CHAPTER 1
CHAPTER 1

INTRODUCTION AND REVIEW OF GEOCHEMICAL RESEARCH IN SEDIMENTS

1.1 INTRODUCTION

The exponential growth of human population and its concentration in coastal and estuarine areas around the world has deteriorated the environmental quality of the urban near shore coastal regions and estuaries. The contamination of coastal regions and marginal seas can be attributed to various factors such as direct input of effluents from industries and communities situated close to the coast, effluents from communities via several outfalls and dumping of waste from ships. The other reasons for coastal pollution, in general, are soluble and suspended load from rivers atmospheric fall out and the waste derived from the extraction of raw materials from the land.

In recent years, there has been renewed interest in environmental studies related to earth, ocean and atmospheric sciences, especially with regard to pollution. In order to understand the problem of pollution at various levels, geochemical studies related to coastal zones have gained considerable significance, as they lead to the understanding of metal cycling, fluxes, budgets, sources and sinks of various chemical elements in nature (Buckley and Cranston, 1991). In addition, the distribution of trace elements in sediments can serve as an indicator of the extent and history of pollutants discharged in specific areas (Chow et al., 1973; Bruland et al., 1974; De Groot et al., 1976).

1.2 SOURCES OF METAL POLLUTION AND ASSOCIATION IN SEDIMENTS

Globally, the contaminants that pose the greatest threat to the marine environment are the bacteria and viruses, excessive nutrients, synthetic organic
compounds (pesticides), toxic metals, radionuclides, hydrocarbons, including oil, polycyclic aromatic hydrocarbons, litter and plastics. Of particular concern are those classes of contaminants, which are not easily broken down and, therefore, persist in the environment.

According to Forstner and Wittmann (1981), there are five different sources from which metal pollution originates to the marine environment and they are characterized in the following order:

1. Geologic weathering in the areas where the metals occur at elevated levels in water and bottom sediments, which are particularly characterized by metal bearing formations. This is termed as a source or back ground level in the environment.

2. Industrial processing of ores and metals is mainly characterized where mine effluents record high concentrations in waters as well as on the biotopes, particularly on the fish population.

3. The use of metals and metal components has numerous sources of heavy metal enrichment in the aquatic environment and the various industries polluting the sea.

4. Leaching of metals from garbage and solid waste dumps are characterized further in accordance with their source of origin, and metal enrichments are mainly from residential areas and domestic effluents which are discharged to receiving water bodies – often to the sea in coastal residential areas.

5. Animal and human excretions which contain heavy metals: The large contributors of non-point sources leading to environmental pollution in aquatic systems are the commercial forest, grassland and cultivated agricultural areas, characterized in this group.
Goldberg (1954) observed that natural metal association in sediments can originate from five different sources. In lithogenous formations, the products are weathered from the source areas or rock debris from the riverbed and this material, regardless of long residence time, undergoes only slight change. In hydrogenous formations, however, the physico-chemical changes in water are attributed to the particles, precipitation products and adsorbed substances. The biological remains are decomposition products of organic substances as well as inorganic siliceous or calcareous shells, which control the biogenous formations. Atmogenous formations are mainly controlled by the metal enrichments resulting from atmospheric fallout while comogenous formations are from the extra-terrestrial particles. Metal enrichments by civilization can be included in the first four processes.

In recent years the estuary-shelf inter-relationships have received increased attention due to more consciousness regarding elemental mass balance between continents and oceans. Under normal physico-chemical conditions, the dissolved metals transported by natural water system are adsorbed on to the particulate material rapidly. However, they do not stay in that condition and may be released as a result of chemical changes in the aquatic systems. The estuarine and coastal sediments represent one of the ultimate sinks for trace elements discharged in to the aquatic environment (Luoma and Jenne, 1976). Many substances that occur naturally, such as trace metals and nutrients, may be mobilized as a result of natural processes as well as by man’s activities and thus may become enriched in coastal and estuarine sediments (Windom et al., 1989). A fundamental property of trace elements is that most of them react strongly with particles (Davis and Leckie, 1978; Benjamin and Leckie, 1981; Balistrieri and Murray, 1982). The high concentrations of metals in sediments, resulting from particle reactivity, enhance the importance of sediments as a direct source of these potential toxins for biota in some
environments (Turekian, 1977; Olsen et al., 1982; Salomons and Forstner, 1984; Luoma, 1983, 1989). According to Oakley et al. (1980), trace metals in estuarine and marine sediments are partitioned between different phases depending on the amount of each phase and the strength of adsorption. The bioavailability of trace elements in marine sediments, however, depends in part on the mineral phase on which the elements are bound (Bryan and Langston, 1992).

The geochemical cycle of wastes from various sources discharged in the coastal marine environment is determined to a large degree by their interactions with sediments. As a result, sediments act as integrators and amplifiers of concentrations of many elements in the waters, which pass over and transport them, and play a vital role in the shallow coastal areas. Thus, coastal marine sediments serve as an ultimate sink for metals discharged into the aquatic environment (Luoma and Bryan, 1981; Hornberger et al., 1999). For this reason, in recent years, sediments have been widely used to identify sources of contamination, to measure their extent, and to diagnose environmental quality of aquatic systems (Luoma, 1989). In addition, coastal sediments are a mixture of inorganic and organic materials that have arrived at the site of deposition as solid particulate matter (detritus) or have been incorporated into the sediments from solution (nondetrital) in a variety of ways. According to Calvert et al. (1993), the concentrations of trace and minor elements in marine sediments reflect the range of chemical oceanographic and sedimentary controls on their distribution and removal from the sea. Such controls include the composition of sedimentary detritus elements delivered to the sea and the partitioning of individual elements between solid and solution phases.

Metals are always a serious source of pollution, not only because they are always toxic above certain levels, but also because they remain at the bottom of the
sea long after the source of pollution has been removed (Taliadouri, 1981). According to Hart (1982), once released to the environment, trace metals are transferred to the sediments through adsorption on to suspended matter and subsequent sedimentation. These adsorption and sedimentation processes of metals mainly depend on the composition such as grain size, carbonate content, level of organic matter, Fe-Mn hydroxides etc. Most metals are associated with the particle surface and are preferentially transported, deposited and eventually buried with fine-grained sediments. Hence, changes in grain size distributions are accompanied by changes in concentrations of organic materials, Fe and Mn (Luoma and Phillips, 1998). Carbonate acts as a dilutor and organic carbon behaves as a concentrator of metals. Therefore, the deterioration of the aquatic environment is clearly reflected by the chemical composition of the sediments (Taylor, 1986).

