CHAPTER-2

Review of Literature
2. REVIEW OF LITERATURE

Estuaries are regarded as one of the most important and unique aquatic ecosystems because they form the place of transition from land to sea and from fresh water to seawater. According to Pritchard (1967) estuary is a semi enclosed coastal body of water having free connection with the sea with measurable quantity of seawater. Estuaries are not in an ideal state but they are affected by surface runoff, tidal wave action and variation in rainfall. The productive estuarine habitats sustain a rich fauna and flora. The present study is aimed at assessing the various physical and chemical aspects of the Manakudy estuary which is a bar built estuary with an area of 150 ha situated about 8 kilometers northwest of Cape Comarin.

The literature pertaining to the study has been reviewed extensively.

Physicochemical parameters
Temperature, Salinity, DO, pH, transparency

Gouda and Panigrahy (1993) studied the hydrographic features such as temperature, salinity, dissolved oxygen pH and transparency of estuaries in relation to the distribution of flora and fauna. Karthikeyan et al, (2004) studied the seasonal distribution of physico-chemical parameters from Uppanar estuary and found that there was a profound seasonal variation in the physico-chemical condition. Prema and Subramanian. (2003) studied the hydrology of Muttakadu backwater of Bay of Bengal and found that the pH
was always alkaline and the temperature negatively correlated with salinity. It was observed that the nutrients, nitrate and phosphate were almost uniform but for a brief period in which nitrate concentration showed an inverse relation with phosphate concentration. However both the nutrients showed higher concentration during the period of low salinity. Ryther and Dunstan, (1971) attributed the increased level of nutrients to eutrophication.

Salinity is an important ecological factor, which influences distribution of plankton in the estuary. Rajagopal (1981) and Rajesh et al, (2001) while studying the physico-chemical parameters in mangrove and non mangrove areas of brackish water impoundments along Nethravathi estuary observed that most of the physico-chemical parameters showed well marked seasonal as well as spatial variations, influenced mainly by the monsoon cycle. Further the waters of impoundments remained Seawater dominated during premonsoon season, whereas freshwater dominated during monsoon.

The physico-chemical characteristics of sewage polluted Kulti estuary was studied by De et al, (1999). There was a negative value of oxygen saturation due to sewage inputs. Das et al, (1997) observed that parameters like water temperature, pH, suspended solids, salinity, dissolved oxygen and nutrients showed varying levels in relation to tidal condition during monsoon, postmonsoon and premonsoon. The pH and salinity increased during high tides while suspended solid showed higher levels during monsoon season.
Further concentrations of dissolved oxygen, \( \text{PO}_4^{3-} \), \( \text{NO}_2^- \) and \( \text{NO}_3^- \) increased during ebb regime and a decreasing trend was observed starting from monsoon to premonsoon. The estuary showed higher values of ammonia during low tides, which was attributed to the discharge of domestic sewage and industrial effluents to the estuary.

Ragothaman and Patil (1995) while studying the physico-chemical parameters of Narmada estuary observed that there was a wide fluctuation in the parameters due to agricultural runoff, common pollutants arising from municipal and domestic waste.

Kadam (1992) found that the water in Thana Creek was highly polluted due to effluents from dye, chemical, pesticide and insecticide industries. Due to disposal of large amounts of pollutants, the BOD, turbidity and heavy metal levels in the Creek crossed the standard limits. Because of increase in organic load the dissolved oxygen was utilized in the process of biodegradation. Kumary and Azis, (1992) monitored the water quality of the Poonthura estuary and was found that light penetration was minimum during the monsoon period and the lowest values were observed in places receiving large quantities of sewage wastes. Further pH was maximum during the pre monsoon period and dissolved oxygen was low but hydrogen sulphide was high. Salinity distribution was influenced by the sea-estuary interaction consequent to the opening of the sand bar. The general distribution of nutrients maintained an increasing trend from the premonsoon to the monsoon period and comparatively high values were observed at the polluted areas.

Murugan and Ayyakkannu, (1991) while studying the ecology of Uppannar back water found that even though wastes were discharged in the backwater the oxygen level was higher probably due to high photosynthetic activity and high flushing characteristics of the Uppanar backwater. Further high transparency was found to be associated with high productivity. The pH values did not follow any definite seasonal pattern and the range of variation was narrow.
Saisasty and Chandramohan, (1990) studied the physico-chemical characteristics of Vasishta Godavari estuary to assess the impact of pollution to which the estuary would be subjected with the exploitation of oil in its basin. The influence of seawater was felt in the estuary up to a distance of 40 km from the confluence towards the upper reaches. Salinity stratification was more marked than that of temperature. The lower reaches were turbid than the middle and the upper. Often the water column was supersaturated with oxygen. It was also found that the concentration of inorganic phosphate was much less and silicate was in sufficient quantities all through the non-flood period. Upadhyay (1988) found a seasonal pattern of temperature, salinity, pH, dissolved oxygen, nitrate and silicate profiles in the Mahanadi estuary. The oxygen concentration in this estuarine system was closely related to biological activity. The pH showed an inverse relationship with salinity. Further dissolved nutrients were mostly non-conservative.

