GEOCHEMISTRY OF TRANSITION, NON-TRANSITION AND RARE-EARTH ELEMENTS IN THE SURFICIAL SEDIMENTS OF CONTINENTAL SHELF OF KERALA AND AN ANNEX TO THE COCHIN ESTUARINE SYSTEM

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Certificate

This is to certify that the thesis entitled "Geochemistry of transition, non-transition and rare-earth elements in the surficial sediments of continental shelf of Kerala and an annex to the Cochin estuarine system" is an authentic record of the research work carried out by Sri Laluraj C.M., under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and no part thereof has been presented before for any other degree in any University.

Dr.S.MURALEEDHARAN NAIR

Declaration

I hereby declare that this thesis entitled "Geochemistry of transition, non-transition and rare-earth elements in the surficial sediments of continental shelf of Kerala and an annex to the Cochin estuarine system" is an authentic record of the research carried out by me under the supervision of Dr. S. Muraleedharan Nair, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, and that no part of it has previously formed the basis for award of any degree, diploma, associateship, fellowship or any other similar title or recognition in any University.

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Preface

The metals present in the surface sediments have high demand on a global perspective, and the main reservoir of these elements is believed to be the ocean floor. A lot of studies on metals are going on throughout the world for its quantification and exploitation. Even though, some preliminary attempts have been made in selected areas for the quantitative study of metals in the western continental shelf of India, no comprehensive work has been reported so far. The importance of this study also lies on the fact that there has not been a proper evaluation of the impact of the Great Tsunami of 2004 on the coastal areas of the south India. In view of this, an attempt has been made to address the seasonal distribution, behavior and mechanisms which control the deposition of metals in the sediments of the western continental shelf and Cochin Estuary, an annex to this coastal marine region.

Surface sediment samples were collected seasonally from two subenvironemnts of southwest coast of India, (continental shelf of Kerala and Cochin estuarine system), to estimate the seasonal distribution and geochemical behavior of non-transition, transition, rare-earth elements, Th and U. Bottom water samples were also taken from each station, and analysed for temperature, salinity and dissolved oxygen, hence the response of redox sensitive elements to oxygen minimum zone can be addressed. In addition, other sedimentary parameters such as sand, silt, clay fractions, $CaCO_3$ and organic carbon content were also estimated to evaluate the control factors on level of metals present in the sediment. The study used different environmental data analysis techniques to evaluate the distribution and behavior of elements during different seasons. This includes environmental parameters such as elemental normalisation, enrichment factor, element excess, cerium and europium anomalies and authigenic uranium.

The thesis is divided into six chapters. The first chapter gives an introduction to the coastal environment, emerging issues, oceanographic investigations carried out along the west coast of India, the shortfall the need for the present study and objectives. The limitations of previous works and the aim and scope of the present study is also mentioned in this chapter.

The second chapter provides the materials, description of the study region, methodology adopted for sample collection and analyses of water and sediment samples. Also, mentioned are the precision and accuracy of metal analyses, environmental techniques such as elemental normalization, enrichment factor, elemental excess, Ce and Eu anomalies and authigenic uranium.

The third chapter elaborates the seasonal changes in the hydrographic parameters and sediment characteristics along the shelf of Kerala and Cochin estuarine system. This includes bottom hydrography, textural property, energy conditions, organic and carbonate contents.

The forth chapter explains the results on seasonal distribution of non-transition elements such as, Be, Al, Ga, Rb, Sr, CS, Ba and Pb along the study region. The relationship between the overlying water environment, sediment texture and elemental concentrations are explained using techniques such as element excess, enrichment factors of the elements and normalization.

Fifth chapter explains the seasonal variation of the 15 transition elements such as from Sc to Zn (except Ti), Y to Mo, Hf and Ta along the study region. This chapter also discusses elemental correlation with hydrographical and sedimentological parameters, element excess, enrichment of elements and normalisation. Comparison of coastal sediments with the marine and estuarine system is given in this chapter.

Sixth chapter deals with the seasonal distribution of rare-earth elements, Th and U in the sediments from the shelf of Kerala and Cochin Estuary. The relationship between organic carbon, $CaCO_3$, dissolved oxygen, temperature, salinity and elements are explained in detail. It also elaborates on the shale normalization; element excess, enrichment factors, Ce and Eu anomalies and authigenic uranium. The statistical techniques such as correlation and multiple regressions used in this study are also given at the end of each chapter.

