CHAPTER-V
DISCUSSION

Estuaries are most productive marine ecosystems in the world, which are both chemically and physically dynamic, complex, and unique. Because of their location at the river–ocean interface, they act as buffers between the land and the ocean (Chapman & Wang, 2001). Estuarine and coastal bays, which are regions of active land–ocean interaction, respond sensitively to natural processes and anthropogenic activities (Li et al., 2007). Estuaries are among the most challenging environments for aquatic life. Faced with fluctuating salinities, estuarine animals must have mechanisms that allow them to adequately maintain osmotic and ionic balance (osmoregulators), or mechanisms permitting them to withstand variations in extracellular fluid osmolarity (osmoconformers). Estuaries are structured by complex gradients, rich in both natural and man-induced types of stress, shaping the distribution and abundance of estuarine animal communities (Gonzalez & Saiz-Salinas, 1998).

The estuarine system is predominantly an area of deposition and acts as an important sink for heavy metals and nutrients in the environment. Metals are transferred from solution to sediments by adsorption onto suspended particulate matter, and deposited with relatively short lag times. Estuaries receive significant anthropogenic inputs from both point and non-point upstream sources and from metropolitan areas, tourism and industries located along the estuarine edges. Heavy metals occur in the environment both as a result of natural processes and as pollutants from human activities (Garcia-Montelongo et al., 1994). Contamination of the marine
environment by metals has risen in recent years due to the global population increase and industrial development (Arellano et al., 2000). It is well known that estuaries can be efficient traps for suspended matter and associated trace metal (Kennedy, 1984; Bewers & Yeats, 1989). These activities represent an important source of pollutants including trace metals for example, Zn, Cd and Cu for which the sedimentation areas are the main reservoir. Estuaries are sedimentary environments of fluvial-marine interaction where an important biomass exchange takes place that favour the accumulation of potentially contaminant elements (Sanger et al., 1999; Ridgway & Shimmield, 2002; Spencer et al., 2003). This sedimentary stock represents a massive repository for contaminants, with the potential of remobilization and transfer to the water column and thus, the pelagic food web (Bloom & Ayling, 1977).

Estuarine sediment contamination is receiving increasing attention from the scientific community, since it is recognized as a major source of ecosystem health stress (Chapman & Wang, 2001; Riba et al., 2002). They provide a record of the natural and anthropogenic inputs of contaminants into the aquatic environment. It plays a key role in the transfer of trace metals to the coastal area (Martin & Windom, 1991). Heavy metals have a high affinity for fine-grained sediments and are the key contaminants in estuarine sediments (Middleton & Grant, 1990; Cundy & Croudace, 1995; Lee & Cundy, 2001; Spencer et al., 2003). Urban estuarine sediments usually contain elevated levels of metals including copper (Cu), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), and zinc (Zn) (Benoit et al., 1998; Sanger et al., 1999).
The present study area, Ennore creek is situated in northeast coast of Chennai city, Tamilnadu, India. Ennore coast consists of alluvial tracts and beach dunes, tidal flats and creek in the eastern part. Ennore comprises of lagoons, with salt marshes and backwaters, which are submerged under water during high tide and form an arm of the sea opening in to the Bay of Bengal.

5.1 PHYSICO-CHEMICAL PARAMETERS OF ENNORE CREEK

The physico-chemical characteristics are playing a significant role in the distribution of organisms, their feeding, reproduction and other aspects. Various physico-chemical and biological processes make it a habitat for vast array of organisms, leading to rich biodiversity (Balasubramanian, 2000) but seasonal variation and anthropogenic pressures bring about a lot of changes in physico-chemical characteristics, which in turn affect the biotic elements. In the present study, physico-chemical parameters of water samples from five sites at Ennore creek were analyzed. The principal physical characteristics are appearance, odour, total dissolved solids and EC.

5.1.1. NUTRIENT PARAMETERS

In the present study, the nutrients (nitrite, inorganic phosphate, ammonia and silicate) were beyond the permissible limits recommended by Australian and New Zealand Environment and Conservation Council (ANZEEC) in all the five sites. The level of nitrate was higher (9.50±1.25 mg/L) in the site IV when compared with other four sites. The elevated levels of nitrate concentration signify that the Ennore creek was polluted. The sources are being anthropogenic activities in all the sites, especially...
the industrial effluents and domestic sewage in site IV. Elevated concentration of phosphate (1.51±0.31 mg/L) observed in the site IV may be due to the addition of detergents and urban wastes entering in the estuary during the monsoon along the Buckingham canal and Koratalaiyiar river. The concentrations of both phosphate and silicate were increased from bar mouth of the creek to back waters, probably as a result of the effects of discharge from the Koratalaiyiar river, and diluting concentration of nutrients through seawater. Several studies have suggested that the excess utilization of fertilizer in agriculture and sewage discharge result in the increase of nitrate and phosphate in the estuary (Aggarwal et al., 2000; Adeyemo, 2003). Nitrite is the main form of dissolved inorganic nitrogen followed by ammonia and nitrate, which is an unstable intermediary transformed to nitrite in nitrification process (Wang et al., 2006). Ammonia is the main form of dissolved inorganic nitrogen in Daya Bay at China during premonsoon season (Wu and Wang, 2007). Silicate is associated with land-based resources, particularly during monsoon in Daya Bay at china (Zhu, 1999). Nutrients exhibit seasonal changes, with concentration higher in monsoon season than in summer season (Huang et al., 2003; Wu and Wang, 2007).

