CHAPTER II
REVIEW OF LITERATURE

2.1. Introduction

Man made impacts along the coastal ocean and in estuaries has increased rapidly over the last decades affecting the natural dynamic equilibrium and the biotic composition of the respective ecosystems. The main cause of such changes are due to the introduction of untreated sewage, which is rich in organic substances and plant nutrients from human settlements, urbanization and growing industries, leaching of nutrients from soils and agricultural fields and animal husbandry. In a highly dynamic environment of an estuary, hydro dynamical, chemical and biological factors vary greatly with different time scales and it is quite likely that these variations may influence sedimentary processes and also physical and chemical characteristics of sediments. The nature and extent of fluctuation in the composition of sediments can indicate the extent of stress on shallow aquatic environment. The sediments in the estuaries indicate the balance between the erosion and depositional forces of the ecosystem.

The nutrient economy of an aquatic system is mostly governed by the sediments and the knowledge on the role of sediment-nutrient is useful in determining the sediments-water interaction, which eventually affects the productivity. Thus the sediment acts as a source and sink and plays a vital role in changing the quality of the overlying water column. Further sediment testing reflects the long term quality situation independent of current inputs. Thus sediment quality indicates the extent
of biological activity and indirectly the fertility of the overlying water and also the actual state of pollution of a water body\textsuperscript{13}.

Nutrient enrichment of rivers, lakes, ground waters and tidal waters is considered to be one of the major environmental problems in many countries\textsuperscript{14}. Although it can stimulate the growth of plants in water, nutrient enrichment ultimately leads to the degradation of entire ecosystem if not controlled in a satisfactory manner. Sediment cores can be used to understand the history of contaminant inputs into a water body\textsuperscript{15}. Estuarine sediment accumulation is a product of continental and marine processes\textsuperscript{16}. Sediment is a very important component of a water body as it influences the type of organism living there\textsuperscript{17}.

Accumulation of trace metals occur in upper sediments in aquatic environments by biological and geochemical mechanisms and become toxic to sediment inhabiting organisms and fish, culminating in death, growth reduction and lower species diversity\textsuperscript{18}. Sediments are normally mixtures of several component including different mineral species as well as organic debris\textsuperscript{19}. Fine sediments have an important role in estuary functioning both as settled material forming intertidal areas and in suspension. Hence the fine sediment regime of an estuary is a key consideration in understanding and managing an estuarine system\textsuperscript{20}. Understanding long-term trend is essential to wise estuary management\textsuperscript{21}.

Various studies have been carried out on the sediment characteristics of estuaries, oceans and rivers throughout the world. The literature pertaining to the study has been reviewed extensively.
2.2. Sediment Texture

The texture of sediment is one of the important physical parameters of an aquatic environment, which influences the physico-chemical and biological characteristics of the system. The geomorphology, granulometry as well as strength and variation in the energy of the transport in current alter the textural characteristics of sediment. Information on sediment and particle size distribution is needed for a variety of water management tasks. Krishnamurthy\textsuperscript{22} reported fairly equal proportions of fine sand and mud near the bar mouth of Pulicat lake. Kurian\textsuperscript{23} observed more of mud and clayey fractions towards the upstream stretches of Cochin backwaters. Bhat\textsuperscript{24} encountered dominance of sand in Nethravati-Gurupur estuary but in the lower stretches of the estuary he found higher percentage of silt mixed with excess of organic matter.

Parulekar \textit{et al.}\textsuperscript{25} noted dominance of sand fractions throughout post and pre monsoon seasons in Goa estuaries. Balakrishnan \textit{et al.}\textsuperscript{10} recorded peak percentage of clay and silt during pre monsoon season in Ashtamudi estuary. The sediment distribution in estuaries depends on the source and texture of sediments supplied and topographic features of the concerned area\textsuperscript{26}. Also the percentage composition of sand in sediments was higher during monsoon season\textsuperscript{26}.

Joseph \textit{et al.}\textsuperscript{27} studied the sediment characteristics of the estuaries around Madras in relation to environmental degradation and reported that the clay content was higher in Adyar sediment compared to other estuaries. Generally in estuaries, fine mud get deposited near the head and other sheltered regions, while along the main channel and at the mouth coarser sediments are deposited\textsuperscript{28}. In the estuarine mouth of
Vellar estuary, the near shore wave action and tidal action remove the finer particles and allow coarser ones to be deposited \(^{29}\).