The summary is given at the end of the thesis, which sum-ups the distribution and geochemical behavior of metals along the two sub-environments. This study contributes significantly to the database of non-transition, transition and rare-earth elements on the west coast India.

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Chapter 1

Introduction

Contents

1.1 General introduction

The oceans covering approximately 70% of the earth crust contain four major sub systems namely; the seawater, suspended particulate material, sediment and the biota. All the naturally occurring elements are considered to be present in ocean in almost all possible chemical forms in varying concentrations. Input of elements is either as dissolved form or as particulate or suspended form. Sediment, which acts as the sink and reservoir, plays the key role in removal. The biogeochemical processes such as acid-base reactions, oxidation–reduction, complexation, adsorption at interfaces, precipitation and dissolution of solid and distribution of solutes between aqueous and non-aqueous phases regulate the bioavailability of the element in the system. The suspended materials on sinking are subjected to changes in composition through processes such as aggregation, disaggregation, scavenging, decomposition and dissolution (Chester, 1990). In surface waters of coastal and estuarine regions, suspended materials are high and variable than in open ocean. Nearshore sediments are strongly influenced by the land masses, while deep sea sediments are influenced by the reactivity between particulate and dissolved components in the water column. The surface runoff delivers elements into the coastal zone, which get progressively diluted in the open ocean. However, the coastal zone is not simply a reservoir of these materials, as they are distributed among water, sediment and living organisms, providing an environment of intense biogeochemical reactions (Figure 1.1). The dominance of one or many of these processes decides the fate of elements and results in their retention in the region or export to the ocean.

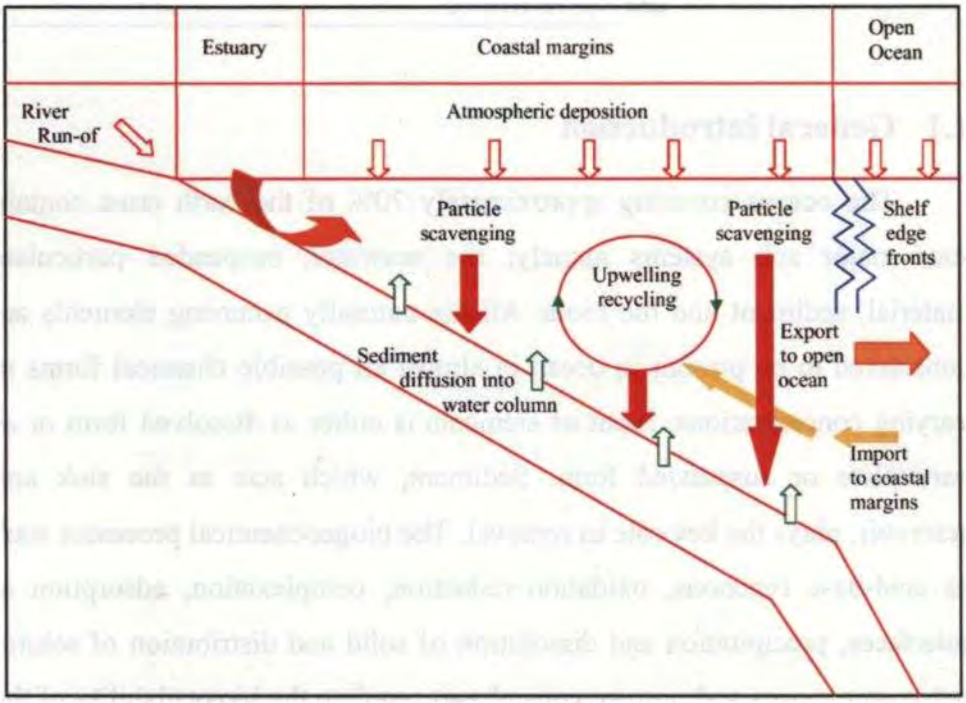

Figure 1.1. Schematic representation on the processes influencing the fate and pathways of elements in the coastal margins (from Simpson, 1994).

The sources of the dissolved and particulate elements in rivers include rock weathering, atmospheric deposition, decomposition of organic matter and anthropogenic activities. The inputs are generally based on the basin properties of drainage area such as lithology, relief, land use pattern, vegetation etc. The materials undergo various physio-chemical changes in the estuary before ultimately reaching the ocean. Fluxes from large rivers are used to estimate coastal inputs (Dupre et al., 1996) and erosional process on a global scale (Stallard and Elmound, 1987). Most of the studies have focused on the dissolved and particulate phases of the river-estuarine systems. Chemical changes are however, noted in the sediments of small rivers (drainage basin <10,000 km^2), which from numerous numbers may actually contribute much more elemental fluxes (Milliman and Syvitski, 1992; Albarede and Semhi, 1995).