Nitrites and nitrates are together measured due to their conversion from one form to the other in the environment. As long as nitrification is stirring in the water, an increase in nitrite and a reduction in ammonia is a normal event (Iscen et al., 2007). High nitrate and nitrite levels are associated with sewage contamination (Ntengwe, 2006). In the present study, the nitrate value reached a peak of 15 mg/l which is rather less than reported by Luiza et al. (1999), who recorded 58 mg/l in the Piracicaba river.
in Brazil. High levels of both phosphate and nitrate can lead to eutrophication, which increases algae growth and ultimately reduces dissolved oxygen levels in the water (Stimson et al., 2001).

Higher concentrations of nutrients were recorded during monsoon and lower concentrations during summer which may be due to discharge of industrial and domestic sewage along sites IV and V of the Ennore creek indicating presence of pollutants largely responsible for atrophic conditions. Olajire & Imeokparia (2001) observed that the nitrate level of Osun River in Nigeria was 20 mg/l. Helen et al. (2005) reported that a nitrate level of 24 mg/l in the upper Thames basin, in Southern England. Nitrate levels found to be slightly higher in Notwane river in south-eastern Botswana (Mladenov et al., 2005) when compared to the present study. Das & Acharya (2003) recorded a nitrate concentration of 14 to 126 mg/l and 173 to 155 mg/l in premonsoon and monsoon season, respectively in Kathajodi river. Ravindra et al. (2005) observed nitrate concentrations of 5 and 9 mg/l during premonsoon and summer seasons, respectively in the Yamuna river. The physico-chemical parameters showed a clear seasonal variation in their distribution.

Grazing and watering (urine and dung) of livestock, frequently observed over the entire sampling period in site IV, also could have been contributed to the higher phosphate concentrations. Olajire and Imeokparia (2001) reported that phosphate level was 0.59 mg/l in Osun river, Nigeria. Mladenov et al. (2005) recorded an average phosphate level of 3.65 mg/l in treated sewage in Notwane river in south-eastern Botswana. In the present investigation, the levels of ammonia were higher in sites II
and IV (Table 12), which may be due to the death and subsequent decomposition of phytoplankton and also due to excretion of ammonia by planktonic organisms (Rajasegar, 1998). The higher level (12.49±2.54 mg/l) of ammonia may be due to the industrial effluents mixing up with estuary. All through the study period, the pH, salinity and total hardness doesn’t show any correlation with nutrients (Tables 13-32).

5.1.2. SALINITY

As shown in the tables 1-12, the salinity level varied from 19.98 to 33.74‰ in Ennore creek, throughout the period of study. The salinity showed a negative correlation ($P<0.01$) with potassium ($r = -0.655$) and Total hardness ($r = -0.500$). The concentration of nutrients decreased greatly with higher salinity. Ouyang et al. (2006) reported that the water temperature had very weak correlations with other water quality parameters such as alkalinity and salinity which were, in general, similar to our findings. It is understandable that domestic wastewater from untreated or overflow sewer pipes constituted a major pollution source for the monitoring sites in sampling sites of Ennore estuary II, III and IV, which could cause a higher concentration of average ammonia and lower values of dissolved oxygen and pH. The annual salinity distribution show an increasing pattern from the eastern to the western part of the creek.

5.1.3. pH

As shown in the tables 1-12, the pH values of the Ennore estuary ranged between 6.6 and 8.45. pH showed a positive correlation ($P<0.05$) with temperature. It may be due to decaying of the domestic and industrial waste litter in the upstream area
contributing to the acidic nature of the water. The seasonal variation in the pH of Ennore creek water may be due to the influx and decay of debris in the area as well as imbalance level of $H^+$ ions input from surface run-offs during rains. This assertion was based on the result of the correlation analyses between pH and nutrients such as nitrate and sulphate levels which were negatively correlated ($P<0.05$) with salinity. They indicate the importance of mixing between polluted freshwaters and costal saline waters. Nutrients were introduced by river and sewage discharges (Paranhos et al., 1998). Negative correlation ($P<0.05$) between nutrients and salinity demonstrates that land sources are the main reason for high levels of nutrients (Liu et al., 2005). The saline and brackish waters typically have high alkalinity, due to high ion concentrations of carbonates and bicarbonates.

High levels of dissolved organic matter devour large amounts of oxygen, leading to anaerobic fermentation and formation of ammonia and organic acids. Hydrolysis of these acidic materials causes a decrease of water pH value (Singh et al., 2004). pH was lower in sites III and IV when compared to other sampling sites. The higher pH values were recorded in the summer (site I) and lower values of pH were observed in the postmonsoon (sites III and IV) season. Similar trend was reported by Ekeh and Sikoki (2003) in the New Calabar river, Nigeria.