Silva et al.\(^ {30}\) observed a relationship between the sediment texture and total organic matter and reported that the coarser sediments have low levels of total organic matter whereas the fine sediments have high levels of total organic matter. The sandy-silty substrate contributed higher percentile values during monsoon in Khamtighowli and Magoori wet lands of Upper Brahmaputra valley while the highest percentile contribution of clay was noticed during pre monsoon\(^ {31}\).

Muraleedharan Nair and Ramachandran\(^ {32}\) reported both silt and clay showed high positive loadings with all the elements in the estuarine region of Beypore estuary. Rajasegar et al.\(^ {33}\) studied the distribution of sediment nutrients of Vellar estuary in relation to shrimp farming and recorded higher clay content during the pre and post monsoon. The sediment texture was found to be the major controlling factor for the adsorption and desorption of the chemical components in both Ashtamudi and Vembanad lakes of Kerala\(^ {34}\). Jeena Pearl\(^ {4}\) studied the metal concentration in Manakudy estuarine sediments and reported that the mouth of the estuary had very low quantity of fine sediments. The study of textural characteristics and organic matter distribution patterns in Tirumalairajanar river estuary revealed that sediment texture was one of the main controlling factors for the distribution of organic matter\(^ {35}\). Sugirtha P. Kumar and Sheela\(^ {36}\) studied the sediment characteristics of Manakudy estuary and found out in estuaries, the sand is predominant at the head of the estuary whereas silt and clay are subordinate constituents. The proportion of sand decreases towards the confluence. The admixture of fresh water and saline water reduces the
velocity of the transporting agent leading to the deposition of coarser particles such as sand in the head of the estuary with little amount of silt and clay\textsuperscript{36}. Further it has been reported that the sand was predominant in the riverine side. The mud (silt + clay) was abundant in the estuarine region than the riverine zone. The estuarine zone was highly silty\textsuperscript{36}.

2.3. Physico-chemical Characteristics of Sediment

2.3.1. pH

Many of the life processes are sensitive to the hydrogen ion concentration (pH) of the surrounding medium. It is an important hydrographical parameter indicating the level of dissolved carbon dioxide in the water, which may in turn reflect the activity of phytoplankton and the level of dissolved oxygen\textsuperscript{38}.

Variation in pH due to chemical and other industrial discharges renders a stream unsuitable not only for recreational purposes but also for the rearing of fish and other aquatic life. The pH of natural water ranges from 6.0 to 8.5. The pH influences to a large extent the speciation of metals in aquatic environments as well as decides their interfacial partitioning between dissolved and particulate. Photosynthesis, salinity, mineralization processes, rainfall, nature of dissolved materials and the discharge of industrial effluents are the major factors that influence pH. Natural turbulence with concomitant aeration can also influence pH\textsuperscript{39}. The acidic pH values of sediment can be attributed to the release of organic acid by mangrove into sediment\textsuperscript{40}.

The sediment characteristics of the estuaries around Madras in relation to environmental degradation was studied and reported that the sediment in Adayar was
acidic due to the sewage accumulation in this estuary and the pH of the sediment at Pulicat was high indicating the highly buffered and uncontaminated nature of the system. An increase in pH in the sediments of AVM canal during rainy season and decrease during summer provides the evidence for the dynamics of H$_2$ producing and consuming microbial population.

The sediment pH of Vellar estuary was high during summer season due to a course of redox changes in the sediment and water column apart from the influence of fresh water and lower values of pH during monsoon was due to inflow of fresh water. Bragadeeswaran et al. studied the sediment texture and nutrients of Arasalar estuary, and found that all stations which lie adjacent to the sea were alkaline due to the influx of marine waters during tidal cycle. The sediment of Okpoka Creek was acidic and the low pH conditions observed were due to the sulphur compounds that characterize the brackish water environment of Niger Delta.

The investigation of the sediment nutrients of Thengapatnam estuary showed higher pH values during the pre monsoon months and lower pH values during the monsoon months. Low pH values were due to the increased rate of decomposition in the organic matter and conversion of released carbon dioxide to carbonic acid. Shijo Joseph and Ouseph carried out a case study from Cochin estuary and indicated high pH values of sediment were due to the influx of marine water into the estuary in high tide time especially in the pre monsoon and post monsoon seasons.

Selva Mohan and Palavesam recorded maximum pH during monsoon and minimum pH during non monsoon period in Rajakkamangalam estuary. The lower pH values during non monsoon periods were due to increased rate of decomposition in
the organic matter and conversion of released carbon dioxide to carbonic acid. Soumya et al. observed that the sediment pH of Ashtamudi estuary was acidic due to an increase in organic pollution throughout the study period. George Sebastian et al. reported that the sediment samples of Vembanad lake in Kerala were highly acidic due to the high organic matter content of sediments undergoing putrefaction, releasing CO$_2$.