The conventional paradigm for the behavior of reactive materials in coastal marine ecosystems has been to identify the processes by which dissolved and particulate materials are associated with minerals settling to sediments. Because of the dynamic nature of these systems, estuarine processes are complex and their transformations often remain obscure. Turbulent mixing of freshwater and seawater can generate rapid changes in Eh, pH, salinity, and trace element concentrations (Feely et al., 1981). Superimposed on this variability are the biological processes acting on time scales of seconds to days (Hedges and Keil, 1999). Hence, it is difficult to understand the origins, pathways, and fates of dissolved and particulate materials in coastal marine systems, and especially in estuaries.

Increase human interventions in estuaries and coastal zones over the last few decades can disrupt the natural equilibrium and the biotic composition of the respective ecosystems. The main causes for such changes are introduction of untreated and partially treated (industrial and urban) sewage rich in organic substances and plant nutrients, seepage from agricultural/aquaculture fields and animal husbandry. Sediments represent one of the ultimate sink for heavy metals discharged into the aquatic environment. These metals occur in sediments, adsorbed as ions, hydroxides, oxides, phosphates, silicates, carbonates, sulphates, sulphides and organometalic compounds (Jenne, 1976). These metals are not necessarily fixed permanently by the sediments and may be released to the water column under favorable conditions. Thus in aquatic system, sediments may be both a carrier and a source of metals. However, factors such as pH, redox potential and salinity play an important role in the mobilization of particulate metals (Kersten and Förstner, 1987).

The role of rivers and estuaries in transporting detrital materials from continents to oceans is paramount, being 10 times that of glaciers and 100 times that of wind (Goldberg, 1976). They carry metals in solution, adsorbed on inorganic solids as cations, on organic solids and in detrital crystalline materials (Gibbs, 1973). The human impact on the geochemical cycling of metals is predominantly a localized one, involving the redistribution of the element from the earth's crust. Though they undergo some perturbation during these processes, some metals are rapidly returned to the lithosphere by sedimentary deposition. As they are persistent and non-biodegradable, they cannot be eliminated but can only be relocated or converted into forms of reduced accessibility or bioavailability (Barbour and Taylor, 1988). Hence, estimation of metals in marine sediments is an important tool for distinguishing between the various carrier phases and to delineate the processes that lead to their enrichment in the sediments. Of special interest is the study of those metals, which have an affinity for biota, such as Cu, Zn, Co, Cr, Ni as well as Fe that have a nutrient-like distribution in the oceans. The enrichment of these metals in marine sediments has been related to the high productivity zone in the hemi-pelagic and pelagic environments, where organic matter in the water column plays an important role in their transport from seawater to the bottom sediments (Collier and Edmond, 1984; Martin and Thomas, 1994). Some metals are accumulated in marine sediments by precipitation from seawater as hydroxides, as is the case of Fe-Mn (Landing and Bruland, 1987) and elements scavenged by them by their incorporation and/or adsorption to authigenic mineral phases (Altschuler, 1980). Sediments are major repositories for metals and, in addition to providing the environmental status; they are also used to estimate the level of pollution in a region (Burton and Scott, 1992; Caccia et al., 2003).

The west coast of India is environmentally more sensitive than the east coast primarily because it is bordering one of the most sensitive ecosystems in the world, the Arabian Sea. The environmental property of the northern Arabian Sea is unique which manifests in rich biological production throughout the year through different processes and thus, explain for the Arabian Sea 'Paradox' (Mathupratap et al., 1996). The mid-depth oxygen deficiency in the Arabian Sea is perhaps the most severely observed anywhere in oceans, as the concentration within ~ 150 – 1000 m are less than 0.1 ml/l within a large part of central and northeastern Arabian Sea (Naqvi and Jayakumar, 2000). This zone is characterised by intense denitrification, which is observed only in 3 regions among world oceans, the other two being observed in the Pacific. With such a delicate biogeochemical balance that exists in the oceanic oxygen-deficient zones, the Arabian Sea will perhaps be among the first to react to potential anthropogenic perturbations such as increased nutrient/organic loading (Naqvi et al., 2000). Any alterations in the rate of mid-depth water renewal or in subsurface oxygen demand may bring about large changes in chemical fluxes. Similarly, an expansion of the oxygen minimum zone, particularly towards the coastal zone, may also have deleterious effects on biological resources as evident from mass mortality of fish reported off Cochin during southwest monsoon, 1998 (Naqvi et al., 1998). It is still not clear as to how the suboxic ecosystem in the Arabian Sea will respond to changes induced by man.