5.1.4. TOTAL HARDNESS

Total hardness values of sites I, II and V were higher than APHA standards (Table 6). Similar findings were also reported in the physicochemical analysis of ground water of Nigeria (Bernard & Ayeni, 2012). Total hardness caused by calcium
and magnesium usually results in excessive soap consumption and subsequent “scum” formation. Depending on the interaction of other factors, such as pH and alkalinity, water with hardness above 300 mg/L may cause scale deposition in the treatment works, distribution system and pipe work and tanks within buildings. Soft water, with a hardness of less than 100 mg/L, may have a low buffering capacity and so be more corrosive for water pipes (WHO, 2004).

5.1.5. IRON

The level of iron (0.68±0.16 mg/L) in site III was found to be higher than the APHA standards. The higher level of iron in site III may be due to the inflow of industrial effluents in the vicinity of Buckingham canal. On exposure to the atmosphere, the ferrous iron gets oxidized to ferric iron, giving an objectionable reddish-brown color to the water. Iron also promotes the growth of “iron bacteria,” which derive their energy from the oxidation of ferrous iron to ferric iron and in the process deposit a slimy coating on the pipes. The iron is released into freshwater system primarily by steel production plants and leaching of cast iron pipes in water distribution system (WHO, 2004).

5.1.6. CHLORIDE, FLUORIDE & SULPHATE

Chloride values in Ennore estuary were within normal ranges for all sites though sites III and V showed values closer to the upper range. Chloride in water originates from natural sources, fertilizers, sewage and industrial effluents, urban runoff containing de-icing salt and saline intrusion (WHO, 2004). Bernard & Ayeni
(2012) have also analyzed the presence and significance of chloride in ground water samples of Kano State at Nigeria. Fluoride was detected within the normal ranges in all water samples of Ennore estuary. Sulphate content recorded in site I of Ennore estuary (1579.91±86.06 mg/l) was three folds higher than the APHA standards. Adefemi & Awokunmi (2010) have reported similar values of sulphate and chloride in their study at Ona river, Nigeria. Presence of sulphate in water is due to mixing up of sewage, industrial wastes, by-product of coal-mines, natural deposits or salt (WHO, 2004). Sulphate and chloride together contribute towards the total hardness of water.

5.1.7. TEMPERATURE

Temperature in Ennore estuary showed a significant seasonal variation (P<0.05) (Tables 13-32). Amakiri (2006) reported a temperature value of 27.6°C in premonsoon and 31.6°C in summer season in Bonny Estuary, Niger Delta at Nigeria. Ekeh and Sikoki (2003) reported a temperature value of 25°C in the premonsoon season and 30°C in the summer season at New Calabar river at Nigeria. The temperature variation is one of the factors in the coastal and estuarine system, which may influence the physico-chemical characteristics and also the distribution and abundance of flora and fauna. Higher temperature values recorded in the Ennore estuary during summer months are expected since heat from sunlight increases temperature of surface water. Similarly the drop in water temperature in the premonsoon season is attributable to heavy rainfall experienced during the period. The results of the correlation co efficient analysis showed a significant (P<0.05) correlation between the variables at different sites (Tables 13-32).
5.2 HEAVY METALS IN SURFACE WATER OF ENNORE CREEK

Heavy metals are one of the serious pollutants in natural environment due to their toxicity, persistence and bioaccumulation (Pekey, 2006). As shown in the Table 32, the present investigation in general reveals that the concentrations of heavy metals in the surface waters of Ennore estuary were above the permissible limits. The sites III and IV are the prime source of heavy metals followed by sites I, II and V. All the metal concentrations recorded in the monsoon were higher than summer. Al-Saadi et al. (2002) investigated concentrations of heavy metals in water of Habbaniya lake (Iraq) and found the following concentrations: 15-86 mg/l for zinc, 5-50 mg/l for copper, 0.3-33.3 mg/l for lead and they reported that all metals except zinc had higher values during spring, whereas zinc had higher concentrations during premonsoon. In general the concentrations of heavy metals of Ennore estuary were lower when compared to Habbaniya lake.

In an earlier study, Kannan & Krishnamoorthy (2006) in Pulicat Lake (India) recorded an elevated level of heavy metals concentration especially iron, cadmium and mercury. In the present study, the average concentration of iron in water samples during premonsoon was 7.62 mg/l and in postmonsoon was 2.25 mg/l. At the same time cadmium concentration was 0.01 mg/l in both the seasons. Rajathy & Azariah (1996) stated that the levels of zinc and copper in water and sediment samples showed seasonal fluctuations in the Ennore and Adyar estuaries of Chennai, India. In addition, the high concentration of metals in sites III and IV may be due to the low salinity region and input of sedimentary fluxes. Seasonal variation in metal distribution is
influenced by strong hydrodynamic and physiochemical conditions prevailing in the estuary (Turner et al., 1992; Zwolsman et al., 1997; Padmini & Kavitha, 2005 a,b). As shown in Table 34, the levels of dissolved cadmium in Ennore water recorded in the present study (0.009±0.002 and 0.025±0.005 mg/l) were in the same magnitude reported by Jayaprakash et al. (2005) in Ennore estuary and for Douro estuary in Portugal (Mucha et al., 2004). The cadmium concentrations of two highly polluted estuaries were 0.045mg/l in Rio Tinto Ria Huelva on southwest Spain and 0.0027 mg/l in Chalk system, UK (Goody et al., 2002; Achterberg et al., 2003). Man et al. (2004) reported a cadmium level of 0.0005-0.004 mg/l for the Mai Po and Inner Deep Bay, on Western Hong Kong, in China. All the values reported by earlier studies in different water bodies are higher, when compared with the concentrations of cadmium in Ennore creek.