The slightly higher pH values in the sediments of Tamirabarani estuary were due to greater input of effluents from different types of industries. Kouamé Mathias KOFFI et al. surveyed the heavy metals concentration in water and sediments of the estuary Bietri Bay and reported that it showed slightly alkaline character. This may be attributed to the effect of bicarbonate ions and penetration of oceanic waters in the bay.

### 2.3.2. Electrical conductivity (EC)

Electrical conductivity of sediment refers to the ability of the sediment to conduct electric current. It is an indicator of the total dissolved inorganic salts and solids. Electrical conductivity varies along an estuary depending on the mixing of freshwater and salt water at a site. Generally, electrical conductivity increases along a coastal stream as it gets closer to the river mouth, where tidal influences are stronger. Freshwater stream generally has an electrical conductivity (EC) of 200–300 µS/cm. Estuaries have a much higher electrical conductivity than freshwater (typically from 20,000 to 40,000 µS/cm). Seawater typically has a conductivity of 51,500 µS/cm. Many aquatic species can survive only within certain electrical conductivity ranges,
so changes in electrical conductivity levels may result in changes to the variety and types of species present.

In estuaries, greater the total dissolved solids in water, particularly salts, the greater is its electrical conductivity\textsuperscript{51}. The rise in EC during summer months suggests the influence of marine water on contributing dissolved ions like Na\textsuperscript{+}, K\textsuperscript{+} and Cl\textsuperscript{−} into estuarine and mangrove environments and enhanced precipitation\textsuperscript{52}. Higher conductivity is an indication of richer ionic and more charged species and lower electrical conductance is the indication of high silicates material\textsuperscript{53}. In Vembanad lake, EC was influenced by industrial effluents, domestic and municipal sewage, salinity intrusion and fresh water influx from rivers\textsuperscript{48}. Kurlapkar and Shakil D.Shaikh\textsuperscript{54} reported that the Bhatey and Kalabadevi estuary showed wide range of electrical conductivity (EC) values according to the vegetation dominated by the site. The EC ranged from 2.9 to 13.1 mS/cm.

\subsection*{2.3.3. Redox potential (Eh)}

The oxidation-reduction condition in sediment depends on the degree of organic enrichment. Redox potential (Eh) of sediments is a convenient index to understand whether the sediment has reduction potential or not. A positive Eh value results from a state that tends towards oxidation and a negative Eh indicates a system causing reduction.

The reducing capacity of marine sediments decreases with core depth. The positive Eh values are generally characteristic of coarse sediments and negative Eh values are characteristic of fine sediments\textsuperscript{55}. Aiyer and Rajendran\textsuperscript{56} reported very low values of Eh when there was high concentration of hydrogen sulphide with total
depletion of oxygen. The redox state in a given place is influenced to a great extent by hydrodynamical and sedimentological conditions\textsuperscript{57}. Under oxidizing sediment conditions, the behaviour of Fe, Pb and Ni were governed by Fe(III) and Mn(IV) oxides; Ba by insoluble complexation with humic compounds, Cu by carbonates and humic complexation. Under reducing sediment condition, the behaviours of Fe and Cu were controlled by the formation of insoluble sulphides, carbonates and humic complexes\textsuperscript{58}.

In Poonthura estuary, the marine and riverine sediments were less reduced than estuarine sediments\textsuperscript{28}. In the Middle Adriatic region, low positive $E_h$ was caused by low to medium organic matter sedimentation rates and negative $E_h$ values were found in areas with higher productivity and organic matter sedimentation\textsuperscript{59}.

2.3.4. Total soluble salts (TSS)

Total soluble salts (TSS), is referred to the total amount of soluble salt present in the soil extract. TSS present in sediment samples consist of ions like calcium, magnesium, sodium, potassium, chlorides, nitrates, carbonates, bicarbonates and heavy metals. The mean values for the total soluble salts (TSS) were higher in dry season than in the rainy season in Epie creek due to its dilution in the rainy season\textsuperscript{60}.

George Sebastian \textit{et al.}\textsuperscript{48} from Vembanad lake established that excessive salts in sediment could cause high osmotic pressure, which prevent the absorption of moisture and nutrients by plants in adequate amounts. TSS was comparatively more in pre monsoon and post monsoon period in Tamirabarani estuary due to the dumping of domestic waste and industrial discharges into the river water ecosystem\textsuperscript{49}. 
2.3.5. Moisture content

Moisture content is the quantity of water contained in a material, such as soil, rock, ceramics or wood on volumetric or gravimetric basis. This property is used in a wide range of scientific and technical areas. The sediment sample containing higher moisture content showed higher organic matter content\textsuperscript{61}.

