10. METAL ACCUMULATION

10.1 INTRODUCTION

Metals in their pure state, present little hazard except those having a high vapour pressure such as mercury and those which may be present in the particulate form in the atmosphere. It is the soluble compound of metals, which create the problems in the aquatic environments. The different oxidation states of metals determine degree of toxicity in aquatic organisms. The priority list of pollutants compiled by the Environmental Protection Agency of United States contains the eight wide spread heavy metals - arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc (Moore, and Ramamoorthy, 1984). Of this mercury, cadmium and lead are known as toxic heavy metals.

Metals are being continuously released into the aquatic ecosystems and they ultimately find their way into biogeochemical cycling. Estuarine and coastal environments are now-a-days affected very much by pollutants, which invariably find their way into the coastal waters through sewage and industrial discharges and shipping activities.
Heavy metals like copper, zinc and mercury have been known to affect the biota of ecosystems and also physiology of the organisms (Abel, 1976). Metals were once thought as non-pollutants and hence mercury, cadmium, copper and zinc were discharged in unknown quantities into the oceans. Only after the Japanese realized mercury and cadmium as the sources of the endemic “minamata” and “Itai – itai” diseases, the world realized the need for promulgating strict regulations for release of such toxic metals into the oceans. Since then, regulations were enforced by the European Economic Community (EEC) and contaminants were classified under two lists namely ‘Black list’ and ‘Grey list’. Metals like mercury and cadmium, were blacklisted and other heavy metals were greylisted and standards were laid down for their levels in effluents (Phillips and Rainbow, 1994).

The concern for these heavy metals in natural cycling, which is often distributed by human activities is on the increase and the heavy metal pollution has been studied extensively in the developed countries. Though heavy metals studies are not extensively carried out like European countries, some preliminary studies have already been carried
out in developing countries, where the coastal waters are presently under
the threat of industrial pollution.

Metals exist in water partly in suspension adsorbed to
particulate matter, which is freely available to filter feeding organisms
(Laws, 1993). The toxicity of heavy metals varies with species and
environment. In aquatic invertebrates, mercury and lead show invariable
impacts and cadmium exhibits high influence. So the impact of
pollutants on marine environment is more acute and its deleterious effects
on living resources are much more evident in coastal and estuarine areas
than in the open ocean. Besides being the most fertile part of the marine
ecosystem and important feeding, nursing and passage zones for a large
number of commercially exploitable aquatic species, coastal and
estuarine regions are chief recipients of man-made and natural pollutants.

The molluscans are known to concentrate metals and species
of *Mytilus, Perna, Ostrea* and *Crossostrea* are considered to be universal
indicators (Rainbow, 1955). The heavy metals get concentrated in
aquatic organisms in considerable quantities and are of several orders
other than observed in seawater (Knauer and Martin, 1973). All these
confirm that certain organisms could be used as ideal indicators of heavy metal pollution for aquatic ecosystems.

The salts of cadmium, lead and mercury are more toxic to fish than the elementary forms (Metelv et al., 1983). The effects of pollution in many cases might be reflected earlier in non-commercial benthic organisms than in economically important organisms, which generally belong to higher trophic levels. Benthic organisms reflect not only condition at the time of sampling, but also condition for sometime previously (Ruvio, 1972). Though significant contributions have been made with reference to the distribution of various heavy metals in seawater (Ganesan et al., 1991; Anand, 1997; Govindasamy and Azariah 1999; Palanichamy and Rajendran, 2000; Angusamy and Victor Rajamanickam, 2000), few attempts have been made on the accumulation of heavy metals in various groups of aquatic organisms (Knauer and Martin 1973; Lopez et al., 1977; Shiber, 1981; George, 1983; Krishnakumar et al., 1990; Lyla, 1991; Sathyanarayana et al., 1994 and Noorjahan Beevi, 1994). However in case of the molluscan only a preliminary survey has been made in India. Seasonal variations in heavy
metals concentrations in molluscs were reported earlier by many workers (Sankaranarayanan et al., 1978; Lakshmanan and Nambisan, 1983; Patel and Chandy, 1988; Ganesan and Kannan, 1995). Noorjahan Beevi (1997) reported that bioaccumulation metals in tissues leads to retardation of growth.