Trace metals in recent sediments can be divided in to two categories according to their predominant source of origin: “lithogenic” and “anthropogenic”, often simply referred to as “geochemical” and “man-made” (civilisational), respectively. Between these two groups, several combinations of metal formations could be developed by their own accumulation and this can influence anthropogenic metal levels in estuaries and nearshore coastal waters. To establish the degree to which the present day environment has been subjected to trace metal pollution, perhaps the most useful way to classify the elements found in sediments is as lattice-held “residual” and nonlattice held “nonresidual” (Agemian and Chau, 1976). According to Chester and Voutsinou (1981), nonresidual trace metals are not part of the silicate matrix and have been incorporated in to the sediment from aqueous solution, by processes such as adsorption and organic complexation, i.e., nonresidual trace metals include those originating from polluted waters. Hence, for the
assessment of trace metal pollution in sediments, analysis of the nonresidual fractions is of prime importance.

According to Yeats and Campbell (1983), marine sediments are the ultimate sinks for particulate material supplied by rivers and the atmosphere to the oceans. Similarly, the transport and cycling of human released contaminants is often strongly coupled to the transport of sediments in rivers, since many contaminants have some degree of associations with the particulate phase in water (Walling and Web, 1983). The coastal area is characterized by wide variations in physico-chemical conditions, with high sedimentation rates, influence of wave motion, variable redox conditions, and high organic matter contents leading to remobilization, release or accumulation of metals in different forms. The transport and fate of heavy metals are associated with fine sediment dynamics. Most of the fine sediment particles on the continental shelf are discharged by river and transported seawards as suspended particulate matter (McCave, 1972). After being discharged into the sea, heavy metals linked with suspended fine sediment particles are dispersed by mixing and adsorption processes (Drake, 1976). The suspended particles tend to be more concentrated in surface and near-bottom turbid layers, although intermediate turbid layers also develop locally. However, the final sink is controlled by the prevailing short-term currents and is the result of dynamic interactions between anthropogenic input and natural processes.

To study the river discharge to the oceans, Ludwig and Probst (1998) investigated the empirical relationships between river sediment yields and a large number of hydroclimate, biological and geomorphological parameters on a global scale. In estuaries and coastal zones where sediments end up, an alteration of the natural river sediment supply can provoke considerable changes in
metabolism in the coastal zone and/or of coastline morphology (International Geosphere Biosphere Program, 1995). In estuarine mixing zone, the river water with low salinity and high metal content encounters marked difference in chemical properties compared to the low saline metal bearing waters. This induces several processes such as flocculation of colloidal particles (Sholkovitz, 1976), leaching and subsequent release of adsorbed elements to seawater from fluvial sediments etc. (Krishnaswami, 1976). The changes in the water chemistry from fresh to saline waters make various solid-liquid interfaces, important loci for many chemical, biological processes, and the estuarine processes can modify the influx of material from continents to the oceans (Bien et al., 1958; Windom et al., 1971; Boyle et al., 1974).

The investigations on the distribution of trace elements in sediments, water and organism are fundamental to the study of environmental pollution, since these elements can be toxic even if they are present in trace amounts (Cosma et al., 1979); moreover, sediment analysis plays an important role in tracing short-term or past pollution (Meiggs, 1980). As most metals associate with the surface of particles, they are preferentially transported, deposited and eventually buried with fine-grained sediments. In addition, sediments can reflect the current quality of the system as well as the historical development of certain hydrological and chemical parameters. Increased human activities have accelerated cycling and increased metal deliveries to estuaries and coastal zone and, as a consequence, higher loadings or concentrations have wide implications on the ecosystems (Hornberger et al., 1999). Industrial effluents and domestic wastes frequently contain amounts of heavy metals far in excess of those in natural waters and when discharged untreated in to the sea, either directly or through a stream, they tend to cause local pollution of the sediments. Hence, a detailed study on grain size, organic carbon and
composition of elements in a source point can be useful tool in identifying metal pollution, particularly when it originates from diffuse non-point sources.

1.3 **Importance of Surface and Core Sample Studies**

In order to derive the total enrichment caused by anthropogenic factors, it is important to establish the natural level of these substances (Pre-civilization) and then subtract it from the existing values. Forstner and Muller (1973) were the first to attempt to study the extent of heavy metal pollution on a global scale. They compared the existing concentrations of elements with natural concentrations in unpolluted sediments; it is recorded as the "Index of Relative Pollution Potential". The study of sediment cores is especially suited for the differentiation of natural metal enrichment, for example in zones of mineralizations and anthropogenic effects occurring in certain areas as a consequence of mining and smelting activities (Allen, 1974). Most studies concerning historical pollution records in marine sediments have been performed in coastal areas under direct influence of rivers, either unpolluted or polluted (Goldberg *et al.*, 1977) and are restricted to temperate regions.

According to Jenne and Luoma (1977), little is known about the potential pathways in which trace metals are concentrated in surface sediments. The historical trends in the changing dominance of these environmental factors reflects the changes in industrial activity, urban growth and changes in the use of metals in paints, domestic and industrial chemicals and in the combustion of fuels. In the past few years, there have been numerous instances of man-induced heavy metal contamination of inland and coastal sediments (Merlini *et al.*, 1971; Sergar and Pellenbarg, 1973, Copper and Harris, 1974; Pasternak, 1974). A large portion of the metal enriched particles is deposited and buried on the shelf and continental slope.
Hence, sediments act as a useful indicator of long and medium term metal flux and when they remain more or less undisturbed with constant sedimentation rates, they can provide us with a historical pollution record and man-induced accumulation of metals (Bruland et al., 1974; Goldberg et al., 1977; Eisma et al., 1989; Macdonald, 1991; Nolting and Helder, 1991).

Generally, fine grained (silt/clay size) materials are the most important fraction of the oxidized layer of the surface sediments and they provide a large surface area that concentrates trace contaminants and other surface-active constituents (Dale, 1974). According to Krumgalz (1989), the geochemical cycle of trace metals in the marine environment is determined by various mechanisms including the interaction of the metals with sediments, the most significant parameter influencing trace metal content in sediment fraction being sediment size dimension. The geochemical cycle of anthropogenic trace metals in the marine environment is determined to a large degree by the interactions of the metals with sediments (Krumgalz et al., 1992). Generally, the smaller the size of the sediment fraction, the larger the amount of trace metals bound to this fraction, and trace elements are mainly present in clay/silt particles (Goldberg, 1974; Groot and Allersma, 1975; Hallberg, 1975; Forstner, 1977; Forstner and Wittmann, 1979; Dossis and Warren, 1980; Mayer and Fink, 1980; Thorne and Nickless, 1981; Salomons and Forstner, 1984; Araujo et al., 1988).