The hydrobiology of various estuaries like Ashtamudi estuary (Nair and Azis, 1987a&b); Vellar estuary (Chandran and Ramamoorthi, 1984); Tapi estuary (Ragothaman and Reddy, 1982); Pulicate lake (Raman et al, 1975); Zuari estuary (Singbal, 1973) and Cochin backwater (Shynamma and Balakrishnan, 1973) were thoroughly investigated.

Other important works on estuarine ecology include those of Joseph et al, (1982) in the Adayar estuary; Evangeline (1975) in the estuaries of

**Sediments**

According to Morris, (1978) estuaries are regions of fundamental importance with respect to geochemical processes on the global scale, for they represent the major route whereby lithospheric material is transported to the oceanic sedimentary domain. Further the studies of estuarine processes also pave the way for predicting the geochemical behaviour of each individual element. Various authors have studied the distribution pattern of sediment mineralization in sediment fractions, sediment mineralisation, exchange and cycling of nutrients, nutrient fluxes, particulate organic matter and other geochemical aspects of sediments. Mucha et al, (2000) studied the sediment quality in Douro river estuary to evaluate the influence of sediment quality on ecosystem degradation. They studied the characterization of the sediments in terms of organic matter and heavy metals, detection of the occurrence of levels of metals above sediment quality guidelines and the probable anthropogenic origin of the metal enrichment through metal normalization to Fe. Further Callender and Hammond, (1982); Wolaver et al, (1986); Bryan and Langston, (1993); Boon et al, (1999); Hopkinson et al, (1999); Carballeira et al, (2000); Christensen et

Paterson et al, (2000) studied the variations in sediment properties of skeffling mudflat, Humber estuary. Crawford et al, (1995) while studying the sources of pollution and sediment contamination in Newark Bay found elevated levels of heavy metals in sediments. Hewitt and Candy (1990) observed very high levels of lead, cadmium and zinc in the soils in and around Cuenea Ecuador.

Considerable literature is available on the sedimentary profile of estuaries on the east and west coast of India. Comprehensive studies on the physico-chemical, biological and mineralogical aspects have been made by various authors in Indian estuaries. Murty and Veerayya, (1981) found that the elemental concentration follow closely the texture of the sediments in the Vembanad lake. Alagarsamy (1991) studied the organic carbon in the sediments of Mandovi estuary and found that the total organic carbon (TOC) showed marked variation in the superficial sediment. There was also seasonal variation being high TOC during premonsoon and low during monsoon and postmonsoon. Seralathan et al, (1993) while studying sediment and organic carbon distribution in the Cochin harbour area found that mud and sand rich sediments predominate in the estuarine mouth and there was high organic carbon content in the sediments. Chandran et al, (1982) observed sandy
sediments near the mouth of the Vellar estuary while silt and clay at the upper reaches. Jegadeesan and Ayyakkanu, (1992) also observed similar trend in the marine zone of the Coleroon estuary. Nasnolkar et al, (1996) observed that the change in the nature of sediment during premonsoon, monsoon and postmonsoon was mainly due to the transport of sediments from one place to another and back associated with tidal currents. The bottom sediments were a mixture of silt and clay in the Cochin mangrove swamps (SuniJ Kumar and Antony, 1994). However silty sand sediments were noticed in Cochin mangroves during monsoon. In many estuaries this trend was noticed as observed by Rao and Swamy, (1991) in Godawari and Krishna river estuaries and Nandan and Azis, (1996) in Kadinamkulam estuary.

The pH of the soil showed marked variations in relation to season (Selvaraj, 2000). Anil kumar et al, (1998) observed the monthly trends of the residual fluxes of salt and fresh water and the transportation of suspended sediments in the Beypore estuarine system. It was found that at the river mouth the water flux was directed seaward during postmonsoon and monsoon seasons. During the premonsoon period the transport was upstream. Maximum flux of the suspended sediment was obtained during the monsoon season at the river mouth and high negative fluxes were obtained during premonsoon at the river mouth. Similar trend was noticed in the distribution pattern of particulate matter in the Netravathi - Gurpur estuary (Vedamurthy et al, 2000). The sediments at the Malpe and Gangolli estuary showed low
percentage of silt - clay fraction mainly because of the filtering capacity of these estuaries. The sediments however were negatively skewed and well sorted (Hande and Madhyastha, 2003).