As shown in the Table 34, the dissolved lead concentrations in the water samples of Ennore estuary were higher (0.090±0.02 and 0.156±0.08 mg/l) when compared to those reported by Vazquez et al. (1998) for Alvarado Lagoon water in Mexico (0.009-0.063 mg/l); by Kraepiel et al. (1997) for the Gironde estuary in France (0.0003 mg/l); by Nayar et al. (2004) for the Ponggol estuary in Singapore (0.020 mg/l). Goody et al. (2002) reported a Pb value of 0.0002-0.0038 mg/l in the cattle slurry lagoons in UK whereas Man et al. (2004) reported 0.0002-0.185 mg/l Pb in the tropical coastal wetland of China. In a survey of trace metal levels along coastal areas of Malaysia, Ismail et al. (1995) reported lead concentrations of 0.0002 to 0.0003 mg/l. In Segara Anakan lagoon of Central Java, Indonesia, lead concentrations
ranged from 0.0002 to 0.0029 mg/l (Tariq et al., 1993). Hall et al. (1996) reported lead concentration of 0.0002-0.0009 mg/l in the dissolved phase of Scottish estuaries. In the present study dissolved lead concentration decreased with increasing salinity (site V) but in lower salinity exists with high concentration (site IV) in the downstream direction. This latter increase in dissolved lead in Ennore creek may be linked to the high industrialization of the surrounding areas, which produces large amounts of lead-based effluents. Moreover, the shallow depth of the river favours re-suspension of sedimentary matter that can contain a significant amount of lead, easily scavenged at the sediment-water interface (Dauby et al., 1994). Lead concentrations observed in the present study were higher than the literature values and permissible limits in all five sites during all seasons, indicating pollution of lead in the aquatic environment.

The maximum concentration of zinc was observed at sites II, III & V whereas minimum concentration was noticed at site IV. The results indicate that zinc is a non-soluble element even at low salinities and shows adsorption which is a major process controlling the distribution of dissolved zinc in Ennore estuary. The high average in site IV and the high values in the mixing zone (Site-V) in Ennore creek reveal that riverine inputs have increased the zinc concentrations along the site IV. Previous studies in other areas particularly, mining polluted area of Roros, Norway indicate that zinc may be complexed with organic ligands in surface waters and this phenomenon may also reflected in site IV (Tanizaki et al., 1992). Zinc concentrations of surface water samples of Bahia blanca estuary are less than 0.001 mg/l (Bryan & Langston, 1992). The present study indicates that the heavy metals were well above the national
environmental board (NEB, 1994) guidelines representing the anthropogenic activities in the Ennore creek.

In Ennore estuary the chromium concentrations ranged between 0.076±0.02 mg/l and 0.136±0.08 mg/l (Table 33). The Cr concentrations ranged between 0.006 and 0.012 mg/l at Likas estuary, North of Borneo Island (Mohd. Harun Abdullah et al., 2010). Moreover, the Cr values in the surface water samples of Ennore creek were moderately higher than the WHO recommended limit of 0.05mg/L.

In the case of Nickel, a minimum level of 0.090±0.02 and a maximum concentration of 0.130±0.07 mg/l were observed in the surface water samples of Ennore estuary. The minimum and maximum Ni values observed in the present study were higher than WHO recommended limit of 0.1mg/L. Similar trend (0.045-0.24 mg/l) was recorded in surface water samples of Ganga river, India (Wasim Aktar et al., 2010). Whereas the minimum Ni concentrations (0.02-0.017mg/l) reported in the surface water samples around Tejgaon industrial area at Bangladesh noticed by Mondol et al. (2011).

Dahuri & Pahlevi (1994) recorded copper concentrations of 0.071 to 0.107 mg/l at Asahan and Deli Serdang in North Sumatra and Lhokseumawe in North Aceh (Indonesia), which are comparatively lower than the values of present study. On an average, site IV had higher concentration of heavy metals than site I, which may be closely associated with suspended particulate matter (SPM) inputs either land-originated or mainly linked with re-suspension and remobilization processes with an active role of benthic biogenic particles (Paulson et al., 1991).
In an earlier study, Al-Saadi et al. (2002) investigated the level of heavy metals in the water of Habbaniya lake (Iraq) and found the following concentrations: 15-86 mg/l of zinc, 5-50 mg/l of copper, 0.3-33.3 mg/l of lead; these reported values were higher when compared to the present study. The levels of Cd observed in the present study (0.009±0.002 and 0.025±0.005 mg/l) are higher than the levels reported by Kannan & Krishnamoorthy (2006) in the Pulicat lagoon, India. The levels of dissolved cadmium in Ennore water recorded in this study were in the same magnitude to those reported by Mucha et al. (2004) at Douro estuary, in Portugal. The values observed in the present study were much lower than those reported for highly polluted estuaries such as Rio Tinto Ria Huelva on southwest Spain (Achterberg et al., 2003).