Tuticorin, in Southern India is a fast growing industrial city. The sea bottom of Tuticorin is mostly sandy mud in nature and having vast coral reef resources and abundance of molluscan fauna. Various industries like the Thermal Power Station, Heavy Water Plant, Petrochemical Industry, Carbide Industry and Sterlite Industry are located here. Tuticorin is one of the most important cargo handling ports as well as a fishing harbour with full-fledged year round mariculture operations. Wastes from naval installations, unloading of bulk cargo such as coal, coke, sulfur and various processed metal ores and metals. Effluents of industries and domestic wastes are the probable pollutants of these coastal waters. Keeping this factor in view, regular monitoring of heavy metal pollution in Tuticorin coastal water attains greater significance. The earlier studies on pollution made on this bay were of

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general nature and largely dealt with the concentration of heavy metals in sea water and sediments. Only limited metal accumulation studies are available in this coast. The present investigation therefore fills up the long felt gap and it deals with accumulation of chosen heavy metals (mercury, cadmium and lead) by marine gastropod *Babylonia spirata*.

10.2 MATERIAL AND METHODS

In the present study accumulation of heavy metals such as cadmium, lead and mercury in the body tissues of *B. spirata* has been carried out.

Monthly samples of *B. spirata* were collected from the Gulf of Mannar region of Tuticorin coastal waters at about 5-15 fathoms for a period of 15 months from August 2000 to October 2001. The animals were brought to the laboratory, washed thoroughly with seawater and the shells were broken without damaging the soft body of the animal. The soft tissues of the males and females were taken, washed well and dried in a hot air oven at a temperature of 105°C for 24 hours. The dried tissues were powdered using a pestle and mortar. Powdered samples were used for metal analysis.
10.2.1 Method for metal analysis

A known quantity of powder samples were weighed and acid digested in a mixture of nitric acid and perchloric acid (2 : 1 V/V) (Topping, 1973), till the samples dried and became colourless. The residue was dissolved in 10 ml of 2 N Hydrochloric acid. These samples were analysed in a GBC Aventa ver 1.33 Atomic Absorption Spectrophotometer. Mercury was analysed by cold vapour technique using mercury analyser (OPEMEC, CECRI, PORT TRUST, TUTICORIN). Blanks and standards were also treated in the same manner as done for the samples.

10.2.2 Statistical Analysis

ANOVA was carried out between metals and sexes to find out the significant variation of metals.

10.3 RESULTS

A general survey of the amount of accumulation of non-essential metals like cadmium, lead and mercury in the body tissues of B.
*spirata* is presented in figs.27 & 28. The results of statistical analysis and comparisons are given in the tables 15, 16 & 17.

The result showed that the concentration of cadmium in males varied from 0.700 to 8.681 ppm, and in females it varied from 0.754 to 8.963 ppm. Higher concentration of this metal accumulation was observed during May 2001 (Premonsoon) in both the sexes, and lower concentration was noted in the month of November 2000 (Monsoon).

The concentration of lead in males varied from 0.037 to 0.899 ppm and in females it varied from 0.107 to 0.998 ppm. Higher concentration of lead was recorded in the month of May 2001 (Premonsoon) in both the sexes. The lower concentration of lead in both males and females was recorded in the month of November 2000 (Monsoon).

The concentration of mercury ranged from 0.019 to 0.089 ppb in males and in females 0.020 to 0.089 ppb. Maximum concentration of mercury was recorded in the month of May 2001
(Premonsoon) and the minimum concentration was recorded in the month of November in both the sexes.

Application of one-way ANOVA for the concentration of these metals between males and females showed that the variation was statistically insignificant tables 15, 16 & 17.

10.4 DISCUSSION

Data on the accumulation of heavy metals such as cadmium, mercury and lead in the body tissue of *B. spirata* revealed that the level of their concentration varied with season and this could be attributed to the fact that this region of Tuticorin is polluted by anthropogenic inputs such as industrial effluents and domestic wastes.