The moisture content was found to be high in clayey sediments of Sewri Mudflats. In general the water content is low in riverine sediments and marine sediments as the texture of the sediment is sand\textsuperscript{62}.

2.3.6. Bulk density and Particle density

Bulk density is an indicator of soil compaction. It is defined as the ratio of dry soil mass to bulk soil volume including pore spaces. Texture and structure are two soil characteristics that govern bulk density. Mineralogy, soil chemistry, parent material and depth in the profile are also influential. Fine-textured soils such as silt loams, clays and clay loams generally have lower bulk densities than sandy soils. Particle density is the volumetric mass of the solid soil. It differs from bulk density because the volume used does not include pore spaces.

A reverse correlation between organic matter and bulk density was found in some Vermont Forest soils\textsuperscript{63}. Arshad \textit{et al.}\textsuperscript{64} pointed out that the bulk density reflects the soil’s ability to function for structural support, water and solute movement, and soil aeration. High bulk density is an indicator of low soil porosity and soil compaction. Yoram Avnimelech \textit{et al.}\textsuperscript{65} studied the water content, organic carbon and dry bulk density in flooded sediments and concluded sediment bulk density is inversely related to the organic carbon concentration. The minimum bulk density
value in pre-monsoon may be due to high rate of evaporation, deep percolation and moist extraction by cultivated plants and trees which ultimately lost from transpiration\textsuperscript{66}.

A strong correlation between bulk densities and organic matter was determined in Harran plain soils\textsuperscript{67}. Pravin et al.\textsuperscript{68} concluded from Coimbatore soils that the bulk density is dependent on calcareous and saline nature of soils but independent on whether soil is acidic or alkaline and there is a high degree of reverse correlation between organic matter and bulk density of soil. Also the bulk density depends on available macronutrients and micronutrients in the soil. It decreases as the total macronutrient or total micronutrient content in the soil increases.

2.3.7. Cation exchange capacity (CEC)

The cation exchange capacity of soils (CEC) is defined as the sum of positive (+) charges of the cations that a soil can adsorb at a specific pH. CEC is an inherent soil characteristic and is difficult to alter significantly. Cations have the ability to be exchanged for another positively charged ion from the surfaces of clay minerals and organic matter. The most important exchangeable cations in the soil are calcium (Ca\textsuperscript{2+}), magnesium (Mg\textsuperscript{2+}), sodium (Na\textsuperscript{+}), potassium (K\textsuperscript{+}), hydrogen (H\textsuperscript{+}), aluminum (Al\textsuperscript{3+}) and ammonium (NH\textsubscript{4}\textsuperscript{+}). The CEC can directly influence the changes in soil pH, because every time the clay particles capture cations, release H\textsuperscript{+} and Al\textsuperscript{3+} ions, which in high concentration acidifies soil. High sandy and low pH soils have low CEC. The cation exchange capacity (CEC) also plays an important role in metal exchanges.

Dorothy Carroll\textsuperscript{69} determined calcium, magnesium, sodium, and potassium as exchangeable cations and observed the CEC was in the order Ca > Na > K > Mg.
Sediments having fresh coating of Fe and Mn oxides had high adsorption and cation exchange capacities and hence augment the retention of trace metals\textsuperscript{70}.

The organic coatings seem to hold, and interfere with the exchange ability of many Ca\textsuperscript{2+} and Mg\textsuperscript{2+} ions and the cation exchange capacity was directly correlated with organic content of the sediments of the Hudson River estuary\textsuperscript{71}. CEC values may be utilized for determining salt water intrusions and pollution effects\textsuperscript{72}. Cation exchange capacity is based on the surface area of sediment grain particles available for binding cations, such as hydrogen (H\textsuperscript{+}) and free metal ions (e.g., Mn\textsuperscript{2+})\textsuperscript{73}. Sediments with a high percentage of small grains, such as silt and clay, have high surface-to-volume ratios and can adsorb more heavy metals than sediments composed of large grains, such as sand.

2.3.8. Nutrient Elements
2.3.8.1. Organic carbon (OC)

A comparatively higher concentration of organic matter was recorded in the pre monsoon sediments than in the post monsoon sediments of Vasishta Godavari river\textsuperscript{74}. Muller et al.\textsuperscript{75} experimentally proved that various clay minerals adsorb substantial amount of organic matter formed by the decomposition of phytoplankton. Organic carbon in the sediment is favoured by the supply of organic matter in the overlying water, rapid accumulation of fine grained organic matter and low oxygen content of bottom water\textsuperscript{76}.