In the Ennore estuary, the concentrations of heavy metals were observed to be significantly higher during summer than those of monsoon. These seasonal fluctuations may be due to fresh water input following rain as well as due to the release of surplus water from the Poondi reservoir in to the sea via Ennore creek; while the higher values in summer may be due to evaporation (Murthy & Rao, 1987). In an earlier study, lower metal concentrations were observed during winter and higher concentrations were noticed during summer season in Florida Bay at USA (Caccio et al., 2003).

The concentrations of selected six metals (Zn, Cu, Cr, Ni, Pb and Cd) in the surface waters of the Ennore creek varied significantly \( P<0.001 \) with the seasons in all the sites (Table 34). The concentrations of heavy metals in surface water were above the permissible limits of National Environment Board (1994). During summer
season the heavy metal concentrations were significantly \((P<0.001)\) higher when compared to other seasons. Since, the study area is being considered as an important source for fishery, the presence of toxic heavy metals in water would be the primary source for the biomagnifications of metals in fish, invertebrates and other aquatic plants and animals, and cause ill effects to those who consume the contaminated fish (Gochfeld, 2003).

5.3 HEAVY METALS IN SEDIMENTS OF ENNORE CREEK

Sediments are known to accumulate trace metals in aquatic ecosystems. They act as storage sinks for various pollutants. If the storage function overtakes its role, they cause problems such as pollution. This is particularly true of depositional sediments in close proximity to anthropogenic metal discharges. The chemical composition of the sediments can be used as a powerful tool to determine the provenance (Vital & Stattegger, 2000). Sediments can be sensitive indicators for monitoring contaminants in aquatic environments. The sediments may be polluted with various kinds of hazardous and toxic substances (Kamaruzzaman et al., 2006).

Sediments can also act as a scavenging agent for heavy metals and an adsorptive sink in aquatic environment. It is therefore considered to be an appropriate indicator of heavy metal pollution (Idris et al., 2007). Determination of metal concentrations in suspended and bed sediments is more sensitive than the dissolved concentrations as indicators of contamination in hydrologic system (Salmons & Forstner, 1984; Luoma, 1989). Sediments not only act as the carrier of contaminants, but also as the potential secondary sources of contaminants in aquatic system (Salomons & Forstner, 1984; Calmano et al., 1993). Such sediments may become so
elevated in trace metals that they pose a risk to the associated benthic biota. For organisms closely associated with surface sediments, the uptake of metals may result from exposure to the overlying water, the sediment pore-water, sediment/food ingestion, or a combination of the three (Ankley, 1996; Lee et al., 2001).

Estuarine sediment contamination is receiving increasing attention from the scientific community, since it is recognized as a major source of ecosystem health stress (Chapman & Wang, 2001; Riba et al., 2002). They provide a record of the natural and anthropogenic inputs of contaminants into the aquatic environment. It plays a key role in the transfer of trace metals to the coastal area (Martin & Windom, 1991).

Heavy metals have a high affinity for fine-grained sediments and are the key contaminants in estuarine sediments (Middleton & Grant, 1990; Cundy & Croudace, 1995; Lee & Cundy, 2001; Spencer et al., 2003). Urban estuarine sediments usually contain elevated levels of metals including copper, cadmium, nickel, chromium, lead and zinc (Benoit et al., 1998; Sanger et al., 1999).

The levels of heavy metals in the sediment samples of Ennore creek are shown in Table 35; the concentrations of heavy metals in sediment samples of Ennore creek showed the following sequential order: Zn > Cu > Ni > Cr > Pb > Cd for all the four seasons. The high concentrations of heavy metals in sediments may not necessarily indicate anthropogenic contamination, because of different background levels in parent materials and sediment properties (Dauvalter, 1998; Demirak et al., 2006; Esen, 2010).
Al-Saadi et al. (2002) reported that the lead, copper and cadmium concentrations were higher in spring in Habbaniya lake’s sediment. In Karakaya dam lake, the heavy metal concentrations were higher in spring and lower in summer (Karadede & Unlu, 2000). The heavy metals in the sediments of different sampling sites are different that probably resulted from the interaction of rock weathering, soil erosion, pollutant emission, and the properties of sediment such as pH, and organic matter, etc (Lu et al., 2005). The above factors may change the toxicity of heavy metals by affecting the activity, bioabsorption and metabolic process of heavy metals (Chen et al., 2010). The heavy metal levels in the surface sediments of Ennore creek in the north sequentially declined from the estuary of Korttalaiyar river to the bay-mouth mainly because that the sea and freshwater mix in the vicinity of the estuary, which could have accelerated the condensation and deposition of the fine particles in which enriched heavy metals may be adsorbed (Wang & Zhang, 2002). Xu et al. (1993) found higher contents of lead, copper and zinc along Xiamen Harbor Jiulong Port-Quanzhou Bay-Xinghua, probably for the considerable metallic mines of lead, copper and zinc distributed along the southeast coast. Zhihao (2010) reported an average Cd concentration of 670 μg/g.

