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Seasonal variation of major elements (Ca, Mg) and trace metals (Fe, Cu, Zn, Mn) in cultured mussel *Perna viridis* L. and seawater in the Dona Paula Bay, Goa

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The major elements and trace metals were analysed from mussel tissue and the seawater taken from three depths (0,5 and 9 meters) from the culture site. Range of variation in Ca, Mg, Fe, Cu, Zn and Mn were 226-399; 708-1329; 0.005-0.084; BDL-0.042; 0.01-0.0375; BDL-0.0099 ppm in the water medium and 1124-1950; 984-4783; 1862-8261; BDL-39; 133-1766 and 44-179 µg/g dry wt in the mussel tissue respectively. The major elements displayed seasonal variation with low values during monsoon period in the water. Among trace metals, Zn and Mn seem to follow almost a close relationship in their contents in the mussel tissue and the water. An inverse relationship of Zn, Mn and Cu to some extent was observed with size in the cultured mussels.

Marine bivalve molluscs, especially mussels have been used internationally as a sentinel organism for pollution monitoring programme[1] as they are suitable for pollution studies due to their remarkable characteristics. Due to bioaccumulative property[2] the bivalves have gained great importance as indicator organisms. Tropical estuarine ecosystem do exhibit wide and abrupt variations in the water quality[3-6]. The need to understand water quality criteria has become a necessity with respect to aquaculture activities and environment protection, as these coastal ecosystems have been widely used for the purpose of discharging industrial effluents, domestic sewage and human interference are responsible for changes in the water quality.

Earlier studies[4,6,7] in Indian coastal waters suggest that these trace metals in seawater are greatly influenced by local topography and hydrological features, and to some extent, play an important role in biological and geochemical processes[8,9]. The major element especially Ca is known to be involved in physiology of bivalves[10,11].

The present investigation (October 1988-September 1989) was taken up at Dona Paula bay (Fig. 1) with an idea to determine the concentration and rate of accumulation of trace metal and other major elements in the mussel tissue under continuous submergence within an estuarine ecosystem. Water quality was also assesed by estimating the above mentioned constituents to obtain the possible relationship between the trace metals in mussel tissue and the medium. An attempt has also been made to define the rate of uptake of these metals by the mussels with the size.

Materials and Methods

A wooden raft with ropes of green mussels (*Perna viridis*) was suspended in the water column at the site of culture (Fig.1). Water and mussel samples were collected at fortnightly intervals for a period of one year from the culture site. Water samples were collected from three depths (0, 5 and 9 m) in the water column. However, average values for the water column were computed to represent monthly data. Twentyfive mussel samples were randomly collected from the suspended ropes at each time. Mussels, after collection were cleaned by keeping them in running filtered seawater in an aquarium for 48 h. The mussel tissue was removed with clean teflon forceps so as to avoid any metal contaminations.

The forceps were cleaned with distilled water before use. The mussel tissue was then dried in an oven at 80°C for 24 h. The dried tissue was stored in glass vials, previously cleaned with concentrated HCl.

Adequate precautions were taken for cleaning sample containers and other glassware. Polyethylene bottles used for storage of water samples were allowed to stand with analytical grade HCl at room temperature for three days. These containers were then rinsed with distilled water and dried at 55°C. The collected water samples were then stored by reducing the *p*H below 4 with 1 *N* HCl. The major elements and trace metals in water were analysed by the standard methods[12]. Standard curve was prepared by re-extracting the extracted seawater samples spiked with known concentration of trace metals. These standards were extracted in a similar way as mentioned above. All these samples were analysed using an atomic absorption spectrophotometer (Varian Spectra AA 30) and the concentrations were expressed as ppm.

The estimation of metals in mussel tissue was carried out by following the AAS method[13]. A known weight of dried powdered sample (pooled for each day of collection) was taken in a glass beaker. To this, 20 ml 70 % nitric acid[14] was added and subjected to digestion on an electric hot plate until the brown fumes completely disappeared and the residue turned whitish in colour. The residue was allowed to cool at room temperature. Then, 2 ml of 30 % perchloric acid[15] was added and digested for about 10-15 minutes to dryness. The dried residue was treated with 10 ml dilute HCl and the metal content measured by AAS (Perkin and Elmer, 5000). Appropriate dilutions were made depending upon the sensitivity of detection of these samples. Reported concentration of metals are expressed as µg/g tissue on dry weight basis. Appropriate blanks and standards were also prepared by using the same method.