According to Abu-Hilal and Bardan (1990), the distribution of trace elements can serve as an indication of time history and extent of pollution discharge in specific areas. Moreover, surface and down core sediment geochemical data indicate the abundance and distribution of the total metal concentrations, and can largely be explained by the variable admixtures of terrigenous components in response to
textural variations and biogenic as well as calcareous components (Bodur and Ergin, 1994). As a result, the distribution of metals in sediment cores sampled from industrialized coastal zone and estuaries has been used as an indicator of past and present pollution events. Such reconstruction studies are useful to improve management strategies as well as to assess the success of recent pollution controls (Ravichandran et al., 1994). According to Szefer et al. (1995), sub-sections of sediment cores reflect the geochemical history of a given region, including anthropogenic impact. Hence, careful analysis of cores sediment samples can provide chronologies of metal concentration, including input of sediment fluxes over a period of time. In addition, geochemical characteristics of sediments can be used to infer the provenance and transport history of the sediment and also to determine the source of pollution (Oliver, 1973; Forstner and Salomons, 1980; Baldi and Bargagli, 1982; Tessier et al., 1982). Hence, surface and core sample studies help to evaluate the most recent changes in sediment contaminant levels due to effluent discharge and subsequent mixing, and also provide proper perspective for predicting system response and formulating future management practice. It is, therefore, important to understand how anthropogenic activities change the concentrations of potentially toxic metals, what processes affect such changes, and which activities have the greatest effects.

1.4 Recent Trends in Surface Sediment Contamination

In urbanized regions, sediments are very often influenced by domestic, industrial and mining activities leading to increased trace metal concentrations (Bruland et al., 1974; Duniker and Nolting, 1976, 1977; Trefry et al., 1985; Martin et al., 1989). Trefry and Presley (1976) inferred that the wide variation in the concentration of all metals in sediments from northwest Gulf of Mexico, especially the Mississippi river delta, might be a function of grain size, organic carbon,
calcium carbonate content and mineralogy. To know the immediate industrial effect on sediment in a clean coastal environment, Knauer (1977) analysed the sediments of Halifax Bay and revealed that within three weeks of the initiation of a refinery, continuous discharge of effluent waters had polluted the sediments in the bay. Loring (1978), in his study on the estuarine sediments of the Gulf of Lawrence, observed that fine-grained material controls the abundance of Zn, Cu and Pb.

Lyons and Gaudette (1979) remarked that in the sediment samples from Jeffreys Basin, Gulf of Maine, a strong correlation exists between the grain size and Fe, Mn, Cu, Cr, Zn, Pb, the highest concentrations being found in the clay-sized sediment fractions. According to Willey and Fitzgerald (1980), organic matter, mineralogy and texture of sediments control the total concentration of trace metals and reactivity in sediments of Miramichi estuary. Further, when compared with the sediments from other areas, Miramichi sediments have at least twice the values. The sources for this addition of metals are the mining activities as well as urban and industrial effluents. Similarly, high levels of metal concentrations (Ag, Cd, Cr, Cu, Hg, Ni, Pb and Zn) were noted in the surface samples of southern California and discharge of municipal wastewater via submarine outfalls could be the main anthropogenic source of pollutant (Young et al., 1978; Hershelman et al., 1981; Katz and Kaplan, 1981).

Surface sediments from Saronikas Gulf and Thermaikos Gulf (Taliadouri, 1981) were analysed in order to determine the main source of pollution. The results revealed that Zn, Fe and Cu concentrations were high in the former whereas, in the latter, Fe, Mn, Zn, Cr, Ni, Pb, Cu, Co and Cd were fairly high and are rich in organic carbon and mud contents. Taliadouri (1995), in his study of Messolonghi region near Pagassitikos Gulf, Greece, observed high organic content in the sediments, and
attributed it to eutrophication. The metal content in the sediments had values that were lower than the mean for unpolluted coastal regions of Greece. However, surface sediment samples analysed from the Pagassitikos Gulf by Taliadouri and Satsmadjis (1982) recorded slightly high concentrations in Ni, Mn, Cr and Zn in an area, which receives input from harbour activity indicating its influence on the marine environment.

Calvert and Price (1983), after examining the Namibian shelf sediments, concluded that major and minor element geochemistry reflects the complex intermixture of several sedimentary components which can be used to examine the extent of minor metal enrichment in the anoxic and diatom ooze sediments. Schafer et al. (1983), in a study on the Saguenay Fjord, Quebec, inferred that the anthropogenic sediment inputs increased the maximum mean monthly discharge of the river sediments. The New York Bight sediments recorded high correlations in organic matter and leachable metals (Zn, Cr, Cu, Pb, Ni, Fe, Hg, Cd) in silty clay component, where most of them were anthropogenic in origin (Krom et al., 1983). Yiyang (1985) found that the geochemical patterns on the shelf sediments of China are relatively close to that in terrestrial rocks and continental crust and the abundance distribution pattern of elements in the shelf sediments is similar to that in the continental crust. According to Nichols et al. (1986), the continuous disposal of toxic waste and the reduction of freshwater inflow has rapidly modified the San Francisco Bay estuary and contaminated its sediments. Similarly, a study conducted on the behavior of some metals in the surface sediments of the Northwest Mediterranean Continental shelf indicated that urban and industrial pollution along the coastal zone has enriched the accumulation of metals (Fernex et al., 1986).
Study on the surface sediments of Gulf of Aquba (Abu-Hilal, 1987) revealed distinct higher concentration in the top layers. Similar enrichment of the top layer was observed in areas receiving anthropogenic inputs of trace metals due to intensive human activities (Young et al., 1973; Crecelius and Piper, 1973; Bruland, 1974; Thompson et al., 1974; Kemp et al., 1974; Knauer, 1977; Hershelman et al., 1981). Elevated levels of trace metals in sediments and biota of several estuaries and embayments of the Gulf of Maine have been noted in the last two decades. Together, these studies suggest considerable variability in the degree of enrichment as a function of source and transport mechanisms (Armstrong et al., 1976; Mayer and Fink, 1980; Goldberg et al., 1983; Larsen et al., 1983; Ray and McKnight, 1984; Gottholm and Turgeon, 1991).

White (1972), Fitzgerald (1980) and Wallace et al. (1988) inferred from their studies that Boston harbour was adversely affected by both domestic and industrial anthropogenic inputs from their associated population centers. Concentrations of Cd, Cu, Ni, Pb and Zn were generally one to four orders of magnitude greater than currently accepted values for concentrations in water as well as in sediments. Results of surface sediment analyses for major and trace elements from 15 Japanese coastal sites recorded higher concentrations of heavy metals than from more open areas (Yiyang et al., 1988). In a baseline study on the heavy metal pollution on the inner shelf sediments of Beaufort Sea, Northern Artic Alaska, Sweeney and Naidu (1989), noted the proportion of silt and clay is the most important factor in the distribution of heavy metal abundance.

