAA guidelines. ERL (Effect Range Low) and ERM (Effect Range Median) guidelines for marine sediment were proposed by US NOAA (Long et al., 1995). The determination and speciation of trace heavy metals in seawater and
sediment for environmental research is of great significance for their interactions with suspended matter, sediment and their uptake by aquatic organisms and has become an area of key interest in present aquatic metal chemistry. Data for distribution of trace metals between the water column, sediment and the suspended particulate material were important and necessary. The various heavy metals such as Cd, Ni, As, Hg, etc. in seawater become toxic if present in excessive quantities and pose a potential threat to the ecosystem. Hence, there has been stable effort to estimate the impact of these metals on fauna (De Silva, 1978). In environmental research and protection, toxic metal particularly Cd, Pb, Hg, As, Ni, Cr, etc. are becoming increasingly signification owing their biological non degradability and chronic toxicity results from their accumulation in vital organs of man (Trinh Xuan Gian, 1999). Cu showed relatively more tendency for stratification. Enrichment of Cu levels was noticed in the bottom seawater layers of both areas, though in Tarut it was nearly more profound. In contrast to Cu, Ni showed an intermittent tendency to enrich in the surface, rather than bottom, layers.

The relationship between Macrobenthic community structure and heavy metals contamination has been studied by previous researchers (Dauvin, 2008). Rygg (1985) studied the relationship between species diversity in benthic fauna communities and concentration of heavy metals (Cu, Pb and Zn). He found a strong negative correlation between species diversity and copper concentration. Hall et al. (2000) studied the metal contamination on macrobenthos community and its effects in estuaries that promoted to respond positively to large reductions in the inputs of contaminants. Warwick (1993) 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. Heavy metals pollutants are conservative and often highly toxic to marine biota. They have been shown to be an important group of toxic contaminants because of their high toxicity and persistency in all aquatic system. Cadmium, copper and zinc are metals with most potential impact that enter the environment in elevated concentrations through storm water and waste water discharges as a consequence of agriculture and industrial activity (Beldi et al., 2006).

It is obvious that the concentrations of heavy metals in marine algal species showed several orders of magnitude higher than the concentrations of the same metals in seawater (Donat and Dryden, 2001). From the environmental point of view, coastal zones can be considered as the geographical space of interaction between terrestrial and marine ecosystem that is of great importance for survival of large variety of plants, animals and marine species (Castro et al., 1999; Hayette et al., 2006). Adverse anthropogenic effects on the coastal environment include eutrophication, heavy metal, organic and microbial pollution and oils spills (Boudouresque and Verlaque, 2002). Dumping industrial wastes in the sea is very common in these areas. According to an estimate, most of the pollutants come from industrial and land based sources: remaining 20% comes from atmospheric sources. Chemicals and heavy metals are found in the industrial wastes. They affect human and severely damage the marine life. Industrial wastes are toxic and remain in the sea for a long time and accumulate in the marine organism. The most serious concerns world over involve Persistent Organic Pollutants (POPs) which have become common in the ocean environment due to industrialization along the coastal lines. They tend to linger in the living tissues of marine species and become more concentrated as they move up the food chain. The industrial toxins can kill or cause hazards to marine life.
Increased river flows could also increase the flux of nutrients and contaminants into coastal systems, which influence eutrophication and the accumulation of toxins in marine sediments and living resources. Both increased temperatures and decreased densities in the upper layers might also reduce the vertical convection enough to prevent oxygenation of the bottom waters, further contributing to anoxic conditions in the near-bottom waters (Justic et al., 1996). Decreased freshwater inflows into coastal ecosystems would likely have the reverse effect, reducing flushing in estuaries, increasing the salinity of brackish waters, and possibly increasing the susceptibility of shellfish to diseases and predators. The natural sources of heavy metals in coastal waters are through river runoff. The mechanical and chemical weathering of rocks serves as another major source. In addition, components washed into the atmosphere, through rainfall, windblown dust, forest fires and volcanic particles also added to this. The natural concentrations of metals in sea water are very low and the possibilities of contamination are high. Virtually, all industrial processes involving water are potential sources of metallic contamination in coastal waters (Vaghela, 2010). The discharge of human sewage and garbage into the coastal waters is practiced throughout the world. The sewage may or may not be treated before discharge. The industrial effluents that are mixing in the study area are causing increasing of metal concentration in the study area. This study proves that heavy concentration will be a bigger problem for this Marine Biosphere Reserve in future.
### Table 9.1. One way ANOVA analysis for tissue sample heavy metals