Reddy et al.\textsuperscript{77} reported that the distributional status of total organic carbon closely follows the distribution of sediment texture in Netravathi-Gurupur estuary. Association of organic matter with fine-grained sediment was well established by
Sajan and Damodaran in Ashtamudy lake\textsuperscript{78}, Purandra and Dora in Vembanad lakeshore sediments\textsuperscript{79}, Chavadi and Bannur in Ramangundi beach of North Karnataka coast\textsuperscript{80}, Nair \textit{et al.} in Cochin estuary\textsuperscript{81}, Sarala Devi \textit{et al.} in some estuaries of North Kerala\textsuperscript{82}, Bijoy Nandan and Abdul Azsis in Kadinamkulam estuary\textsuperscript{83} and Sunil kumar in mangrove sediments of Cochin\textsuperscript{84}. Anilakumary \textit{et al.}\textsuperscript{28} studied the sediment characteristics of Poonthura estuary in relation to pollution and found out OC in the sediment is a reliable index of nutrient degradation and productivity of the water body. Further they suggested that the combined effect of low rainfall, reduced flow rate, settling of detritus matter and decay of leaf litter and associated macrophytes results in high sedimentary OC during premonsoon. Low levels of water and poor flow rate may also account for high sedimentary OC. Organic enrichment of mangrove sediment in the intertidal zone is from leaf litter derived from mangrove trees and from detritus\textsuperscript{85, 86}.

Das and Sabu\textsuperscript{87} observed low sedimentary OC during monsoon in Rushikalya estuary and found that it may be the result of increased flow rate due to heavy rains, which prevent the settling down of organic carbon. The same observations were made by Murugan and Ayyakkannu in Cuddalore Upanar back water\textsuperscript{88}. Muraleedharan Nair and Ramachandran\textsuperscript{32} investigated that in Beypore estuary total organic carbon showed strong positive correlation with both silt and clay and an inverse relationship with that of sand in the estuarine sediments. In marine sediments only the clay content exhibited a strong positive correlation with total OC. Total OC was negatively correlated with sand and silt. Rajasegar \textit{et al.}\textsuperscript{33} pointed out that in Vellar estuary the organic carbon content in the sediment was high during summer season and low during the monsoon. The high organic carbon content at some stations of
Paravur-Kappil backwaters may be due to the deposition of terrestrial organic matter from the excessive land runoff, settling of material and decay of vegetation. The higher levels of sedimentary OC during summer months is due to high evaporation of water in the reservoir and decomposition of algae while low levels during colder months is due to less evaporation of reservoir water.

Jeena Pearl observed a high positive correlation between organic carbon and nitrogen in Manakudy estuarine sediments and revealed that the accumulated fine sediments are nitrogenous organic matter. Saha and Hossain found that the sites which contained higher organic matter showed higher heavy metal concentration in the Buriganga river. Soumya et al. studied the sediment characteristics along the Ashtamudi estuarine system and reported that in Kandachira kaiyal the organic carbon content was high due to hectic coconut husk retting activity. George Sebastian et al. observed a significant seasonal and locational variation in OC, a significant positive correlation of OC with clay, silt, EC,TSS, total nitrogen, moisture content, phosphate and sulphate and significant negative correlation with sand in Vembanad lake. Sugirtha P. Kumar and Sheela noticed a significant correlation of organic carbon with silt fractions and clay fractions in Manakudy estuary. The finer fractions (silt+clay) showed an efficacious relationship with organic carbon, while coarser fractions have no patent kinship. The high percentage of organic carbon and organic matter could primarily be attributed to input from the mangrove in the form of dead leaves and decaying prop roots.

2.3.8.2. Total Nitrogen

Kemp studied the organic carbon and nitrogen in the surface sediments of Lake Ontario and found that nitrogen content in the sediment depends on local
The condition of rainfall, quantities of freshwater inflow, turbulence and biological activities. The maximum value of nitrogen due to the decay of a large number of phytoplankton which settled from the water column was observed during summer\textsuperscript{92, 93}. Low values of nitrogen during monsoon in Vellar estuary were due to low level of organic matter\textsuperscript{94}. Knicker \textit{et al.}\textsuperscript{95} studied the fossil algal residues and found a positive correlation between total nitrogen and percentage of clay.