The sedimentological studies along the east coast of India pertain to the work of many authors. Rao (1971) studied the bottom sediments of Pulicat lake and Joseph (1991) studied the sediments of Ennore estuary in relation to mitigation of mercury loading in biological system. Rao et al, (1992) made a correlation between mangrove environment and its sediment characters in Godavari estuary. It was found that high density of mangrove population was observed where salt was high in the sediments. The mangrove sediments are characterised by muds, sandy muds and clayey muds and the sand content was very low. However relatively high content of sand was observed at the landward side corresponding to the waterfront side. Further Venkateswaran and Natarajan, (1983) studied the distribution of free phosphates in the sediments of Porto-Novo. The chemical and textural characters of Vasishta-Vainateyam Godavari delta and the Cauvery estuary were studied by Murty and Murty, (1993) and Ramanathan et al, (1988) respectively.

The concentration of suspended matter (CSM) in Gautami – Godavari estuary increased during southwest monsoon due to increased runoff. However during premonsoon and northeast monsoon season the CSM was
mainly controlled by the tidal currents as the fresh water discharge during this period was minimum (Reddy et al, 1994).

Mohan (2000) studied the sediment transport mechanism in the Vellar estuary. It was found that sand predominate in the head of the estuary with silt and clay as subordinate constituents. The proportion of sand decreases towards the confluence. The silt content was comparatively lower than the clay content in the downstream direction. However the central part of the estuary showed a decreasing trend of sand and an increasing trend of clay content. The variations in the textural characters suggest that tidal activity has significantly affected the sediment population and minor disturbances of other transporting agencies might have affected the depositional processes which are marked in the deposited sediments.

**Metals in Sediment**

Trace metals, or heavy metals have been major environmental contaminants since the advent of industrial revolution. Several of the elements are highly hazardous to aquatic life and humans. Being basic elements, they are not biodegraded and very long lived in the environment (Larsen, 1992). Heavy metals are critical in the environment because of their uptake in food chain and because of bioaccumulation processes (Beijer and Jernelov, 1986).
Various authors have studied the distribution of elements in the sediments of estuaries. Caetano et al, (2002) showed that in shallow highly productive estuarine environments intense biogeochemical activity is concentrated in the upper sediment layer. However, pore water compositions of permeable inter-tidal sediments change as water flows over the areas during ebb and flood tides. It was found that Fe is mainly cycled inside the sediment but Cu and Cd exhibited different patterns. When Cu and Cd reach the sediment surface they are rapidly released to the water column.

Further the equilibrium between pore water and sediments in shallow productive environments is greatly influenced by the presence and activity of benthic organisms (Aller, 1977), the pressure variation induced by wave motion (Shum and Sundby, 1996) and the mixing linked to the tidal excursion (Hemmond et al, 1984; Agosta, 1985). Equilibrium in inter-tidal permeable sediments of macro- and meso-tidal environments is repeatedly altered by the tidal flushing, which causes a partial renewal of pore waters and the export of solutes to the water column twice a day (Falcao and Vale, 1995). For example NH$_4^+$ weakly sorbed to the sediment particles and of Fe, a redox-sensitive element, change dramatically their concentrations during tidal inundation (Caetano et al, 1997). When sediment temperature increases during exposure to the atmosphere, solute concentrations changes due to density gradient currents (Rocha, 2000).
Muller et al, (2002) studied the elemental composition of the sediments of Lake Baikal and found that the trace metal concentrations in sediments and pore waters of Lake Baikal was scarce. There was a slight increase in Pb and it was attributed to atmospheric transport from anthropogenic sources.

Warwick (2001) found that due to extensive mining in the catchment area of the Fal estuarine system in the past, metal concentration in the intertidal sediments are the highest. Due to heavy metal toxicity for a long time there was induction of metal tolerance in some species and in others by the evolution of tolerant strains.

Chiffoleau et al, (2001) studied the spatiotemporal changes in cadmium contamination in Seine estuary and found that cadmium was among the major contaminants of the estuary.