As shown in the table 35, the Cd concentration in the sediment of Ennore estuary ranged between 19.14±1.80 and 57.25±4.65mg.kg⁻¹. Contamination level of cadmium is lower than that of copper and zinc in the sediment samples of Ennore creek. High values may be attributed to the continental input and runoff from the Araniyar river in Ennore creek. The above inferences are very well supported by the
high levels of cadmium, copper, lead and zinc which are all components of the fertilizers used in agricultural activities (Krumgalz et al., 1992).

Higher levels of lead and zinc (435 and 1090 μg/g, respectively) observed in the sediment samples of Tamilnadu coast reported by Srinivasalu et al. (2005). Distribution of trace metals in the sediment samples of Bay of Bengal, India (Selvaraj et al., 2004) indicating enrichment of trace metals in the river basin which is due to the large-scale industrial input into the river on the upstream side as well as in the coastal region. Srinivasalu et al. (2007) reported copper in the northern, central sectors indicating a two fold increase in concentration (3320-6230 μg/g) than the background samples in Kalpakkam, India. The enrichment of copper, lead and zinc in site IV indicated local contamination. The above inference is also well supported by earlier studies, indicating the enrichment of these metals in the tidal and coastal zones around the study area. In addition, the sampling area is a backwater region with large-scale tourist activities (especially pleasure boating) for more than two decades (Hornberger et al., 1999; Tam & Wong, 2000; Selvaraj et al., 2004).

The average concentration of total trace elements indicates marginal higher concentration of copper ranging from 625.2 to 729.33 μg/g; lead 24.68 to 26.64 μg/g; cadmium 4.45 to 6.0 μg/g; zinc 59.3 to 61.5 μg/g in Bay of Bengal of Chennai, India (Raju et al., 2010). The higher values could be due to the low flow conditions of the coastal waters in the study area which is attributed to the change in current direction (Srinivasalu et al., 2005). In an earlier study, the concentration of trace metals in the samples which are very close to the shore line in Ennore creek indicates that the higher
concentration is may be due to the anthropogenic activities in coastal areas (Muthuraj & Jayaprakash, 2007).

Lead also showed similar distribution pattern in the study area. These elements are known as markers of paint industries and omnipresent in the study area. The concentration of lead in the sediments of this region would have also originated from the atmospheric deposition of automobile exhaust (Leopold et al., 2008). Zinc used as markers or tracers of motor vehicles. The sources of pollution include industrial effluents such as food and beverage factories, and also domestic effluents from the population living along Kortalaiyar river (Srinivasalu et al., 2007; Jayaprakash et al., 2010).

Kehrig et al. (2003) reported that metal concentrations in sediment samples have significantly exceeded the natural concentration of heavy metals, which is due to significant anthropogenic input of zinc, lead, chromium, copper, nickel, cadmium and methyl mercury in a tropical coastal estuary and a Mangrove in Brazil. Various river channels which may act as pathways for sediment inundation to the nearby lands with heavy mineral content, the high metal content may affect the productivity of estuarine environment in future (Turner, 2000; Bob et al., 2005; Sujatha et al., 2008). Comparisons of sediment metal concentration along various other coastal regions around the world indicate increase in cadmium and copper concentration in the Ennore creek area which are well supported by the observations of Muthuraj & Jayaprakash (2007).
The concentrations of different heavy metals in the sediment samples of Ennore estuary are shown in Table 35. The level of heavy metals sediment samples is in the following order: Zn > Cu > Ni > Cr > Pb > Cd. In a study conducted by Sulochanan (2007), maximum zinc level of 29,400 μg/g was observed in Palk Bay sediment. Zulkifli (2009) reported a cadmium level of 0.16 μg/g in peninsular at Malaysia, which is comparable to the present study. Hwang et al. (2008) have reported the following levels of heavy metal concentrations in the sediments of San Francisco Bay, USA: copper: 101-541 μg/g, cadmium: 0.69-7.75 μg/g, lead: 218-750 μg/g and zinc: 280-1430 μg/g.

Edinger et al. (2008) investigated the sediments of north Sulawesi, Indonesia and reported a lead concentration of 2.5-12.0 μg/g; zinc concentration of 34-932.2 μg/g and copper concentrations of 10.0-62.9 μg/g. Copper concentrations in the sediments of mangrove area of Singapore varied from 1.03 to 46.32 μg/g; Zinc concentrations varied from 11.27 to 134.13 μg/g and cadmium concentration of 0.44 μg/g (Cuong et al., 2005). Glasby et al. (2004) reported Cu, Zn, Cd and Pb concentrations of 20 -103, 256 - 1310, 1.2 - 6.3, 42 - 167 μg/g, respectively in the sediments of Szczecin lagoon, Singapore.