In order to create a basic data for the geochemical study, sixty chemical elements were analysed from the sediment samples from river Honghe and the continental shelf sea of river Changjiang (Yi Yang, 1985). To create a baseline
data for the first time Zhao et al. (1995) made a study on element abundance from China Shelf sediments on 286 samples and 62 elements were analysed. Similarly, Krumgalz et al. (1992) established the “finger prints” of pollutants in Haifa Bay and found that the distribution of anthropogenic trace metals (Cd, Cu, Fe, Pb, Zn) was high in several fractions. The Gulf of Maine which was once set as a standard to compare other coastal regions, with its high quality sea foods, unspoiled beaches and pristine waters, has lost its nature and is as polluted as other heavily populated and industrial coastal sites (Larsen, 1992; Gottholm and Turgeon, 1991). Taliadouri and Bogdanos (1992) reported that the domestic wastes of four million people in the Greek Metropolitan region and the discharges of the many industries concentrated there have seriously affected the bottom sediments of the Elefsis Bay. Yucesoy and Ergin (1992) inferred that the main sources of the elevated concentrations of Cr, Ni, Cu, Zn and Pb in sediments of Black Sea are related to the ultramafic/volcanic rock series and associated ore deposits of the drainage basin. Higher organic carbon and CaCO₃ contents reflect the proportion of the biogenic material in the samples and contributions from near shore terrigenous sources in southern Black Sea.

Nolting and Hoogstraten (1992), in their study on the horizontal and vertical distribution in the sediments of Mediterranean Sea, concluded that Rhone is probably the major source for several trace elements to the Gulf of Lions. However, the potential source of contamination on the shelves of Kara and Barents Seas was nuclear waste dumped by the former Soviet Union and the river discharges from large industrialized watersheds of Siberia (Yablokov et al., 1993). Detailed study on the surface sediments and mineralogical composition of Sulu Sea and South China Sea reveal that the sediments are carbonate rich and organic matter poor silty clays. The compositional variability of the sediments is low and it is controlled to a considerable extent by variations in sediment supply and grain size and not
due to differences in bottom oxygen levels (Calvert et al., 1993). Results of geochemical analysis of sediments from the Sea of Marmara indicate that the surface and down core total metal concentrations of Fe, Ni, Zn, Cr, Co, Cu and Pb are largely explained by the variable mixtures of terrigenous components and biogenic calcareous components poor in metal content. However, a significant amount of increase is recorded in Cu, Zn and Pb in sediments, which could be the pollution effect from the coastal region of Turkey (Bodur and Ergin, 1994).

According to Palanques et al. (1995), the Gulf of Cadiz has long been affected by mining activities since the Tartesians and Romans. But recent studies indicate high heavy metal accumulation due to the industries implanted during recent decades, which have supplied the input of contaminants to the marine system. Elaborate studies from the marine sediments of Halifax harbour and Central harbour regions reveal high concentrations of contaminant metals (Hg, Pb, Cu and Zn). The accumulation of waste in the sediments is mainly attributed to the discharge of untreated domestic sewage, development and expansion of harbour, shipping terminals, light industries and storm water drainage (Buckley et al., 1995). Taliadouri and Varnavas (1995) observed an increase in Cd, Pb, Cr, Cu, Zn, Mn, Ni, Co and Fe in the surface sediments from Thermaikos Gulf, mainly attributable to sewage outfall, the industrial zone and the river input. Loring et al. (1995), in a study on the Pechora Sea, Russia, using grain size, organochlorines, major and trace elements in surface and core samples, inferred high concentrations in the region.

According to Drake et al. (1996), each element in the Congo Basin is transported to the ocean by the so-called “dissolved” load by rivers. The clean up program by the Massachusetts Water Resource Authority on the Boston harbour have yielded positive results as some heavy metal concentrations has
decreased during the period 1977 – 1993. The concentrations of some metals, however, are high and might induce adverse biological effects (Bothner et al., 1998). Surface sediments in the discharge area of the river Oder reveal enrichment in heavy metals compared to their pre-industrial background levels where anoxic environment is present in the sediments (Neumann et al., 1998). Szefer et al. (1998), in their study on rare earth elements distribution, observed lack of positive Ce anomalies indicating that they are formed under less oxidizing conditions in the Southern Baltic sediments.

1.5 Recent Trends in History of Metal Contamination from Core Sample Studies

Most studies concerning historical pollution records in marine sediments have been carried out in coastal areas under direct influence of rivers, either unpolluted or polluted (Goldberg et al., 1977) and are restricted to temperature regions. Carefully dated cores through sediment deposits can provide chronologies of metal concentration or input in area of net sediment deposition (Nriagu et al., 1982; Christensen and Goetz, 1987).

Sediment cores of the Western Baltic Sea (Erlenkeusar et al., 1974) analyzed for heavy metal and carbon isotope contents indicate enrichment of Cd, Pb, Zn and Cu whereas, Fe Mn, Ni and Co remain unchanged. Goldberg et al. (1977), in his study on the pollution history of Narrangansett Bay in sediments using box corer, observed that the metal input was of higher magnitude, greater than the normal values. Similarly, the record of pollution history from the study of a sediment core recovered near regions of high human population and high industrial activity around Southern Bay of California (Bruland et al., 1974; Bloom and Crecelius, 1987) indicates high metal concentrations in the top layers.
According to Swift et al. (1995), in a review of chemical pollutants of the New York Bight, the major perceived threats to sediments are from chlorinated pesticides, lead, mercury, polynuclear hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and plutonium. They also studied the physical processes governing pollutant dispersal for several time and space scales. They also elucidated the sediment transport mechanisms, made an analysis of transport climate, and estimated the sediment transport budget in the coastal environment. Calvert et al. (1985) inferred that the sediments off the Peruvian shelf were enriched in Cr, Cu, Ba, Mn, Rb, Sr and Zr and attributed the high values to their delivery to the sediment inorganic association and their incorporation in to the high molecular weight polymers formed during burial diagenesis. Guoxian et al. (1988) observed that the marine environmental quality around Jin Zhou Bay, Bohai Sea, China, became a serious threat as the heavy metal pollutants were discharged in to the bay continuously and the contamination level reached a peak around 1971. However, core sample studies on the pollution history indicate a decrease in metal fluxes owing to regulation and control of pollutant discharges.