Cortesao and Vale, (1995) studied metals in sediments of the Sado estuary and found that element / aluminium ratios showed considerable variations along the different sediment origins and metal anthropogenic inputs. Association types of the metals can be divided into 2 groups; metals with relatively high potential for mobilization such as Cd, Zn, Mn, and Ni and those that are bound on particles - Cr, Cu, Pb and Fe (Calmano and Wellershaus, (1982).
According to Larsen et al, (1983) a nearly universal consequence of urbanization and industrialization of estuarine shores is an elevation of environmental levels of various trace metals. Of the three compartments where metals reside in an aquatic environment, the biota, the water and the sediments, the sediments are the major repository. Metals anthropogenically introduced to the marine environment are removed from the water column close to the point of entry (Helz et al, 1975; Lyons and Fitzgerald, 1980) and hence metal levels of estuarine and marine sediments can act as sensitive indicators of environmental quality while the sediment record in depositional environments can serve as a historic index of change.

Several authors have studied the speciation and behaviour of trace metals and heavy metals in the Indian estuaries. Joseph and Srivastava, (1993) recorded that in Ennore estuary the concentration of metals in sediments were higher in the head of the estuary and decreased towards the estuarine mouth, while in Adyar estuary higher concentration were noticed in the middle of the estuary. Further the concentrations of metals showed an observable seasonal variation in the estuarine sediments. The concentrations of the metals were found to be higher during the monsoon period. Similar observations were made by Subramanian and Mohanchandran, (1990) in the studies on heavy metals distribution and enrichment in the sediments of Southern East Coast of India.
George (1993) has extensively studied the speciation and behaviour of Pb, Cd and Cu in Zuari estuary in relation to rainfall. It was found that dissolved labile and nonlabile forms of Cd, Pb and Cu showed lowest concentrations during the southwest monsoon while maximum concentrations were observed during the premonsoon season. The iron content in sediment in relation to monsoon was studied by Biksham and Subramanian (1988a&b) in Godavari estuary and Subramaniam et al, (1988) in the Ganges estuary. Further a variable but systematic increase in the concentration of metals was observed towards the high salinity region. Chlorinity plays an important role in the adsorption / desorption character of a metal. An increase in salinity causes a decrease in the adsorption. In addition other mechanisms like ionic strength pH, redox potential, microbiological activity, organic matter degradation and the residence time of the particle in the mixing zone also play an important role. Precipitation of Fe has been one of the factors for the increased level. Further co-precipitation with the iron hydroxide could have led to a decrease in the concentrations of Cd, Pb and Cu towards the high salinity region.

Nair et al, (1993) studied the surficial sediments of the Cochin estuary and delineated five metal fractions namely exchangeable, carbonate bound, easily reducible, organic / sulfide bound and residual. It was found that there was selective accumulation of Mn and Ni in carbonate bound and organic / sulphide forms along with marginal amounts of Co in the exchangeable
fraction. Large portion of Fe and Cr occurred in the residual fraction, whereas composite fractionation of Zn species was noticed. The exchangeable fractions of Fe and Cr as well as of easily reducible Co were below detection limits. The levels of Cr and Zn indicate anthropogenic inputs in the estuary, whereas Co and Ni showed regional contamination exceeding natural levels. Shanthi et al. (1990) studied the sediment concentration of Zinc and Copper in the Vellar estuary and found maximum values of Zinc during monsoon and postmonsoon. However the maximum value of Copper was recorded during premonsoon season.

Mohan (1995) applied the enrichment factor to represent the trace elemental concentration in Vellar estuary. It was found that elemental concentrations were higher in the clay fraction than in the bulk samples. However, the enrichment factor showed that the elemental concentrations were higher in the bulk samples than in the clay fractions. Further the enrichment factor suggested that the enhancement of trace elements due to ionic exchanges in clay minerals was negligible and might be due to the adsorption and absorption by iron oxide coating on clay minerals and other matters. Based on the results of the elemental concentration of combined bulk and clay fractions, Mohan (1995) provided four factors influencing the overall contribution of these elements. The first factor is “grain size factor” which mainly influences the concentrations of elements, except Ti and Cd. These
two elements may be influenced by coarse size i.e. titanium minerals available in the size ranges of fine sand to fine silt and cadmium normally available in the carbonate phase as shell fragments mostly available in the size ranges larger than silt.

The second factor is called the "solution factor". i.e. Fe, Mn, Cr and Co are mainly provided from a hydrogenous source and not by any other processes. But other elements could have been provided by organic matter, carbonates, clay minerals, etc.

The third factor suggests that mineralogical composition has also played an important role in the overall concentration of elements in the environments, so it is called as "mineralogical composition factor". Al, Fe, Ni and Co are the major elements, which are influenced by this factor. However, the remaining elements have not shown any influence in this factor.