Anupam Sharma and Biswas\textsuperscript{31} made a comparative account of carbon, nitrogen and phosphorus of two wetlands of Upper Brahmaputra valley. They reported that the seasonal variations of available nitrogen depends upon the grain size of the sediment and also higher values for nitrogen during pre monsoon may be due to abundance of macrophyte vegetation. The most important source of NO\textsubscript{3} is biological oxidation of organic nitrogenous substances, which originates through sewage and industrial wastes\textsuperscript{96}.

In Manakudy estuary, Jeena Pearl and Abbas Fenreji\textsuperscript{97} observed low C/N ratio due to lack of suspended matter in the estuary. Agricultural runoff, domestic and municipal sewage, retting of coconut husk and other anthropogenic activities facilitate an increase in the concentration of nitrogenous material in the sediments of Vembanad lake\textsuperscript{48}. Kannappan and Karthikeyan\textsuperscript{98} noticed a minimum value of nitrogen during summer and a maximum value of nitrogen during monsoon season in Manakudy estuary.

2.3.8.3. Phosphate-Phosphorus

Qasim and Gopinathan\textsuperscript{99} reported a decrease in phosphorus content starting from estuarine mouth to the fresh water zone in Cochin back water. Saha\textsuperscript{100} studied
the changes in the properties of bottom soil of two fresh water ponds in relation to ecological factors and concluded that phosphorus content is high during rainy season and low during summer season. Similar trend was also observed by Umayoru Bhagan et al.\textsuperscript{41} in the sediments of AVM canal.

The continuous adsorption and desorption of phosphates by sediments serve both as a source and a sink for phosphate in phosphorus cycle\textsuperscript{81}. Nasnolkar et al.\textsuperscript{101} carried out a study on organic carbon, nitrogen and phosphorus in the sediments of Mandovi estuary and concluded low values of phosphorus encountered during monsoon is attributed to the leaching of phosphate from sediments to the overlying water.

Parry\textsuperscript{102} studied the agricultural phosphorus and water quality in Australia rivers and reported that the increased phosphorus loading in aquatic systems from cultivated lands, domestic and industrial sewages have created the eutrophication problems in rivers and reservoirs. Vinithkumar et al.\textsuperscript{103} studied the organic matter, nutrients and major ions in the sediments of coral reefs and sea grass beds of Gulf of Mannar biosphere reserve and reported detritus is the main source of organic phosphorus in the sediment. It gets bound with the shells and bones of invertebrate animals and when the shells break phosphorus is released into sediment and water. A high monsoonal value of phosphorus in Vellar estuary was due to heavy rainfall, land run off from agricultural fields contaminated with super phosphates and from soap and detergents used by the public\textsuperscript{104}.

Vasantha\textsuperscript{44} studied the distribution of sediment nutrients of Thengapatnam estuary and found a high phosphorus concentration during monsoon and low
concentration during pre monsoon. She reported high values of phosphorus were promoted by the deposition of inorganic phosphate due to runoff from the land during monsoon, domestic sewage and agricultural effluents. Similar observation was informed by Anitha and Sugirtha P. Kumar⁹³. They concluded high values of phosphorus were due to the dead organic matter settling from top and are related to the permeability of the sediments and the lower values may be due to the removal of top layer of sediments by heavy flood, deposition of sand and the leaching of phosphate from sediments to the overlying water. Increased application of fertilizers, use of detergents and domestic sewage play a great role in contributing to the heavy loading of phosphorus in the sediment. Further it was evidenced by obtaining positive correlation between organic carbon and phosphorus. However a similar pattern of variation of nitrogen and phosphorus and the significant correlation between them revealed that the concentration of one is dependent on the other and indicated a common source for both. Metal concentration in Manakudy estuarine sediments was studied by Jeena Pearl⁴ and found that higher concentration of phosphorus was due to the larger supply of terrigenous material by the river, organic productivity and agricultural waste discharge from the paddy fields of the region. Low concentration of phosphorus was due to the process of flocculation, change in salinity and low quantity of fine sediments.

2.3.9. Major elements

2.3.9.1. Sodium

Many industrial wastes and domestic sewage are rich in sodium and would increase its concentration in the natural water after their disposal¹⁰⁵. High value of sodium observed during post monsoon season may be due to high salinity and low
value during monsoon season may be due to rain and flow of river water in Tapi estuary\textsuperscript{106}. Anitha and Sugirtha P. Kumar\textsuperscript{93} studied the seasonal variation in physico-chemical parameters of Thengapattanam estuary and reported a minimum value of sodium during monsoon and maximum during summer season.