Abu-Hilal and Bardan (1990), investigated the core samples from the Gulf of Aquaba and recorded high concentrations of Cd, Co, Cu, Fe, Mn, Pb and Zn; they inferred that the metal pollutants discharged in to the water of the Gulf are from permanent sources of pollution. Analyses of hydrocarbon residues and metals in a dated core from an undisturbed sedimentary basin in Halifax Harbour clearly demonstrate that the sediments have been accumulating fuel residues and industrial wastes for the past 100 years. The level of contaminants in these sediments is amongst the highest recorded for coastal marine areas in the world (Gearing et al., 1991). Chemical analyses of core and surface sediments from northern
Euboekos Bay, Greece, reveal that the area is markedly enriched in metal relative to the Aegean Shelf sediments. The enrichment is partly related to the presence of a Fe-Ni ore body on the sea floor formed by dumping of a metal rich slag and partly to natural geological processes (Taliadouri and Varnavas, 1995). The concentrations of Cd, Cr, Cu, Ni, Pb, Sn and Zn in the surface sediments of Mid-coast Maine are distributed heterogeneously between sub-regions of the area and they generally exceed pre-industrial levels (Larsen and Gaudette, 1995).

According to Buckley et al. (1995), the accumulation of contaminant metals (Hg, Cu, Zn and Pb) in the bottom sediments of Halifax Harbour is a result of discharge of untreated sewage and industrial waste, leaching of landfill waste and surface drainage. Geochemical data from 4 cores taken in the Eastern Gotland Basin of the Central Baltic Sea show that depositional conditions for heavy metals were similar prior to anthropogenic influences. However, after the onset of industrialization, the sediments became characterized by high organic carbon and heavy metals. Geochemical analysis on sediments from the continental slope of the Banc d’Arguin (Mauritania) reveals that the trace metal concentrations measured in the area are low and comparable to those found in “pristine” environments (Nolting et al., 1999).

1.6 REVIEW ON SEDIMENT GEOCHEMICAL RESEARCH ON INDIAN COAST

1.6.1 WEST COAST

In the past, few workers have worked on the bulk as well as the partition geochemistry of sediments of the western continental shelf of India (Marchig, 1972; Murthy et al., 1973; Nair, 1975; Gogate et al., 1976). The non-lithogenous fractions of the outer shelf and slope regions composed of calcium carbonate
recorded low concentrations in iron, manganese and nickel in the west coast of India (Murthy et al., 1973). The outer shelf topography off the Gulf of Cambay and further south indicates that the algal and oolitic ridges originated during Holocene transgression (Nair, 1975). The abundance of skeletal components in the inner shelf and topographic data suggest the presence of onshore sediment transportation and the influence of bottom current on the outer shelf in the western continental shelf. A detailed report was presented on the major and trace element distribution pattern, deposition and partition patterns of elements in different compositions of the northern half of the western continental shelf sediments (Hashimi and Nair, 1976).

According to Bhosle et al. (1978), the shelf sediments from the Arabian Sea recorded high concentrations of organic carbon from the continental slope, whereas the shelf samples were characterized by low values. Distribution patterns of calcium and magnesium carbonates, organic matter, phosphate, sulphide-sulphur and sulphate-sulphur were investigated in surface and core samples collected between Bombay Harbour and Bombay High (Paropkari et al., 1978). Low values of organic carbon (0.95%) were recorded on the western continental shelf sediments, which is far below the world average near shore sediments (Parpakari, 1979). The marine environment along Bombay coast has deteriorated drastically due to the wastewater discharge from domestic and industrial establishments in and around the city (Zingde et al., 1979). Borole et al. (1982) made a detailed study on the suspended particulate matter and core samples on Narmada, Tapti and Arabian Sea sediments, which presented a clear picture on the ultimate fate of suspended load, riverine input and deposition rates of the elements.

The bulk and partition geochemistry of the surface sediments and the complex intermixture of several sedimentary components in the surface
sediments of west coast of India helped in identifying the geochemical processes responsible for the incorporation of elements into the sediments (Rao and Murthy, 1990). Sebastian et al. (1990) collected seasonal samples from Mahe estuary, Northern Kerala, and the sediments were analysed for texture, organic matter and carbonate content. Narayana and Venkatesh Prabhu (1993) investigated the distribution and textural variations of sediments off the west coast of India. Surface sediments of Cochin estuary indicated variations in texture resulting from detritus settlement influenced by mixing conditions in the estuary (Nair, 1975). George et al. (1993) described the depositional, sedimentary, and textural variations in the sediments of Ettikulam lagoon, west coast of India. Venkatesh Prabu et al. (1997) analysed the textural characteristics of near shore sediments off Hannovar, southwest coast of India, and opined that the transportation agencies were incapable of separating the sediments into different size grades. Rajamanickam and Gujar (1997) collected 256 sediment samples and, based on detailed studies on textural parameters, they described the possible changes in the depositional environments on the nearshore sediments of Jaigad, Maharashtra.

1.6.2 **EAST COAST**

The earliest report on the sediments of the Bay of Bengal was by Sewell (1925); he analysed the data collected during the expeditions by NOVARA and RMIS INVESTIGATOR and presented his findings in a number of papers (Sewell, 1925, 1928, 1929, 1932). International Indian Ocean Expedition (IIOE) data on the Bay of Bengal was presented in the form of an atlas (Wyrtki, 1971).

The Bay of Bengal has attracted a fair share of attention with regard to its sedimentation geology, notably the origin and history of the Bengal sediments (Stewart et al., 1965; Schott, 1968). Geochemical investigations of this vast
expanse are, however, limited, and confined to the deep (Nair and Pylee, 1968; Ramesh, 1997). The continental shelf off the east coast (Rao, 1978; Paropkari, 1990) Visakhapatnam (Gogate et al., 1970; Siddique and Mallick, 1972; Rajamanickam and Setty, 1973), river Godavari (Rao and Rao, 1975) and the Andaman Islands (Pandarinath and Narayana, 1991) also has been studied.