Results and Discussion

Monthly variations in major elements (Ca and Mg) and trace metals (Fe, Cu, Zn and Mn) in the water and mussel tissue have been depicted in Figs 2 and 3 respectively. In the present study, major elements reported a seasonal pattern of variation. The concentrations of these elements were observed to be high during major period of study except during monsoon season. The observed pattern of variation was attributed to non-conservative behaviour of Ca in view of its involvement in biological and geochemical processes[4]. Low values of these elements during monsoon could be due to dilutions and drainage

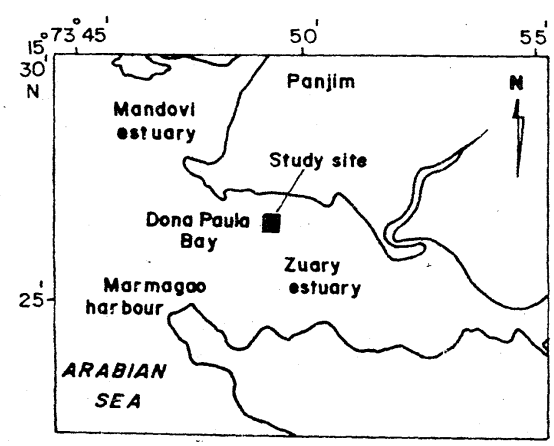

Fig. 1—Map showing location of raft culture site at Dona Paula Bay, Goa

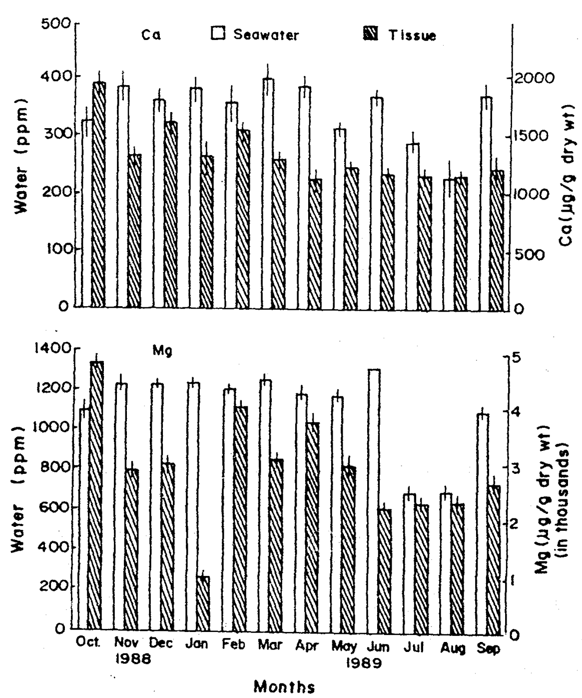

Fig. 2—Monthly variation in Ca and Mg in seawater and mussel tissue

from riverine sources[16]. The Ca content variation observed in the present study was found to vary with salinity, registering higher values in more saline waters. Such higher values in Ca content in more saline waters were attributed to the geochemical processes[4,8], and freshwater runoff[17]. The Ca content in mussels during the present study is in descending order, which indicates that as the size increases there is reduction in Ca content. Silverman *et al.*[18] stated that Ca content deposited by the mussel tissue get reduced during spawning season. Steffens *et al.*[10] reported that Ca concentration in bivalves may account for up to 50% of dry weight of gills and are composed primarily of $CaPo_4$ with an associated glycoprotein. Ca content of mussel tissue is greatly influenced by the composition of the sediment, acting as substrate for their food materials[19]. It can be seen from Fig. 2, that higher values of Ca in the seawater were closely associated with high values in the tissue. This suggest that the required Ca is taken up by organisms from the seawater[20]. Seasonwise, during monsoon period (June-August), Ca values were low, which could be the result of dilution of medium due to precipitation or runoff thereby reducing availability of uptake of this element by the raft-grown mussels.