2.3.9.2. Potassium

Umayoru Bhagan \textit{et al.}\textsuperscript{41} reported maximum values of potassium during the non monsoon period in Thengapattanam estuary. Vasantha\textsuperscript{44} studied the distribution of sediment nutrients of Thengapattanam estuary and found a maximum potassium concentration during monsoon and low concentration during pre monsoon. Selva Mohan and Palavesam\textsuperscript{46} noticed maximum potassium content during monsoon and minimum during non monsoon in Rajakkamangalam estuary. The high value of potassium registered may be due to the leaching of potassium through rain water from the surrounding coconut fields, which contain potassium in the form of fertilizer. Anitha and Sugirtha P Kumar\textsuperscript{93} studied the seasonal variation in physico-chemical parameters of Thengapattanam estuary and reported a minimum value of potassium during monsoon and maximum during summer season.

2.3.9.3. Chloride

Hattersley\textsuperscript{107} studied the negative health effects of chlorine and reported chloride occurs in all natural waters in widely varying concentrations. Plants do not thrive on chlorinated as well as on unchlorinated water and wild animals develop atherosclerosis by consumption of chlorinated water. De \textit{et al.}\textsuperscript{108} studied the soil status in and around Satpura thermal power station and concluded rainfall leaches salt out of soil may be the reason of lowest value of chloride during monsoon and highest in pre monsoon. Gadhia \textit{et al.}\textsuperscript{106} studied the seasonal variations in physico-chemical
characteristics of Tapi estuary and found that the value of chloride was higher during pre monsoon which might be due to high salinity, tidal flow and low fresh water mixing. Low value found during monsoon season was due to rain and more mixing of fresh water from river. Prabhahar et al.\textsuperscript{109} carried out a study on the seasonal variation in physico-chemical parameters of Palar river and concluded sewage water and industrial effluents are rich in chloride content and discharge of these waste water results in greater chloride level in fresh waters.

2.3.10. Carbonate elements (Calcium and Magnesium)

Vijayakumara and Vijaya Kumar\textsuperscript{110} studied the water quality of mangrove ecosystems of Kundapura and reported that the sediments had maximum calcium content in the month of February (summer) and minimum value in the month of November (monsoon). Calcium concentration was highest in estuaries due to the influx of riverine sources. Similar results were reported by Anitha and Sugirtha P. Kumar in Thengapattanam estuary\textsuperscript{93}. Further maximum values of magnesium were observed during the month of February and minimum values during the month of November\textsuperscript{93}. Using the ratio $\text{Ca}^{2+}/\text{Mg}^{2+}$, it was found that Thengapattanam estuary was affected with sea water intrusion. Anitha and Sugirtha P. Kumar\textsuperscript{111} studied the geochemistry of sediments in Thengapattanam estuary and concluded that Ca at the surface sediment is higher than the remaining middle and bottom sediment due to the abundance of skeletal components.

2.3.11. Mobile elements

2.3.11.1. Iron and Manganese

Carrol\textsuperscript{112} stated that iron appears in the lake sediments as an essential component of clay minerals which is the major one in the lakes. Rengasamy
Alagarsamy\textsuperscript{113} studied the distribution and seasonal variation of trace metals in surface sediments of the Mandovi estuary and found enrichment of iron and manganese reflects the intensity of anthropogenic inputs related to iron ore processing in the upstream region of the Mandovi estuary, however, the highest enrichment levels were not found near the mouth region. $I_{geo}$ values calculated for iron and manganese showed higher values in the pre monsoon period in the upstream region of the estuary than in the post monsoon and monsoon seasons. Selvaraj \textit{et al.}\textsuperscript{114} stated that Mn is precipitated as hydroxides in the estuarine and near shore areas as the less saline river water rich in Mn mixes with high saline low Mn sea water. However the dissolved Mn in sediments are dissolved in the pure water below the surface sediments due to the biogeochemical processes and it can also diffuse up to the oxidized sediment interface and can be precipitated as oxide or oxy-hydroxide in Ennore Creek.

Fe-Mn oxy-hydroxides are the major controlling factor for trace metal accumulation when compared to organic carbon\textsuperscript{115}. Nadia \textit{et al.}\textsuperscript{116} recorded from his study in some Red Sea coastal areas manganese is an element of low toxicity having considerable significance when manganese bearing fertilizers contributes to air and water pollution. It is one of the more biogeochemical and active transition metals in aquatic environment. Anitha and Sugirtha P. Kumar\textsuperscript{111} reported that iron can be combined with a variety of anions to form complexes and minerals in Thengapattanam estuary. The common mineral forms are present as silicates, oxides, sulphides and phosphates. Under a variety of natural environmental conditions, Fe also changes its oxidation state steadily with changes in the amount of oxygen and variations in pH conditions in the aqueous phase.
2.3.11.2. Sulphur