Cadmium, lead and mercury have not been known for biological function in molluscs. The high levels reported in the present study was in accordance with the earlier reports (Graham, 1972; Thrower and Eustace, 1973; Ratkowsky et al., 1974; Talbot *et al.*, 1976; Fowler and Oregioni, 1976; Bloom and Ayling, 1977; Eisler *et al.*, 1978; Phillips, 1977 and 1979). Eisler *et al.*, 1978 and Nair, 1984 stated that the - 153 -
high concentration of metals in the edible portions of the molluscan species may reflect the result of man's activities of natural perturbations.

Dog whelks *Nucella lapillus*, which feed heavily on limpets, *Patella vulgata* contained more than twice as much cadmium as in the whole body than the whelks which do not feed on limpets or those which include them only occasionally in the diet. This was attributed to the fact that limpets rapidly reflected environmental metal levels especially cadmium. *Crossostrea virginica* and *Mercenaria mercinaria* showed higher concentration of cadmium during the exposure to seawater and algae contaminated with cadmium (Peden *et al.*, 1973). In the present study also the mollusc has used as an indicator of metal pollution in the environment as in the case of previous studies.

Seasonal maxima in cadmium levels of mussels were observed, but this coincided with the periods of high precipitation and run-off with a simultaneous increase in the suspended load in coastal waters. This increase could enhance the ambient concentration of metals in both soluble and particulate forms (Fowler and Oregioni, 1976).
In various lamellibranches and temperate gastropods, it was reported that the fluctuation of metal accumulation was due to flood, water, run-off, direct rainfall and discharge of industrial wastes (Krishnamoorthy, 1969; Segar, 1971; Kumaraguru and Ramamoorthy, 1978; Ireland, 1977; Wooten and Lye, 1982; Mathew and Menon, 1983; Cheung and Wong, 1999). For many of the heavy metals, seasonal differences are reported. Monsoon recorded higher copper, zinc and lead content in sediments than in dry seasons (Mohapatra, 1992).

*B. spirata* samples from the Gulf of Mannar of Tuticorin coastal region show seasonal variation in the accumulation of these heavy metals in their body tissues. Since these molluscs are carnivore, they could accumulate these metals not only from ambient water, but also through the food chain and from inorganic particulate mater and hence the seasonal fluctuation of metals could be attributed to the available food and organic matter and their fluctuation reflects on the accumulation. The levels of heavy metals particularly the toxic elements like cadmium, lead and mercury in the Gulf of Mannar coastal water and sediment was studied by Palanichamy and Rajendran, (2000). They
observed higher concentration of cadmium in sediments than water. This could be attributed to the discharge of industrial effluents from chloralkali chemicals.

In the present study, *B. spirata* show higher levels of metals in their body tissues during premonsoon season. It has been observed that the breeding season for *B. spirata* was premonsoon. This could be related to higher feeding activity during the breeding season and also probably due to biomagnification through food chain relationship (Joseph and Srivastava, 1993). However a definite seasonal variation with an increased metal load (zinc, copper, lead, cadmium and mercury) during monsoon period and decrease level during summer period in *Perna viridis* and *Crossostrea madrasensis* in the southeast coast of India is reported by Senthilnathan *et al.*, (1998).

Kumaraguru (1980) recorded increased levels of metals during monsoon season in the Vellar estuary and Killai backwaters. Lyla (1991) also recorded increased levels of metals in sediments during monsoon followed by postmonsoon and premonsoon. However the premonsoonal increase of metals in the present study could be attributed
to the higher feeding activity during breeding season. It is also obvious that carnivores normally tend to accumulate more metals than the herbivores. In mollusc also the same condition is applicable (Noorjahan Beevi, 1994). *B. spirata* being a carnivore the accumulation of metals is highly noticeable.

Luk-Yanova and Marten Yanova (1996) reported the accumulation of lead and zinc in the body tissues of *Marcia recens* and found that the concentration of these metals in the body tissues of females were higher than the males. In the present work also, the same result has been observed. The higher accumulation of metals in the body tissues of females may be due to their rapid feeding nature.