The Mg content displayed stable values in the water during major period of study except in monsoon season. Low values of Mg were observed in monsoon season (July-Aug; Fig. 2). These low values of Mg content could mainly be due to dilution of water medium during the monsoon season. The Mg content in the mussel tissue and the surrounding water did not bring out any specific relationship. Published reports [16] on the distribution of Mg in coastal waters indicate that this element does not appear to take part in biological cycle and the only factor that alter its content is geochemical nature and is relatively stable[4] as compared to Ca.

The Fe content in the present study at the culture site was stable and registered low values, which indicated uniformity in distribution. Such distribution in Fe was reported[21] in Baltic surface waters and observed that high Fe content was also associated with large amount of organic matter in the water column. In another study similar observations were made in Indian waters[22] and reported that such higher values were associated with high content of organic matter. In the present study, high suspended matter was observed to coincide with high Fe content values[23]. Another probable reason for high Fe content could be terrestrial pollution and anthropogenic local inputs as documented by earlier workers[21,24]. Furthermore, it was also inferred that Fe content in coastal water is a function of freshwater input and is greatly influenced by riverine waters[7]. In this context it is worth mentioning that the major contribution of iron in the water column was from suspended load. It can be stated that the living material contributes

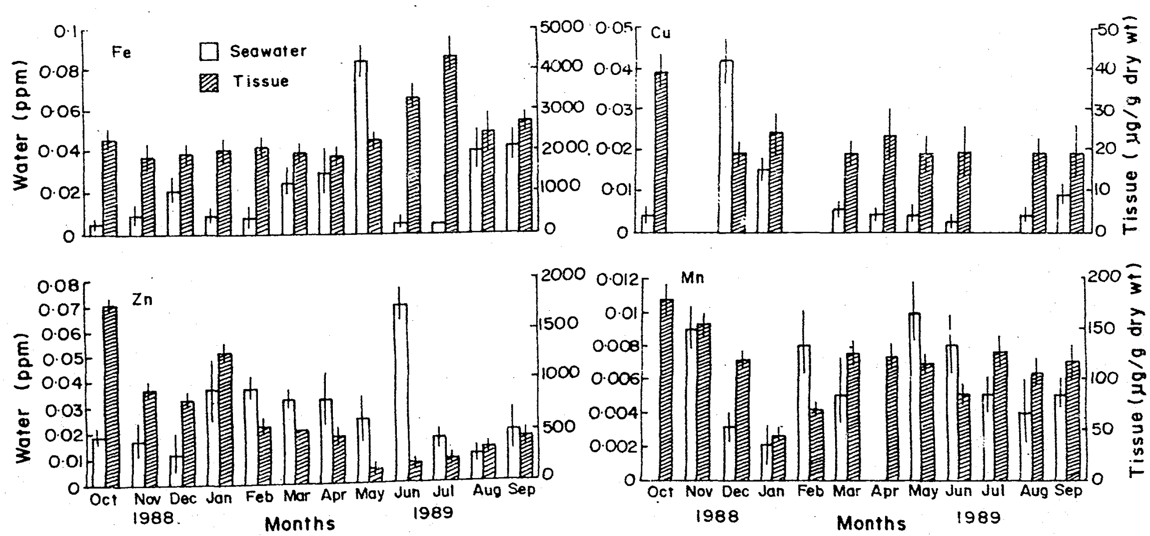

Fig. 3—Monthly variation in Fe, Cu, Zn and Mn in seawater and mussel tissue

to the majority of suspended load formed primarily by the primary producers[23]. Such low values in coastal waters of Goa have been reported earlier[25].