Subba Rao (1958) and Rao and Rao (1969) have reported calcium carbonate content in certain parts of the eastern continental shelf of India based on few samples. Several workers have worked on the continental shelf sediments of Visakhapatnam (Subba Rao, 1964, Venkataratnam, 1968; Rao et al., 1980; Murthy et al., 1987 and Murthy, 1989). Further, several workers have focussed on the chemical (Ramaraju et al., 1987; Sarma et al., 1982; Ganapati and Raman, 1979) and geochemical (Satyanarayana et al., 1985) studies of the Visakhapatnam harbour and coastal environment. Subba Rao (1962) inferred that the sediments of Visakhapatnam and Puri to Port Novo (Mohapatra et al., 1992) are sandy near shore and fine seaward becoming clayey silt or silty clay. Sarma and Rao (1988) reported on the distribution of organic carbon, total nitrogen, total phosphorous and total aminoacids of Visakhapatnam harbour sediments collected each month during 1986-1987. The textural characteristics and clay mineralogy of shelf sediments of Visakhapatnam were reported by Murthy (1994), opined that molluscan shells, shell fragments and foraminifera control the distribution of calcium carbonate in these sediments. Purnachandra Rao et al. (1998) studied the clay minerals and the influence of source rock and fluvial input on the shelf sediments of east coast of India. Similarly, Rao and Sarma (1993) collected 75 sediment samples of the coast between Bhimunipatnam-Amalapuram, central east coast of India and an overall analysis revealed that the geochemistry of sediments of the Bay of Bengal is controlled by their texture. Raman (1995) made a detailed study spread over more
than a couple of decades of the physico-chemical characteristics of the Visakhapatnam harbour; he revealed that during the past two decades the benthic conditions have been affected and the harbour is also subjected to high degree of pollution caused by industrial and urban wastes.

According to Pragatheeswaran et al. (1986), the sediments off Chennai are more contaminated in heavy metals and organic carbon than Visakhapatnam shelf sediments. The enhanced levels of Cu, Hg and organic carbon were attributed to input from industrial sources including organo-mercurial paint industry and oil refineries. Ramanathan et al. (1988) analysed major and minor element geochemistry of water and suspended and bed sediments collected from the upper reaches of the Cauvery estuary to understand the geochemical processes in tropical estuarine systems. The investigation of the characteristics of the sediments from a core collected from the Gulf of Mannar revealed high concentration of CaCO₃ (61.4%) and low organic carbon values, distinctly different from the anoxic sediments of Bombay (Ray et al., 1990). Palanichamy et al. (1995) inferred that industrial effluents pollute the waters of Arumuganeri region, Gulf of Mannar; they also recorded higher suspended solids due to discharge of effluents from the chlor-alkaline industries and land drainage. Vanmathi (1995), in her study of sediments of Tuticorin coast, concluded that heavy metals, especially cadmium, are significantly higher than in other coastal regions, affecting the biota in the region. Selvaraj (1999), in his study on the Kalpakkam coastal waters and sediments, recorded high concentrations of Fe, Cu, Hg and Pb; he attributed the enriched levels of Pb, Cu, Cr, Cd and Zn in sediments to mainly anthropogenic input along the coast and the river Palar.
The review of geochemical research carried out so far on and off the east coast reveals that considerable amount of work still remains to be done with regard to geochemistry and metal pollution in sediments. It is well understood that very few studies have been carried out on these aspects, especially in the Gulf of Mannar. With an aim to assess the impact of industrial and urban revolution on sediment quality, an investigation related to environmental quality of sediments along the Tuticorin coast, Gulf of Mannar, has been taken up. With this objective, a geochemical approach, comprising of the determination of sand-silt-clay ratio, CaCO₃, organic matter, total and nondetrital trace metals, rare earth elements, overall sediment accumulation rate and their horizontal and vertical geochemical distribution patterns in surface and core sediment samples, was initiated four years ago leading to the level of a Ph.D. thesis. The research problem is addressed under the title “Geochemical Characteristics of Surface and Core Sediments, off Tuticorin, Gulf of Mannar, South India: Implications for Metal Pollution”.

1.7 GEOLOGICAL AND COASTAL SETUP OF TUTICORIN COAST

The Gulf of Mannar receives riverine input through a number of rivers and streams, of which the Tambraparni followed by Vaipar River, are the major sources. The catchments of these rivers and streams covers an area of approximately 50 sq. km., draining an area essentially comprising crystalline rocks of Precambrian age and Holocene to Recent sedimentary formations situated on the coastal margins. A brief description of the geology of the area is presented to understand the nature of the source rocks for the sediments, which are transported by the rivers.

The region forms the southern part of the South Indian Granulite terrain (SGT), which is a high-grade terrain metamorphosed under granulite facies. The SGT is dissected by a number of shears, which have been used to divide it in to
crustal blocks. Radhakrishnan and Naqvi (1986) classified the SGT in to Northern Marginal Zone, Central Zone and Southern Zone. The Southern Zone is separated from the Central Zone by the Palghat -Cauvery shear and it is further divided in to two blocks separated by the Achankoil-Thenmalai shear (ATS). The ATS is a NW-SE trending shear terminating in the east coast 50 km south of Tuticorin.

The area north of ATS is essentially composed of hornblende-biotite gneisses and their granulite facies equivalents, the charnockites. They contain enclaves and linear bands of metasedimentary rocks represented by quartzites, garnetiferous biotite gneisses locally named as khondalites, calc-granites and crystalline limestone, which are inter banded with mafic granulites. The intrusive events include emplacement of anorthosites and granites. The khondalite suite of rocks dominates the area south of ATS and forms inter banded sequence with quartzofeldspathic gneisses and charnockite masses for isolated outcrops.

The hornblende-biotite gneisses, which form the most predominat rock types, are essentially composed of plagioclase, potash feldspars and quartz with minor amounts of hornblende and biotite. The charnockites are rather similar in mineralogy but contain hypersthene as the mafic mineral with less hornblende and biotite. The khondalite suite of rocks is quartzo-feldspathic and contains abundant garnet, biotite and sillimanite. Graphite occurs in considerable amount in some areas. The calc-granulites, which are limited in extent, are rocks with varied mineralogy, comprising calcite, scapolite, diopsidic pyroxene, Ca-garnet. The minor accessories are represented by zircon, monazite, rutile and ilmenite.

Geochronological data on the terrain is scanty and the available data indicate that the protoloths of the gneisses and charnockites may belong to Early Proterozoic
(2.1 Ga) as evidenced by the isotopic characters of the Kodaikanal charnockites. The granulite facies metamorphic event, which transformed the gneisses in to charnockites is dated as 550 Ma (Choudhary et al., 1992; Santhosh and Radhika, 1994). The P-T conditions of metamorphism indicate that the rocks have been metamorphosed under high temperature of 650 to 720°C and pressure in the range 5.3 to 6.0 K.bar. The P-T estimates imply that the rocks have been buried to a depth of 25 km during 550 Ma and have been exhumed to the present level due to erosion. This gives an idea about the denudation and quantum of sediments removed from the region during its geological history.