The fourth factor is "deporption factor" i.e. the elements desorbed from the precipitate. The elements Mn, Cu, Ni, Zn, Cd and Co are mainly influenced by this factor but the remaining elements have not shown any significance in this factor. The chemical constituents such as organic carbon, carbonates, Al, Fe, Mn, Ti, Cu, Ni, Zn, Cr, Cd and Co which are present in the Vellar river, its estuary and nearshore environments are mainly influenced by grain size variation or Fe and Mn precipitation or composition of the
minerals in the sediments or desorption of elements from the precipitate, or by a combination of one or more of these processes (Mohan, 1995). Similar correlation between trace metals and the soil texture of the sediments in the Gulf of Mannar have been observed by Kumaresan et al, (1998). Sankaranarayanan et al, (1998) found the trace metal supplied to an estuary is mostly in particulate form which in turn is related to the organic and manganese concentration of particles. Further it was observed that anthropogenic discharge of heavy metals into the environment forms part of the suspended matter in rivers, which acts as an effective scavenger of these trace elements.

Panda and Sahu, (1999) observed in the Bahuda estuary that residual fractions of the sediment played an important role in enrichment of trace metal ions like Co, Zn, Cr, Cu and Pb, indicating locked nature of these elements. Further Fe-Mn oxide bound phase contributes a significant amount of trace metal load to the sediments followed by carbonate phase, which is of minor quantity.

Kumar et al, (2001) studied the levels of certain heavy metals in the sediments of Mangalore, West coast of India in relation to industrial effluents and found that zinc concentration was high followed by chromium, copper and cadmium. Further heavy metals exhibited a distinct seasonal and spatial variation.
The estuarine core sediments in the tidal zones between Chennai and Pondicherry of the east coast of India also showed marked variations in the elemental composition (Achyuthan et al, 2002). Further calculated enrichment factor with respect to upper sedimental crust showed that analysed sediments were depleted in Mn, Co, Pb and enriched in Ni and Cr.

Sarkar et al, (2004) made a detailed document of geochemical and mineralogical aspects of the muddy to sandy mud sediments of the Hugli river, north east coast of India. It was found that the level of the metallic and non-metallic elements showed a wide range of variation all along the course of the estuary and this could be attributed to their differential discharge from the source rocks and differential discharge of untreated effluents originating from industrial, agricultural, aquacultural as well as domestic sewage. The elemental contents, particularly the heavy metal content in the sediments were lowest in the upstream part of the estuary but higher in the intermediate stretch and highest in the mouth of the estuary.

Loska et al, (2004) studied the metal concentration of farming soils affected by industry. The contamination of the soil was assessed on the basis of geoaccumulation index (Igeo), enrichment factor (EF), contamination factor and degree of contamination $C^i_r$. The geoaccumulation (Igeo) was used to assess the metal contamination of soil by comparing current and preindustrial concentration. Based on this value, six classes of the
geochemical index were distinguished (Muller, 1981). The enrichment factor (EF) was based on the standardisation of a test element against a reference one. The reference element is the one characterized by the low occurrence variability. The most common reference elements are Mn, Ti, Al and Fe (Pacyna and Winchester, 1990; Quevauviller et al, 1989; Reimann and de Caritat, 2000; Schiff and Weisberg, 1999; Sutherland, 2000). Loska et al, (2003) used calcium as the reference element because calcium is one of the main components of the earth’s crust and its concentration in the soil is connected mainly with the matrix. Further the mining interference factor (MIF) for calcium is similar to the value for Rb and higher than MIF for Al and Zn which are most often used as reference elements.

According to Hakanson (1980) the study of the contamination factor and degree of contamination would be necessary to assess the soil contamination through reference of the concentrations in the surface layer of bottom sediments to preindustrial levels. Loska et al, (2004) found elevated contents of cadmium, lead, arsenic, antimony, and mercury in farming soils of Poland due to industrialization. However the contents of Chromium, Nickel, Lead, Zinc and Mercury were similar to the levels in the Earth’s crust or pointed to metal depletion in the soil.

Webster et al, (2000) studied the source and transport of trace metals in the Hatea river catchment and estuary. The study of Cu, Pb, Zn, Cr and As
concentration in bed sediments, fresh water, storm water and suspended particles (SPM) revealed that the most recently deposited sediment in the Hatea River estuary has elevated levels of Cu, Pb, and Zn. This was attributed to the metal derived from tributaries draining the more densely populated side of the catchment and Cu-bearing antifoulants used in the marina. Further it was noted that the trace metals were transported in both dissolved and particulate form in the fresh water tributaries. There was also evidence to show that the trace metals were conveyed by coarse SPM during periods of highest river flow. It was found that of the metals, Pb showed the strongest association with coarse SPM and the greatest potential of accumulation in estuarine sediment, demonstrating little tendency to be leached from sediment under stimulated estuarine conditions.