Sediments of Florida bay, USA contained 7-32 μg/g of copper, 10-48 μg/g of zinc and 3-15.7 μg/g of lead (Caccia et al., 2003). Strait of Johor (Malaysia) sediments contained copper (11-93 μg/g), zinc (54-334 μg/g), cadmium (0.08-0.34 μg/g) and lead (19-160 μg/g) (Wood et al., 1997a). Pekey (2006a) noticed copper concentrations of 9.6-43.7 μg/g, 75-271 μg/g zinc, 0.005-0.25 μg/g cadmium and
22.3-89.4 mg/g lead in sediments of the Izmit Bay, Turkey. Kucuksezgin et al. (2006) reported 3.3-8.6 µg/g cadmium 23.8-178 µg/g lead and 60.6-139 µg/g Zinc in sediments of the Izmir Bay, Turkey.

The cadmium concentrations of sediment in the South China Sea around Malaysia were below detection limit (<0.01 µg/g to 5.57 µg/g). Cadmium concentrations in sediment of Singapore estuary were 0.2-0.8 µg/g (Sin et al., 1991). Everaarts et al. (1994) reported that mean copper concentrations in the Intertidal zone of Pattani Bay, Thailand varied from 22.9 to 26.9 µg/g. There was no concentration gradient associated with surface sediment.

As shown in the table 35, the maximum (288.46±24.68 mg/kg⁻¹) and the minimum (109.35±9.1 mg/kg⁻¹) ranges of nickel in surface sediments of Ennore estuary show some harmony with the nickel values observed in the earlier studies; 7-357 mg/kg⁻¹ in Ulla estuary, 33.14-49 mg/kg⁻¹ in Medway, 1.2-24.6 ppm in Kabini river estuary (Taghinia Hejabi et al., 2010), 60.2-122.0 mg/kg⁻¹ in Ennore estuary (Joseph & Srivastava,1993), 31.0-68.1 mg/kg⁻¹ in Adyar estuary (Joseph & Srivastava,1993), 7-357 mg/kg⁻¹ in Ulla river estuary (Prego et al., 1999), 19.8-42.1 ppm in Yangtze estuary (Zhongyuan Chen, 2004), 0.16±0.11µg g⁻¹ in Poxin river estuary (Elisangela de Andrade Passos et al., 2011), 21.9-46.5 mg/kg in Pearly river estuary (Xiujuan Yu et al., 2010). The lower and higher ranges of Ni observed in the sediment samples of Ennore are significantly higher than the Effect range medium (ERM) of 51.6 mg/kg recommended by National Oceanic and Atmospheric Administration (NOAA).
Lead concentration in sediments around Singapore ranged from 16 to 250 μg/g (Sin et al., 1991). The concentration of lead in surface sediments of Pattani Bay (Thailand), which was apparently more contaminated, was found to be 79.4-97 μg/g (Everaarts et al., 1994). Most studies from Malaysia were concerned with the west coast of Peninsular Malaysia and the concentrations ranged from 1-180 μg/g. Samples of sediments from various locations along the coast of Malaysia analyzed by Ismail et al. (1995) contained 6.1-27.5 μg/g of lead.

At Bintulu, on the east coast of Peninsular Malaysia, Ismail (1993) documented lead concentrations of 11-36 μg/g in sediments. Jakarta Bay sediments contained relatively higher concentrations of lead, which may be attributed to the heavy ship traffic and discharges from industries directly into the Bay (Ismail, 1993). The concentrations of lead (site IV) observed in sediments in this study were several orders of magnitude less than industrial regions of New Zealand and Brazil (Baptista et al., 2000; Mathew et al., 2003; Amaraneni, 2006).

As shown in Table 35, the concentrations of chromium in the sediments of Ennore estuary ranged between 100.36±8.9 and 298.32±23.68 mg.kg⁻¹. Both the lower and higher ranges of chromium observed for Ennore estuary were significantly lower than the ERM value of 370 mg/kg (Long & Morgan, 1990). The chromium concentrations of sediment in the previous studies from various estuaries worldwide: 1.1- 4.63 nmol g⁻¹ in Gironade (Sebastein Rober, 2004), 10.1 - 92.1 ppm in Yangtze estuary (Zhongyuan chen, 2004), 1.35 ± 0.57 mg/kg in Poxin river estuary (Elisangela de adra passors et al., 2010), 74.1-123 mg/kg in Pearl river estuary (Xiujuan Yu et al.,
2010), 106-590 ng/g in Vasai creek of Mumbai (Pravin et al., 2012), 37.4±1.3 mg/kg in upper sediment layers of Jequia mangrove, Brazil (Kehrig et al., 2003), 19.40±1.51 in Ligas estuary (Mohd.Harun Abdullah et al., 2007), 7.8-38.8 mg/kg in Swartkops estuary (Karen binning & Dau Baird, 2001), 31-144 mg/kg in Medway estuary (Spencer & Mac Leod, 2002) and 1.2-21.2 ppm in Kabini river (Taghinia Hejabi et al., 2010).