Fe variation in mussel tissue did not indicate any particular rythm of variation. In small mussels, the Fe content was reported to be low. These low values in young and newly transplanted mussels at the new site were mainly due to the changing environmental conditions probably leading to inefficient feeding during such acclimatisation period. Subsquently, with the increase in size, higher values of Fe content were reported. Such elevated levels of Fe with increase in growth were mainly due to proximity of culture site to anthropogenic point sources such as electroplating plants, ironworks and waste outfalls[2]. The high values of Fe in marine fauna could be attributed to inflow of mine drainage[25]. Fe accumulation in these organisms is supposed to be regulated by other factors such as sex, salinity, season, turbidity and depth[26]. Seasonally low values of Fe were reported in winter. The pattern of variation of Fe content as shown in Fig. 3 indicates that the rate of increase of Fe from the medium and the mussel was of very high magnitude. This further indicates that the uptake capacity of mussels towards this particular metal is relatively high as compared to other metals.

The Cu content at the site of culture was low except in the month of January. Higher values of Cu at this time were mainly due to higher rate of dissolution of Cu in the upper layers[27]. In the present study, the higher rate of dissolution of Cu at this time was influenced by high content of oxygen. This substantiates that the low concentration of oxygen is not favourable for dissolution of Cu in upper layers. Therefore, low values of Cu observed during the present study could be attributed to low values of oxygen.

Cu content in the mussel tissue was observed to be high in the initial period of growth. A report [26] suggests that higher values were recorded in young mussels. In the present study, Cu content did not reveal any specific trend of variation. Cu uptake in mussels was erratic and seem to be influenced by the available concentration of other metals [2]. However, other abiotic factors are also supposed to influence the Cu accumulation in mussels such as salinity and proximity to point source[28]. Higher ability to accumulate Cu by mussels in postmonsoon could not be wholly explained by temperature regime. Possible causes for higher accumulation of Cu in October could also be due to moisture content[2], availabiity of food[29], local pollution[30] and land drainage[2]. The elevated levels of Cu were primarily attributed to proximity to anthropogenic sources and secondarily to various biological and abiotic modifiers capable of modifying Cu uptake and retention in molluscs. In few cases it can be seen that the Cu content in the selected mussels was less (Fig. 3) as compared to the medium. This could be due to random selection of mussels which contained less Cu as compared to the medium.

Distribution of Zn during the present study reported higher values from January to March. These higher values could be mainly due to terrestrial contamination, anthropogenic local inputs and or from local sources and river runoff areas[21]. During monsoon season, Zn values were reported to be low and such low values were expected to be due to colloidal and adsorbed forms of Zn in the suspended matter[7].

The pattern of Zn variation in the mussel tissue displayed a decreasing trend in the size range of 40-62 mm shell length. Such decrease in Zn with size has been reported earlier[26]. However, in the size range of above 62 mm shell length, a reverse pattern was observed. Published literature[31] indicates an increase in Zn content with increasing body weight. Marked variations in Zn content were noted to be influenced by season, geographic locale and Zn specific sites of accumulation. It has been reported that Zn content in nearshore waters coincided with periods of high precipitation and runoff with concomitant increase in suspended load in coastal waters[30]

The Mn content at the site of culture reported two peaks, primarily in November and later in May. High values of Mn at this site were mainly due to transportation of mining ore in this area, as this site happens to be near the route of barges transporting mining ore. In monsoon, low values of Mn were observed indicating that riverine input does not enhance the Mn content of the water body. Similar observations were made earlier[7] and low values of Mn were reported during monsoon season. The present data also reveal that nearbottom waters harvest more Mn as compared to columnar waters. In this context, redox potential play an important role in the distribution of Mn [7,32].

The Mn content in the mussel tissue was found to be of high magnitude (179±7 μg/g dry wt) in immature as well as adult mussels. Such high values in mussels could be mainly due to pollution by automobiles, small crafts and substrate composition[33]. The present site of raft culture happens to be in the vicinity of a major port and is known for high rate of pollution by small crafts operating in this area for the purpose of recreation. Industrialised port areas exhibit higher Mn values as compared to other areas [30]. During the present study the Mn content did not seem to follow specific trend of variation with size.

Interpretations made from statistical analyses highlight that no definite, as also the significant, relationship could exist among the trace metals in the medium and the mussel tissue with the size. Earlier reports[29] illustrated that the diet and the food chain presumably play major role in accumulation of trace metals as compared to the medium. Hence, the present study confirms to a certain extent that trace metal content in the mussel tissue is not regulated by the composition of the medium.

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