Ayyamperumal et al, (2006) made the base line sediment quality study for trace metals in the River Uppanar, Southwest Coast of India. It was found that acid leachable metals, Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn and Cd showed peak value at the sulphidic phase and the enrichment of metals in the surface layers were due to anthropogenic activities. Factor analysis showed that anthropogenic activities have affected both the estuarine and fresh water regions of River Uppanar. Wong et al, (2006) studied the urban environmental geochemistry of trace metals. Wair et al, (1993) made elaborate studies on the sediment characteristics in relation to changing hydrography of Cochin estuary.
Acevedo-Figueroa et al, (2006) made extensive studies on the trace metals in sediments of two estuarine lagoons from Puerto Rico. It was found that there was an elevated concentration of As, Cd, Cu, Fe, Hg, Pb and Zn in the sediments of these lagoons. Further the average concentrations of Hg, Pb and Zn in the sediments were above the effect range median (ERM) that predict toxic effects to aquatic organisms. Enrichment factors using Fe as a normalizer and correlation matrices showed that metal pollution was the product of anthropogenic sources. The sediment metal concentrations in some areas were of natural origin and were comparable with other regions of the world.

Duquesne et al, (2006) showed evidence of decline in levels of heavy metals in the Severn Estuary and Bristol Channel, UK and their spatial distribution in sediments. It was found that sediment metal concentrations were highest at sites close to industrial centers but levels have decreased significantly in other areas of the estuary. Further greatest metal concentrations in deposited sediments were usually associated with the finest particulates at locations with muddy sediments, but this was not always true at sites with predominantly sandy sediments. Further it was shown that the metals bound to suspend particulates at all sites were remarkably consistent, presumably reflecting the mixing capacity of the macro tidal estuary. The sediment redistribution due to strong seasonal currents also attributed to differences in the sediment characteristics.
Ray et al, (2006) studied the trace metals in the particulate matter and sediments in the Godavari estuarine mangrove ecosystems. It was found that the trace metal concentration in the particulate matter and in sediments were higher compared to the Bay. This was a positive evidence to show that the mangrove environment was a source of these trace elements. There was a significant correlation between several couples of metals in different regions of the estuary. Further, there was significant correlation between heavy metals like Fe, Mn, and Zn with total suspended matter (TSM) in particulate organic matter indicating that complexation with organic materials may play an important role in the distribution of these metals. Significant correlations existed between organic carbon (OC) and Cr, Co, Pb, Cu and Mn in sediments indicating the fact that organic matter is acting as a metal carrier. The insight into the correlation matrix in the estuarine mangrove ecosystems showed that the trace elements may be divided in to three combination viz i) Fe, Mn and Cr. ii) Cu, Co, and Ni. iii) Pb and Cd. It was observed that high concentrations of trace metals in mangrove sediments indicate that the mangrove systems are physical traps for fine material and their transported load of metals, constitute of chemical group of metals from selection (Harbison, 1986)

Menounou and Presley, (2003) studied mercury and other trace elements in sediment cores from Central Texas lakes in relation to local anthropogenic effect from coal- fired power plant. It was found that mercury and other trace metals could be transferred to an aquatic environment through
atmospheric deposition. Sediment cores from lakes near to the power plant showed higher trace metal concentration in the upper part of the cores compared to the bottom layers. This was an indication of deposition of trace metals in the recent sediments.

Presley et al, (1992) studied trace metal concentration in sediments of the Eastern Mississippi Bight. It was found that there was considerable variation in trace metal concentration both spatially and temporally, largely as a result of natural variability in grain size mineralogy. Clay rich samples from deep water were always more metal rich than sandy samples from shallow areas. There was evidence to show that biochemical activity in the sediment was capable of solubilizing reducible and adsorbed metals.

Nair and Ramachandran, (2002) studied the textural and trace elemental distributions in sediments of the Beypore estuary along the South west Coast of India. They opined that textural characteristics, major elements and total organic carbon (TOC) content of the sediments have substantial influence on the elemental distribution. Significant variations in the concentrations of Mn, Cr, Ni, Cu, Pb and Co were observed in riverine and estuarine sediments whereas except for Mn the variations are not so pronounced in the innershelf regions. Both silt and clay showed high positive loadings with all the elements in the estuarine regions. However it was found that in the innershelf sediments, the trace elements showed better affinity with
clay fractions than silt. Further TOC had significant positive correlation with trace elements in both estuarine and innershelf sediments. Finer fractions and TOC played a major role in the distribution and retention of trace elements in sediments. It was also observed that estuarine inputs had a profound influence on the trace metal flux in the immediate vicinity of the adjoining innershelf.