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>4970.212</td>
<td>11</td>
<td>451.8375</td>
<td>0.305708</td>
<td>0.982574</td>
<td>1.924308</td>
</tr>
<tr>
<td>Within Groups</td>
<td>106416.2</td>
<td>72</td>
<td>1478.003</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>111386.5</td>
<td>83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 9.2. One way ANOVA analysis for water sample heavy metals

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>16.41767</td>
<td>11</td>
<td>1.492515</td>
<td>0.102401</td>
<td>0.999881</td>
<td>1.924308</td>
</tr>
<tr>
<td>Within Groups</td>
<td>1049.414</td>
<td>72</td>
<td>14.5752</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1065.832</td>
<td>83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 9.3. One way ANOVA analysis for sediment sample heavy metals

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>SS</th>
<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>93017.74</td>
<td>11</td>
<td>8456.158</td>
<td>0.023655</td>
<td>1</td>
<td>1.924308</td>
</tr>
<tr>
<td>Within Groups</td>
<td>25738101</td>
<td>72</td>
<td>357473.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>25831118</td>
<td>83</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 9.4. Shows seasonal variation of heavy metals in water

Figure 9.5. Shows seasonal variation of heavy metals in sediment
Figure 9.6. Shows seasonal variation of heavy metals in tissue samples of *Trochus radiatus*
10. SUMMARY AND CONCLUSION

Molluscs especially the gastropods form an important group of marine organisms next to fin fishes in providing rich nutritional source of seafood for mankind. The natural production of fishes appear to be declining year by year and there is an urgent need for conserving and managing them properly for the future in addition to popularize and utilize molluscs for edible purposes. For this purpose detailed studies on the biology of marine molluscs become inevitable. Biology of many gastropod species occurring in Indian waters is studied extensively while some of them are found untouched. One such species found left out is *Trochus radiatus*, which is found commonly distributed along the Gulf of Mannar – Palk Bay area. The present study was planned and carried out to understand the biology of this gastropod for a period of one year from May 2011 to April 2012.

This study indicated that these gastropods predominantly inhabit sandy area of the neritic zone of the Gulf of Mannar area in the Bay of Bengal. The abundance of this gastropod in the bed was found to be 75 numbers per square meter area. The population was found to be dominated by the medium and large sized gastropods (20–36 mm size groups) and the numerical abundance was found to be more in January due to the new recruits. *Cypraea annulus, Cypraea caurica, Cypraea moneta, Cypraea teres, Hemifusus pugilinus, Murex trapa*, was found to occur in moderate numbers in the trochid bed.

The length - weight relationship of the gastropod showed a proportional relationship (for males, females and combined) as the length increased, the weight also increased obeying the cubic law.
The life span of this species estimated to be around four years and the age and growth were studied using five different methods. The growth was found to be more during the 1st year and it decreased subsequently in the 2nd and 3rd years.

Four different maturity stages could be recognized and these stages were found to occur throughout the year indicating prolonged breeding. It attained sexual maturity at 22.3 mm. Two spawning peaks were found, one during October – November and the other during April. The condition index showed a direct relationship with the maturity and spawning of the gastropods. Higher index was noticed during September and low during October – November months.

Study on the biochemical composition of this gastropod did not show any difference between sexes and the fluctuations were found to be minimum. The fluctuations were in relation to the spawning season. From this study it is suggested that the best size group for consumption is above 26.0 mm.

The results of the present study showed that the growth of *T. radiatus* faster during the initial years and have a longevity of 3 - 4 years. This is similar to other tropical gastropod species studied by various other authors. Also as reported by various authors the allometric relationship was also similar to many of other tropical gastropod species.

Study of the biology of a species is very essential for the judicial exploitation and sustainable management of any resource. This study of the trochid gastropod *Trochus radiatus* gives some of the vital information on its various aspects of biology and reproduction. These informations will be useful for the fishery managers for formulating various management strategies. Findings on the reproduction of this species will be useful for regulating minimum sizes and season for exploitation.
Gastropods are considered as a cheap and best source of protein for human consumption and other commercial uses. Gastropods are also has a very high potential for farming and to increase production. Consumption of gastropods is not so common in India, and use of this untapped resource having a high protein of 53.5% can be promoted as an alternative protein source for human consumption. Success of any farming practice is dependent on the availability of the technology for seed production. This study is providing a basement for further more developments on larval rearing, stock assessment and management on this species to conserve it from exploitation activities.