The surface sediments in all sites of the Ennore creek were contaminated with heavy metal concentrations and were subjected to interim sediment quality guideline (ISQG) values for interpretation of present study. The average concentration of heavy metals in the sediments of Ozuki lagoon, Japan was 109 mg.kg⁻¹ for Zn, 27 mg.kg⁻¹ for Pb, and 21 mg.kg⁻¹ for Cu. Similarly, 169 mg.kg⁻¹ of Zn, 37 mg.kg⁻¹ of Cu and 9.48 mg.kg⁻¹ of Pb were recorded in the sediments of Ogous lagoon, Japan (Azadur Rahman & Hiroaki Ishiga, 2011). These reported values for heavy metals were very low when compared to the Ennore creek ecosystem. The high concentrations of heavy metals in sediments may not necessarily indicate anthropogenic contamination, because of different background levels in parent materials and sediment properties (Dauvalter, 1998; Demirak et al., 2006; Esen et al., 2010).

5.4 HEAVY METALS IN DIFFERENT BIOTA SPECIES OF ENNORE CREEK

Estuarine environments are vulnerable to stress and if a key species disappears due to heavy metal pollution no other species can replace it. A vast number of chemicals, as well as large amount of nutrients, are released into the environment daily
and transported via rivers and lakes into estuarine and marine environments. Hence there is need to monitor environmental changes, with quantitative laboratory and field investigations integrated to link ecological metrics with metal body burden in sentinel aquatic organisms (Padmini, 2007).

Metals are a natural component of aquatic ecosystem. Excessive levels of metals in estuarine environment can affect aquatic biota and pose risk to people consuming them. Human activities have drastically altered the biogeochemical cycles and balance of some heavy metals by increasing the fluxes of several chemical elements into the ocean. Nonessential heavy metals are of concern to welfare of mankind. The distribution of metals amongst water, sediments and biota in a estuarine eco-system is a function of the metals concerned and reveals the contamination status of the system (Salomons et al., 1987; Saeki et al., 1993; Lopez-Sanchez et al., 1996; Smith et al., 1996).

Heavy metal contamination causes epidemic that last for several years often causing genetic disorders. For instance, lead poisoning from utensils has been considered as one of the main factors in the wiping out the oldest Roman civilization (Takeuchi, 1972). Mercury poisoning in the Minamata Bay, Japan lead to a number of birth defects and presently the fishes in the bay are contaminated with mercury above the permissible limits (Takeuchi, 1972). Mercury poisoning is also referred to as “Minamata disorder” (Takeuchi, 1972). Cadmium poisoning is called as “Itah Itah” disease in Japan (Takeuchi, 1972). Though documented evidence for mass poisoning due to essential elements are lacking, cases on individual poisoning are abundant.
Heavy metal contamination of the environment is recognized as a serious pollution problem. Variability in metal concentrations of marine organism depends on many factors, both environmental and biological factor (Phillips & Rainbow, 1993). Fishes are widely used as sentinels of contamination as sufficient background knowledge enables the use of certain species as bioindicators of heavy metal pollution (Pastor et al., 1994 & 1996). In particular, mercury has received much attention due to its well known toxic effects. Metal analyses of water samples and fish tissue have revealed that metal accumulation is inversely proportional to ecosystem changes (Birge et al., 2000).

The results of present study indicate that *O. mossambicus* accumulated higher concentrations of zinc (521.30±28.30 mg.kg⁻¹) and copper (410.36±30.5 mg.kg⁻¹), which may be due to its ability to retain zinc and copper than cadmium and lead. *O. mossambicus* are more contaminated than *C. batrachus*. So *O. mossambicus* may be used as a good indicator of pollution. The higher concentrations of heavy metals in fish have been attributed to the fatness of liver and fat-content in muscle tissues and its great affinity to combine with heavy metals (Shenouda et al., 1992).

In the present study, higher concentrations of zinc were found in *P. monodon* (568.12±34.20 mg.kg⁻¹) than *F. indicus* (521.30±28.30 mg.kg⁻¹). Aquatic invertebrates show a large variability in heavy metal concentrations in the tissues (Rainbow, 2007). It is well known that heavy metals can be accumulated in tissues of aquatic animals (Yilmaz & Yilmaz, 2007). Generally, crustaceans accumulate some metals in direct proportion to the increase in the bioavailability from water and food.
chains (Rainbow et al., 1990). The crab species *S. serrata* accumulates maximum concentration of all the heavy metals for all seasons when compared to *P. pelagicus* (Tables 37-42).

Environmental factors, such as freshwater runoff, particulate matter re-suspension, and primary production might have been influenced the bioavailability of trace metals in Ennore creek. Many of these processes are highly variable on monthly and even daily scales. Besides, the heavy metals were found to be higher in sites that were located near industrial areas (Praveena et al., 2008). In the present study, concentrations of all the heavy metals in fish, crustaceans and mussels were exceeding the permissible limits recommended by FAO (1983), USFDA (1996) & European Commission (2001). The higher concentrations of Cu, Cr, Zn, Cd, Ni and Pb in the biota samples, particularly in the bivalve species from Ennore creek may be due to anthropogenic influence particularly the inflow of industrial effluents (thermal outlet, fertilizer industrial effluent and cement industrial effluent). The results of this study reveal the valuable information about the metal contents in fish, crustacean and molluscan species from the Ennore creek. In the present study bivalve molluscan *C. madrasensis* have been identified to accumulate higher concentrations of non-essential and essential heavy metals than other animals, suggesting that they could serve as bioindicator of severe heavy metal pollution.