The distribution and seasonal variation of trace metals in surface sediments of the Mandovi, a tropical estuary in the west coast of India were studied by Alagarsamy (2006) to determine the extent of anthropogenic inputs from mining activities and to estimate the effects of monsoon on geochemical processes. It was observed that the concentrations of iron, manganese, cobalt, copper, zinc and lead showed marked variations. Further the metal concentration was invariably lower during monsoon compared to the pre and post monsoon. There were detectable anthropogenic inputs in the estuary due to iron ore processing in the upstream of the estuary as evidenced by the high enrichment levels of iron and manganese. The Igeo levels were also high in the estuary. Further there was Cu and Zn enrichment in the mouth of the estuary due to organic load from the municipal sewage entering the estuary.

**Metals in Water**

Industrialisation leads to pollution of the aquatic ecosystem. Pollutants are discharged into rivers and lakes and leaches into the soil and ground water.
Many authors have studied the major and trace metals in estuarine waters. Kraepiel et al, (1997) studied the geochemistry of trace metals in the Gironde estuary and found that Cd, Ni and Zn appeared to have a mid-salinity maximum in dissolved concentration. However both conservative and nonconservative behaviours have been observed for dissolved Cu in the estuary and there was not a mid-salinity maximum. The dissolved Pb behaves quasi conservatively in the estuary and follows a simple dilution line. The Fe concentration was higher at low salinities and there was a decreasing trend seaward. Chiffoleau et al, (2001) found Cd contamination in the Seine estuary. There was partition of Cd between the dissolved and the particulate phase and was characterized by an intense phenomenon of solubilization in the mixing zone fresh water - sea water, however the colloidal Cd fraction remained low along the whole salinity gradient.

The dissolved labile and nonlabile forms of Cd, Pb and Cu in Zuari estuary showed lowest concentration during the monsoon, while maximum concentration during the premonsoon season. The metal input due to desorption and dissolution of the particulate phase was not very significant in Zuari estuary (George, 1993). Similar observations were made by Shibu et al, (1995) in the Cochin estuary.

Senthilnathan and Balasubramanian, (1997) found an inverse relationship between the metal concentration in water and sediment in the
Vellar and Uppanar estuaries. They opined that the inverse relationship between metals in water and sediments was due to variation in salinity. When the metal rich river water mixes with the metal impoverished seawater there was rapid sedimentation process. In addition, the sharp increase in salinity as the fresh water mixes with seawater would result in the precipitation and coagulation of metal with or adsorption on to the particles and remove considerable amount of metals from the solution.

Sankaranarayanan et al, (1998) found that there were seasonal fluctuations in trace metals in the Cochin Backwater.

Dash et al, (2000) found that there were seasonal variations in dissolved and particulate fractions of Cd in the Rushikulya estuary. The dissolved and particulate fractions of the element showed a significant behaviour in different seasons because of their involvement in the biochemical cycles. Further, the physico-chemical parameters indicated a significant variation due to estuarine mixing.

Nagaraju et al, (1994) found that in the water of Pulicat Lake the concentration of the trace elements increased with increase in pH, chlorides and sodium in both monsoon and dry seasons. Further, the concentration and the behaviour of trace elements were controlled by adsorption, supplemented by organic reactions and by precipitation in sulphide rich environments.
Diagomanolin et al, (2004) found that the metals like Ni, Cr and Cu showed higher concentration during winter and minimum concentration during spring. Further heavy metals like Cr, Ni and Cu were found in higher concentrations at downstream compared to upstream. The higher concentration of Ni and Pb was due to discharge from agricultural industries (Rauret et al, 1988). Das and Sahu, (2002) made toxicity studies in the Rushikula estuary.

Jeyaprakash et al, (2005) made a base line study of physico-chemical parameters and trace metals in waters of Ennore Creek and found that the discharge of effluents from major industries near the Creek was responsible for the heavy stress on the estuary. There was positive correlation between Na⁺ and K⁺ and salinity. Manganese showed a conservative behaviour with high values at low salinity. Iron and Manganese showed similar trend, being removed by colloidal flocculation on the downstream side and showed very high concentration on the downstream side. The high concentration of Cr, Cu, Ni, Co, Pb, Zn and Cd was also related to high temperature (Jeyaprakash et al, 2005).

**Organic carbon** OC

The organic carbon in sediments is reported to be a reliable index of nutrients regeneration and the productivity of a water body. Redox potential is
a readily obtained description of organic matter within the sediment and of its oxidizing or reducing power.