The study area from Tuticorin to Tiruchendur in the south extends to about 60 km. This stretch is mainly comprised of Archeans, Quaternary and Recent geological formations. Moreover, sedimentary formations to a stretch of 10 to 12 km from the coast, south of Tuticorin, also occur consisting of Tertiary formations of sand and calcareous sandstones. Garnet sand, ilmenite sand and gypsum are observed along the coast and mouths of Vaipar, Kallar and Nambiyar rivers, which flow during monsoon periods. According to a report in 1973, heavy mineral estimates in this coastal belt accounts for nearly 40,000 tonnes of ilmenite and 15,000 tonnes of garnet. The physiographical features present a raised beach with sand bar parallel to the present coastline north of Tiruchendur. However, sand bars on the northern and southern sides of Tambraparni River are slightly angular to the coastline. Beach, coastal ridges, cliffed coast, sand dunes, beach terraces, spits, salt marshes and teri sands are some of the geomorphic features observed in this stretch. The coastline of Tuticorin district has been developed by sediment accretion and broken by spits developing in to prominent cuspates as observed in the study area. To the south of Tuticorin, a huge sand bar has developed in to a northward trending beach cusp 4 km from the main shore. The coast is also influenced by the
Tambraparni river delta and the coastline south of Tiruchendur is marked by a narrow beach beyond which extends the coastal ridge over which sand dunes, beach terraces and calcareous rich limestone beds have formed. A number of coral islands rim the coastal zone and support diverse fauna.

The Gulf of Mannar is a transitional zone between the Arabian Sea and Indian Ocean proper and is connected with the Bay of Bengal through a shallow sill, the Palk Strait. The area under investigation off Tuticorin, presents great interest because it is an industrial belt consisting of many major industries involved in production of chemicals, petrochemicals and plastics. In addition, a thermal power plant and heavy water plant and human activities in and around Tuticorin have altered the ecosystem prominently; the total population of Tuticorin town, according to census 1991, is around 20 lakhs. Further, the river Tambraparni carries heavy metals discharged from agricultural activity and finally drains in to the inner shelf of the Gulf in the southern part of the study area.

The Gulf consists of several coral reef islands and of the 21 coral islands present along the coastline between Tuticorin and Pamban, most of them are situated close (2 to 18 km) to the main land. These coral reefs are on the decline and are almost facing a struggle for survival due to degradation of the ecosystem by industrialization. Likewise, the inner shelf of the Tuticorin coast was once a prominent nursery ground for pearl culture which, however, has almost ceased, in recent years due to the anthropogenic activities in the region.

1.8 **Industrial Scenario Around Tuticorin Coast**

The total extent of the coastal stretch of Tamil Nadu 1,026 km and solid waste 9,112 tpd and wastewater (3,78,364 m³/day) are let out in to the
open sea. In recent years, development in Tamil Nadu has gained momentum and a number of large and small industries have been commissioned in and around Tuticorin district. The large-scale industries are mostly located on the coast or very near the coastline. In addition, Tuticorin has the oldest harbour and the largest port in Tamil Nadu next to Chennai Port Trust. The Port of Tuticorin handles a variety of consignments, which includes coal, fertilizers, oil, gas, and various container goods of different types. The fishing harbour of Tuticorin started during 1911 has about 300 mechanized boats, which carry out fishing activities. This activity also exerts considerable stress on the marine environment in the region.

Tuticorin Thermal Power Station (TTPS) at present has five units and it generates about 1050 MW per day. The total area of the coal yard for TTPS is 2,50,000 sq.m and the consumption of coal by these units is up to 16,782 MT per day. The ash ponds located in 187 hectares of land are filled up by nearly 6000 MT/per day of fly ash. In addition, the wastewater (ash & water) let out in to the open sea through ash ponds is 74,500 KL/day. Cooling water of more than 1,65,000 cu.m/hr is used in the TTPS. Inside the thermal power plant, the temperature reaches a high of 1360°C and chemicals like HCl, H2SO4, HNO3, caustic soda, ferrosulphate, ammonia, potassium bisulphate, hydrazine hydrate, trisodium-phosphate, acetylene, nitrogen, carbon dioxide, chlorine, hydrogen and argon gases are used daily for various activities. In addition, lubricant oil, grease and transformer oil are also used in this unit.

The Southern Petrochemical Industries Corporation Limited (SPIC) manufactures urea and di-ammonium phosphate, aluminium fluoride, sulphuric acid, caustic soda, hydrochloric acid, liquid chlorine and ammonium chloride. The unit generates 620 KL of trade effluents per day. SPIC effluents have high
concentration of total suspended solids, total dissolved solids, chlorides, sulphides, ammonia, BOD, COD etc. The effluents are being let in to the sea through a 300 mm dia cast iron pipe extending for about 1 km from the coast. The main solid wastes generated by SPIC are arsenic sludge, chromium sludge, gypsum, CaCO₃, calcium fluoride and calcium phosphate.

Tuticorin Alkali Chemicals (TAC), located on the coast next to SPIC, manufactures 6300 MT/month of high soda ash and ammonium chloride. The unit generates 1800 m³/day of trade effluents, which are high in TDS and in addition contain oil, grease and ammonia. A submersible outfall located in the sea, 500 m from the coast, transports the effluents from TAC. The Heavy Water Project (HWP) manufactures 1500 KL/per day of heavy water. The effluents mostly contain ammonia, hydrogen, nitrates, fluorites and phosphates.

Further, on the banks of the river Tambraparni, south of the study area, Dharangadhara Chemical Works (DCW) produces 4000 ML/month of caustic soda. Domestic effluents of 10,000 L/per day and 9000 KL/per day of trade effluents are let out in to the sea through an open channel. The Indian Rare Earths Limited (IREL) produces ilmenite, rutile, zircon, monazite, garnet and zirconium dry frit, and the unit discharges 1170 KL/per day of trade effluents. The Tuticorin Spinning Mills, Madura Coats and Arasan Textiles produce cotton yarn whereas the South India Carbonic Gas Industry produces carbondioxide. All the industries are located along the coast and the effluents are directly let out in to the open ocean with minor treatment.

In addition, various industries located in the adjoining coastal town drain their effluents in to the sea through different channels. Tuticorin
municipality and the small-scale industries around Tuticorin district generate 14 ML/per day of sewage, which ultimately reaches the gulf. The small scale industries located in SIPCOT Complex, spread over an area of 400 acres are engaged in diverse activities, including manufacture of paper bags, sea food processing, senna leaves, iodized salt, fibre boxes, fish meal, industrial sheds, industrial oxygen, cement concrete blocks, body building, species powder, calcium carbide and low metallurgical coke. All these units are located in the northern part of the town and the effluents are discharged in to the sea with minor treatment. In addition, there are many units concentrating on food processing (403 units), metal bases units (274), paper based production (117), textile associated (107), mineral based (100) and transport equipment and services (85) and distributed in the district, which account for 80% of the small scale industrial units. Further, 4800 to 5000 units of handicrafts, match factories and cottage industries are located in the surrounding regions of Tuticorin. Therefore, the gulf receives wide range of contaminants from the aforesaid industrial and urban activities.