Low concentration of these metals during monsoon might be attributed to the spent period of *B. spirata*. During this period, feeding rate would also be low, resulting in the probable low accumulation of metals through food.

A definite seasonal variation with an increased metal load (zinc, copper, lead, cadmium and mercury) during monsoon period and
decreased level during the summer period in *Perna viridis* and *Crossostrea madrasensis* in Southeast coast of India is reported by Senthilnathan *et al.*, (1998). But in the present study in *B. spirata* the metal concentration was found to be high in premonsoon and low during monsoon due to their reproductive behaviour.

Benthic macrofauna such as polychaete-worms, crustaceans, molluscs and echinoderms, occur in the sediment, rich in heavy metals in their tissues, resulting in high contents in habitats with low metal concentrations (Everaats *et al.*, 1989). The carnivores accumulating relatively higher concentration of metals than herbivores were evident (Noorjahan Beevi, 1994). *B. spirata* is also a carnivore accumulating higher level of metals in its body tissues.

It could be understood that the effluents discharged from the chloralkali plants are the prime source of mercury in the Gulf of Mannar. When analyzing the metal accumulation, it was observed that the seasonal variations on the bio-availability of metals could not only be related to the concentration of metals in the environment, but also to the food and particulate matter. Bryan (1984) and Hutchins *et al.*, (1996)
also opined that the bioaccumulation of metals by marine organisms is highly dependent on the above-said parameters. From the present study, it could be concluded that the concentrations of these metals (cadmium, lead and mercury) noted in the body tissues of *B. spirata* were less than the maximum permissible limit of the Indian standard, recommended for fish and fishery products for human consumption (FAO, 1983; table 18), and hence the study animal can be recommended as safe for human consumption.
Table 15. ANOVA on the accumulation of cadmium between male and female *Babylonia spirata*

<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>2.48</td>
<td>1.00</td>
<td>2.48</td>
<td>*0.32</td>
<td>0.58</td>
<td>4.20</td>
</tr>
<tr>
<td>Within Groups</td>
<td>220.73</td>
<td>28.00</td>
<td>7.88</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>223.22</td>
<td>29.00</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

* Insignificant

Table 16. ANOVA on the accumulation of lead between male and female *Babylonia spirata*

<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>0.67</td>
<td>1.00</td>
<td>0.67</td>
<td>*2.34</td>
<td>0.14</td>
<td>4.20</td>
</tr>
<tr>
<td>Within Groups</td>
<td>7.99</td>
<td>28.00</td>
<td>0.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8.66</td>
<td>29.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Insignificant

Table 17. ANOVA on the accumulation of mercury between male and female *Babylonia spirata*

<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>0.00</td>
<td>1.00</td>
<td>0.00</td>
<td>*1.83</td>
<td>0.19</td>
<td>4.20</td>
</tr>
<tr>
<td>Within Groups</td>
<td>0.01</td>
<td>28.00</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>0.01</td>
<td>29.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Insignificant
Table 18. Indian Standards for Trace elements in fish and fishery products*

<table>
<thead>
<tr>
<th>Element</th>
<th>Standard</th>
<th>Approximate date of Adoption</th>
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</thead>
<tbody>
<tr>
<td>Hg</td>
<td>0.5 ppm</td>
<td>1982</td>
</tr>
<tr>
<td>As</td>
<td>1.0 ppm</td>
<td>1982</td>
</tr>
<tr>
<td>Cd</td>
<td>10.0 ppm</td>
<td>1983</td>
</tr>
<tr>
<td>Pb</td>
<td>5 ppm</td>
<td>1982</td>
</tr>
<tr>
<td>Zn</td>
<td>50 ppm</td>
<td>1971</td>
</tr>
<tr>
<td>Sn</td>
<td>250 ppm</td>
<td>1982</td>
</tr>
</tbody>
</table>

* Source: FAO 1983
Fig 27 Concentration of cadmium and lead in the body tissue of male and female *Babylonia spirata*
Fig 28 Concentration of mercury in the body tissue of male and female *Babylonia spirata*