Several authors have studied the organic carbon in sediments. Muller *et al.*, (2003) by the study on the deposition of organic carbon in the sediments found that almost all settled organic carbon was degraded from calcite with oxygen at shallow depths and only a fraction was decomposed aerobically at the deepest location.

Das *et al.*, (2001) found that organic carbon contents showed seasonal fluctuations influenced by rainfall. Higher values of organic carbon were found during the postmonsoon period and it was attributed to influx of land runoff containing considerable amount of terrigenous organic matter due to monsoon showers. Similar observations were made by Nasnolkar *et al.*, (1996).

Normally the level of organic carbon in sediments is a reliable index of productivity of the water body. Positive relationship between the abundance of benthic fauna and concentration of organic carbon in sediments has been recorded by several workers (Damodaran, 1973; Parulekar and Dwivedi, 1973; Parulekar *et al.*, 1975; Chandran, 1987b). Further it is noteworthy that organic carbon and nitrogen contents of the sediment types with higher content of clayey silt or silty clay substrates and lower content of sandy substrates (Chandran, 1987a). However in a confined saline pond the organic
carbon in sediment was related to the prawn crop even though the sand content of the sediment was relatively higher. This was due to gradual accumulation of manures, residual feed and metabolites in the confined saline pond (Das et al, 2001).

Nandan and Azis, (1996) made elaborate studies on organic matter of sediment from retting and non-retting areas of Kadinamkulam estuary southwest coast of India. It was found that organic matter like pectin, pentosan, polyphenols and tannins released from retting areas by microbial decomposition increases organic pollution in the estuaries. Further increase in the salinity and temperature accelerated the retting process which in turn increased the organic load of the medium. This was evidenced by the fact that organic carbon in sediments was higher in the retting areas when compared to the nonretting sites. Further the organic carbon content was highest during the premonsoon period and there was considerable seasonal variation in the distribution of organic carbon. The very low rainfall during premonsoon period resulted in the development of a stagnant condition in the estuary leading to a sharp rise in the organic carbon content. But during the monsoon there was heavy river discharge and the organic carbon content decreased.

Sunil Kumar (1996) found that there was vertical and horizontal distribution pattern of organic carbon in the sediments of Cochin mangroves. There was correlation and predilection between organic carbon and the
texture of the sediment. Organic carbon has a proportional and patent relationship with the fine fractions (silt and clay) of the sediment. However in the tidal areas of the mangrove swamp there was inconsistent pattern of organic carbon in the sediment with regard to vertical as well as horizontal distribution.

Seralathan et al, (1993) observed a positive correlation between sediment texture and organic carbon. Mud sediments showed the highest organic carbon values followed by sandy mud. However silty sand and muddy sand showed low organic carbon content in the Cochin estuary.

Packard et al, (2000) while studying the role of dissolved organic carbon in transferring carbon between planktonic components of the gulf of St. Lawerance pelagic system found that there was a relationship between DOC and phytoplankton primary production in the euphotic zone during the bloom and a relationship between DOC and bacterial production in the euphotic zone after the bloom. Further a dial study showed DOC production in the morning and DOC degradation in the evening implicated phytoplankton in generating DOC during the day. There was a positive correlation between DOC and ammonium, and DOC and urea because ammonium and urea are products of zooplankton and nekton excretion. DOC – Dissolved organic carbon

Tharadevi (2002) found seasonal variations in the organic carbon content in the Manakudy estuary which showed higher mean values during
premonsoon. Dora and Rao, (1975) recorded comparatively higher concentrations of organic matter in the premonsoon sediments than in the postmonsoon sediments in the Vasishta-Godavari estuary.

The relationship between clay content and organic carbon has been worked out by many authors. Clay content of the soil showed a positive correlation within the Manakudy estuary (Tharadevi, 2002). Almost similar results were reported from other estuaries of India. Rajamanikam and Setty, (1973) have expressed the possibility of greater accumulation of organic carbon in the case of clayey sediment, which offers larger surface area for the adsorption of organic matter. Reghunath and Murthy (1996) also found that organic matter increases with silt percentage and mean grain size and decreases with increase in depth and sand percentage. Ghosh and Choudhury, (1990) observed that the texture of the sediment controls the organic carbon content. Further several workers have found that fine grained sediments generally have higher amounts of organic matter than coarse grained one (Krumbein, 1939; Trask, 1939; Van Andel and Postma, 1954; Rao, 1967; Naidu, 1968). Alagarsamy (1991) reported that in areas where organic pollution is high, the total organic carbon often exceeds 5%.