1.9 ECOLOGICAL SCENARIO OF TUTICORIN COAST

Tuticorin is one of the well-known old age fishery ports of India, especially by virtue of the production of valuable, good quality, natural pearls and chunks in addition to marine food products. A survey of fishery statistics reveals that there was a gradual decline in fishery output which reached an all time low of 1,320 tonnes in 1992 when compared to 4202 tonnes in 1988.

In addition, all the coral islands situated along the Tuticorin zone are subjected to human interference and activities carried out by them. They are disturbed by the collection of coral rubble, quarrying of coral stones, operation of bottom set gills for lobsters, marine algal collection and trap fishing operations in
and around the islands. Evidences are available for the removal of boulder type corals in the shallow waters, thus creating imbalances in the islands. As a result of the mining activities during the past years few years, a few islands are now completely submerged during high tide. In the Gulf of Mannar, *pearl oysters* known as *pearl banks* or *paars* lie about 12 to 20 km away from the coast at depths of 15 to 25 m. Pearl collection was intensive during 1805 to 1961 when abundant coral reefs existed. After 1961, however, trawler fishing was introduced and has gradually intensified over the years. During a survey in 1975-76, considerable fluctuations in the pearl oyster settlement were recorded and the pearl banks were not productive at all.

As per the overall industrial scenario, many large and small scale industries have come up along the coastal zone in recent years and the large coral islands and marine community have shouldered the burden in receiving the heavy load of effluents let out in the coastal zone.

1.10 **OBJECTIVES OF THE RESEARCH WORK**

The Tuticorin coast of the Gulf of Mannar is one of the most important areas to be investigated in detail as developmental activities in the city are rapidly increasing day by day and especially in the coastal zone. The decline in pearl fishing as well as marine food production warrants environmental monitoring of the inner shelf in order to evolve strategies to control environmental degradation. As sediments in the inner shelf are good indicators of the quality of marine ecosystem, a detailed study of the geochemistry of surface sediments was taken up. Further, as the history of pollution in the shelf can be better brought out by the variation of geochemical characters of sediments collected at depths, three short cores and 64 surface sediments were collected for this study.
The objectives of the present study are:

a) To study the horizontal, vertical grain size variations in surface and core sediments and to interpret the sediment type and texture.

b) To understand the spatial and vertical distributions of calcium carbonate, organic matter contents and to identify their role in trace metal accumulation.

c) To comprehend the geochemical behaviour of major and total trace elements in the coastal environment and their distribution.

d) To study the weak acid extracted nondetrital trace metals of coastal sediments and to decipher the anthropogenic fingerprints.

e) To study the importance of rare earth elements as pollution indicators

f) To estimate the overall sediment accumulation in the coastal zone and, finally,

g) To compile the data from the above study and evaluate the present as well as past environmental, sedimentological and geochemical conditions and provide a reliable data base for future research.

1.11 SAMPLING OF COASTAL SEDIMENTS

Sediments in the coastal regions consist of a mixture of organic and inorganic materials. They have been incorporated in to the sediments from solution (nondetrital) and solid particulate matter (detritus). Hence, undisturbed sediments in the coastal zone can provide a historical record of metal accumulation with regard to time, while surface sediments provide an immediate assessment of the levels of contamination at present.

In the present study, three core samples (Fig. 1.1 and Table 1.1) were collected using a PVC pipe of 8 cm dia with serrated bottom and Petersen mud
Fig. 1.1. Study area and sampling locations.
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grab was used to collect 32 surface sediment samples during each season (premonsoon and postmonsoon). The core samples were collected at 10-15 m water depths. They were brought to the shore laboratory, kept at –20° C immediately after collection and sub-sampled at 2.5 cm interval. The length of the core sample varied in order of the retrieving capacity and totally 103 sub samples were obtained, 33 each in Core 1 (C1) and Core 2 (C2), and 37 in Core 3 (C3). Surface sediment samples were collected in a grid pattern along five transects in two seasons viz., premonsoon (November, 1996) and postmonsoon (May, 1997). Traverse 1 (T1) (Stations 1-4) is located in southern end of the study area opposite to the temple town Tiruchendur, traverse 2 (T2) (Stations 5-10) is located opposite to the mouth of River Tambraparni and traverse 3 (T3) (Stations 11-23) is placed just opposite to SPIC. The northern section traverse 4 (T4) (Stations 17-23) is collected opposite to the main harbour and the final traverse 5 (T5) (Stations 24-29) is located north of Tuticorin and stations 31-32 are located close to the shore near TTPS and fishing harbour. Special care was taken to avoid leakage of fine-grained material between sea-surface and the deck of the launch. Samples of about 1 kg each were collected from each station and kept in numbered, clean plastic bags.

1.12 SAMPLE PREPARATION AND STORAGE

The sediment samples were prepared for sedimentological and geological analyses, which involved drying, sub-sampling, wet and dry sieving and finally crushing and storage (Loring and Rantala, 1992). The samples were air dried for 48 hours and the pebbles, coarse organic fibers and shell fragments were removed using respective sieves. The samples were then homogenized and crushed softly to remove the lumps. Air-drying was preferred in this study as most of the changes are related to oxidation/reduction phenomena, which affect the proportion of metals weakly held in the sediment (Kersten and Forstner, 1987). After drying, the
various core samples and surface sediments were stored in neatly numbered plastic bags. The schematics flow-chart (Fig. 1.2) explains the sediment sample preparation and analytical methodology adopted in the present study.

1.13 **SCOPE OF PRESENT INVESTIGATION**

In developed countries, the problem of pollution of the marine ecosystem has been realized and periodical monitoring of the coastal waters is being carried out during the past three decades. Measures have been undertaken to bring down the level of pollutants and, in many areas, success has been reported partially though not fully. In developing countries like India, due to limitation of funds, detailed monitoring has been seldom undertaken and only during the recent years environmental awareness is picking up. The review of various reports reveals that the Gulf of Mannar has either been neglected or studies related to pollution are very scanty; some work has been carried out, however, on the coastal and beach sediments and waters. The complex nature of the Tuticorin coast with its numerous industries and the degrading coastal islands warrant a detailed study. The present study will provide a history of accumulation of trace metals and their present level and the data can be used as a baseline to monitor the coast in future. Hence, the present research investigation on the sediments is imperative to assess the environmental degradation of the coast as well as the coastal islands.
Fig. 1.2 Flow chart depicting methodology for sediment analysis.