There is an apprehension that environmental deterioration of coastal and estuarine waters will inevitably have consequences for the Arabia Sea's ecosystem. The symptoms are there to show considerable impact of deterioration of estuarine waters on the coastal as well as shelf ecosystem (Nair et al., 1991; Naqvi et al., 2000; Jayakumar et al., 2001). The emerging industrial establishments and human settlements along the west coast of India, thus necessitates a critical evaluation of the nature and quantum of inputs to the Arabian Sea as well as their regional assimilative capacities. If there is a possible threat to the well being of the living resources of EEZ of India, then the southeastern Arabian Sea is one of the prime locations affecting the most.

As estuaries are geochemical barriers regulating the export of materials, emerging metropolises like Cochin necessitates information on the fate of metals in the coastal environment. The booming city of Cochin has population of nearly 1.5 million (Anon, 1998) and 60% of the chemical industries of Kerala are situated in this area. Cochin estuarine system is the largest of its kind on the west coast of India with an area of 256 Km^2. Cochin estuarine system comprises one of the most important harbour and industrial centers in the west coast of India. It was reportedly unpolluted, sustaining a rich shell and fin fishery and variety of other organisms (Sankaranarayanan and Qasim, 1969). The anthropogenic influence in the estuary began in the second part of 19th century and continues to compound

(Gopalan et al., 1983; Balachandran, 2002). The resident population (3 Million in 2002, @ > 4000 person.km^{-2}) and associated industrial activities result in a release of 0.104 Mm^{3}d^{-1} of industrial wastes and 260 t.d^{-1} of domestic sewage without proper treatment, polluting the lower estuary with nutrients, trace metals, organic matter and pesticides (CPCB, 1996; Sujatha et al., 1999; Menon et al., 2000; Balachandran et al., 2005). Even though numerous researchers have reported the trace metal distribution in the Cochin estuary (Venugopal et al., 1982; Nair et al., 1990; Nair, 1992; Padmalal et al., 1996; Balachandran et al., 2005; Balachandran et al., 2006) as well as in the coastal region (Murthy et al., 1973; Rajamaniamma, 1994; Laluraj and Nair, 2006), an integrated geochemical study involving trans-boundary exchange of the potentially toxic elements has not been carried out so far. The industrial typology includes fertilizer, pesticide, radio- active mineral processing, chemical and allied industries, petroleum refining and heavy metal process and fish processing. The fertilizer consumption in Kuttanad region (the main agricultural field draining to Cochin estuary) alone is reported to be 20,239 t y^{-1} (Anon, 1998). The estuary receives organic wastes (~ 260t d^{-1}, Anon, 1998) and an annual dredge spoil from the harbor area to the tune of 107 m^3. A recent study on this coastal environment has brought out the different pathways of metal associations in coastal sediments on an annual scale (Balachandran et al., 2003; Balachandran et al., 2006). They observed that succession of southwest monsoon by winter and inter monsoon periods brought a distinct transformation in the behavior of metals from a rapid deposition to an organic association followed by sedimentary modifications to normalize the geochemical distribution. To summarize all, as the system has been subjected to irrational economic exploitation during the past five decades, the environmental deterioration has ultimately resulted in ecological degradation.

1.2 Metals in aquatic system

In aquatic system, metals are present as dissolved ions, colloids, suspended and solid forms (sediments). The metal concentration strongly depends on the redox condition, pH, ionic strengths and scavenging activity. The ecological impact of metals largely depends on their form in water, capacity for complexation, sedimentation and bioaccumulation. Some trace metals are adsorbed on surface of suspended material or may be incorporated into the lattice of mineral such as iron and manganese oxides or in organic matter (Rognerud et al., 2000). Wayne and Markovics (1997) stated that the trace metals in sediment depend on the rock and on the weathering processes. Tang (1987) pointed out that the composition of a parent rock is the major factor affecting the trace metal content. The variability of metals in fine sediments is controlled more by hydraulic than geochemical activity by which, the sediments are transported and deposited (Marcus, 1996). The transition metals are present in sediment as insoluble hydroxides, carbonates and sulphides. $Fe(OH)_3$ and MnO_2 also influence the heavy metal deposition and distribution in sediments (Janne, 1976). Hence, metals in suspended and bed sediments are more sensitive than the metals in dissolved form and their level of contamination in an aquatic system (Turner and Millward, 2002).