Sulphate concentration in lake sediments play an important role in the release of phosphorus which leads to eutrophication of lakes\textsuperscript{117}. Under anoxic conditions, sulphate reduction takes place and promotes the release of phosphorus from sediments. Ayyamperumal \textit{et al.}\textsuperscript{118} assessed acid leachable trace metals in sediment cores from river Uppanar and concluded that the decrease in sulphur from riverine to estuarine sediments is attributed to oxidation of H\textsubscript{2}S along the riverine sediments resulting in low values in estuarine sediments. The sulphur removed from the organic phase in the form of elemental sulphur is insoluble and accumulates in sediments. Sugirtha P. Kumar and Sheela\textsuperscript{36} studied the sediment characteristics of Manakudy Estuary and concluded higher values of sulphur were due to the coir retting pits where hydrogen sulphide is released. The hydrogen sulphide formed by most decomposing bacteria is oxidized to sulphate and finally to elemental sulphur. Sugirtha P. Kumar and Sheela\textsuperscript{37} made a comparative study of textural and chemical characteristics of riverine and estuarine sediments of Manakudy estuary and found that the average values of sulphur decreased from riverine to estuarine.

2.3.12. Trace metals (Cd, Pb, Cu, Cr and Zn)

Analysis of bulk sediments from the Mandovi estuary by Rengasamy Alagarsamy\textsuperscript{113} showed that lowest metal concentrations were found during the monsoon, compared to the pre- and post-monsoon. Comparison of the metal levels in the sediments from different areas of the estuary indicates that there was a detectable anthropogenic input to the Mandovi estuary. Cu and Zn enrichment in the river mouth region, associated with high organic carbon contents, is indicative of the influence of organic wastes from municipal sewage entering the estuary. The inter metallic
relationship revealed the identical behaviour of metals during its transport in the estuarine environment. Pragatheeesswaran et al.\textsuperscript{119} reported an increase in the concentration of copper during the monsoon period in Vellar estuary which may be due to spraying copper sulphate as an algaecide in the rubber plantations and agricultural fields that reach the water bodies during rainy season. Chromium (IV) is the most toxic form for bacteria, plants and animals\textsuperscript{120}. Municipal refuse, automobiles and agricultural use of pesticides and fungicides contain ZnSO\textsubscript{4} as the additional sources of environmental pollution\textsuperscript{121}. Mido and Satake\textsuperscript{122} studied about the chemicals in the environment and found blue green algae are particularly susceptible to Cu because it inhibits the nitrogen fixing properties of these algae.

Muwanga\textsuperscript{123} studied the environmental impacts of copper mining at Kilembe and reported trace amounts of heavy metals are always present in fresh waters from terrigenous sources such as weathering of rocks resulting into geo-chemical recycling of heavy metal elements in these ecosystems. Similar conclusion was made by Zvinowanda et al.\textsuperscript{124}. Many metallic ions form stable complexes or chelates which may tend to concentrate in the food chains and can act as cumulative poisons in high level consumers\textsuperscript{125}.

Heavy metals may enter into aquatic ecosystems from anthropogenic sources, such as industrial wastewater discharges, sewage wastewater, fossil fuel combustion and atmospheric deposition\textsuperscript{126}. Cr (VI) being mobile and extremely toxic is more harmful than Cr (III)\textsuperscript{127}. Trace metals are co-adsorbed with other elements as oxides, hydroxides of Fe, Mn or may occur in particulate form\textsuperscript{128, 129}. Okafor and Opuene\textsuperscript{130} assessed trace metals in sediments and found out trace elements may be immobilised
within the stream sediments and thus could be involved in absorption, co-precipitation and complex formation. Harikumar and Jisha\textsuperscript{131} studied the distribution pattern of trace metal pollutants in an urban wetland and revealed that the enhanced concentration of trace metals in most populated urban areas like Kottuli wetland is due to strong anthropogenic influences. Mohiuddin \textit{et al.}\textsuperscript{132} also reported the same in an urban river.

The higher concentration of lead in sediments is indicated by the low degree of desorption of the metal under estuarine conditions\textsuperscript{4}. Sekabira \textit{et al.}\textsuperscript{133} studied the heavy metal pollution in the urban stream sediments and concluded that lead, cadmium and zinc can be co-precipitated (inclusion, occlusion and adsorption) with manganese and iron hydroxides. Sudarsan Raj \textit{et al.}\textsuperscript{134} reported that the sediment samples were moderately polluted with Cd due to the fertilizer based industrial effluent that has taken place in the river basin of Mahanadi estuary.