In anoxic condition, metals and minor elements can vary as a function of prevailing redox potential (Calvert and Perdersom, 1993). Elements such as Cu, Cr, Co, Zn, Ni, V and Mo, which are soluble in oxic condition, are reduced to insoluble specious of lower valency under anoxic conditions. Hence, behavior of Cu, Cr, Co, Zn, Ni, V and Mo can be used as indicator of sedimentation under different environmental conditions (Calvert and Perderson, 1993).

Metals are introduced into the ocean by river run off, winds, hydrothermal venting and anthropogenic activities. Rivers are a major source of particulate and dissolved metals, both of which are mobilised during the weathering of granitic and basaltic crust (Jérôme et al., 2008). Some of the cations are adsorbed onto the surface of clay minerals. Metals undergo different chemical reactions during estuarine mixing, which play an important role in establishing the oceanic composition of elements and act as a link between continent and oceans (Sholkovitz, 1993). The increase in ionic strength and pH in the estuary precipitates the resolubilised metals as oxyhydroxides and organomettatlic colloids (Feely et al., 1981; Balachandran et al., 2005). The dissolved metals reaching the ocean tend to be more reactive than major ions and get deposited in sediments. Some of the metals are deposited as a component of wind-borne dust particles. In fact, atmospheric fall out is one of the largest oceanic inputs of some metals like, lead (Nel, 2005). Once metals are introduced into aquatic systems, the sinking particles carry them to sediments, where chemical reactions re-dissolve a significant fraction and diffuse across the sediment-water interface. Organic rich sediments are major sources of remobilized metals due to their affinity to organic matter (Derek and Elizabeth, 1986; Liang et al., 2008). In addition, the hydrothermal fluids associated with tectonic centers are enriched in trace metals as sulfides (Katja et al., 2007). Metals are also introduced by human activities via rivers and atmospheric transport. The alternate pathways include direct dumping of industrial and municipal wastes. The metal present in seawater undergoes rapid and efficient removal by adsorption, precipitation and incorporation into biogenic particles (Turner et al., 2008). These particles enriched in metals eventually sink into the bottom, the process being termed as scavenging. The organic rich coastal and shelf sediments are susceptible to suboxic as well as oxic diagenesis. The suboxic condition leads to the enrichment of redox elements such as V, Cr, Co, Ni, Cu, Mo, Pb, U and Ce, whereas oxic sediment remove Mn and Fe under changing redox conditions (Jennifer and Steven, 1999; Shumei et al., 2008). The anoxic coastal sediments release metals diagenetically, while a fraction of these can escape back into the overlying waters.

Estuarine and oceanographic processes play an important role in linking the composition of sediments from rivers to oceans. Hence, geochemical composition of sediments provides global metal inputs to ocean. Some of the metals are removed during estuarine mixing (Martin et al., 1976; Sholkovitz and Elderfield, 1988; Elderfield et al., 1988). Sediment metal enrichment has been reported along the southwest coast of India (Nath et al., 2000). Metals introduced by domestic, industrial and mining activities are incorporated into sediments. Metals get accumulated in the estuarine and continental shelf sediments. The rare-earth elements (REEs) can be used to understand the geochemical evolution of earth's crust. REEs mobilize during weathering and undergo modifications (non-conservative) in the estuary (Sholkovitz et al., 1994). River sediments generally have a residual fraction and a liable fraction. REEs are sensitive to environmental changes such as redox condition, salinity, chelates, pH adsorption-desorption, complexation, precipitation etc. The metals can be divided into nutrient type and scavenging type according to their absorption capabilities (Chester, 1990). Nutrient-type metals behave similar to nutrients (NO_3, PO_4, and Si), suggesting their regulation through biological process. Scavenging-type elements are reactive and their distribution is determined by their adsorption (hydrolytical and or/ oxidative) or removal onto particulate matter. For the present study, three groups of metals considered are non-transition, transition and rare earth elements, thorium and uranium.

1.2.1 Non-transition elements

The elements representing S and P block are included in the non-transition group. The metal reactivity depends on the ease with which electrons can be removed or their affinity towards electrons. The reactivity of elements in the periodic table decreases from left to right across a period and increases from top to bottom in a group. The group I elements are very reactive, soft, light and easily fusible. These alkali metals lose an electron readily and hence, are very reactive in water. The present study considers Rb and Cs from alkali metals. The alkaline earth (II group) elements posses a property intermediate between alkalis and rare earths metals. They lose two valence electrons to form ions with two plus charge. Beryllium is the least metallic element in the group and tends form covalent bonds in compounds. Alkaline earth metals are less active than the alkali metals. They react readily with halogens to form ionic salts, but react slowly with water. The present study includes Al and Ga from XIII group, representing P block. Aluminum is the third most abundant element in the earth's crust (7.4 %). Its oxide is stable and prevents corrosion, whereas Ga does not have this property. Bauxite (ore of aluminium) contain small amount of gallium. The two metals (tin and lead) in the XIV group of the periodic table are fairly unreactive and form ions with a $^{+}2$ or $^{+}4$. The non-transition elements are generally classified into conservative metals (Rb, Cs and Sr), nutrient and scavenging metals (Be, Ga and Ba), reactive and scavenging metals (Al and Pb) and anthropogenic and redox sensitive metals (Pb).

1.2.2 Transition elements

Transition elements (TEs) comprise of a series that share similar electronic configuration [ns^2 (n-1) $d^{1\text{-}10}$] and hence, similar chemical properties. The transition elements are commonly defined as the 30 elements with atomic numbers 21 to 30, 39 to 48, and 71 to 80. They are called transition elements because they are placed between the most reactive metals on the left and non-metals on the right. They resemble each other in several physical and chemical properties. As with all metals, the transition elements are both ductile and malleable, and conduct electricity and heat. The interesting thing about transition metals is that their valence electrons, or the electrons they use to combine with other elements, are present in more than one shell. This is the reason why they often exhibit several common oxidation states and showing redox nature under oxygen minimum condition / anoxic. The redox process may strongly affect the distribution of metals. The most distinctive manifestation of redox processes are encountered in suboxic and anoxic waters. In such waters, consumption of oxygen during the reminerilisation of organic matter exceeds supply, so that NO_3, Fe/Mn-oxyhydroxides and finally SO_4 are microbiologically reduced to continue this process. Suboxic waters contain neither dissolved oxygen nor dissolved sulphide and are poised by the intermediate electron acceptors (NO_3, Fe/Mn-oxyhydroxides). Anoxic waters are more strongly reducing and sulphide is present. Under these conditions, many metals change their oxidation state, which is mostly accompanied by dramatic change in solubility of metals such as V, Cr, Mn, Fe, Co, Ni, Zn and Mo. For the present study, 15 transition elements were selected on the basis of abundance in nature, toxic effects and environmental interactions.

1.2.3 Rare earth elements (REEs), thorium and uranium

The REEs comprise 15 lanthanide elements (atomic numbers 57 to 71) as well as yttrium (at. no. 39). Because of the unique chemical properties, REEs are very useful in geochemical studies of earth and planetary systems (Goldberg et al., 1963; Taylor and McLennan, 1985; Bwire et al., 2003). They are extremely coherent in chemical behavior and have been subjected to intense investigation in marine geochemistry. All rare-earth elements occur in trivalent state with exception of Ce^{4+} and Eu^{2+}. In lanthanide series, the progressive filling of electron in the shielded inner 4*f* orbital leads to gradual decrease in the ionic radii from La^{3+} to Lu^{3+}, which is called *lanthanide contraction.* With decreasing ionic radii, there is a systematic change in the strength of complexation between REEs and ligands (de Baar et al., 1991; Hemberger et al., 2004). Due to this difference, they are used as tracers in studying fundamental processes that govern the oceanic cycling of REEs. For instance, the heavier lanthanides were predicted to be more strongly complexed in seawater and hence more resistant to scavenging (Michael, 1999). The fractionation between particles and ligands in solution depends on the relative affinities of these phases in the REEs (Turner et al., 1981; Sholkovitz, 1993; Kelly et al., 2004). The most important source of REEs is riverine input. The concentrations of REEs in river waters are significantly higher than seawater (Elderfield et al., 1988). The behaviors of REEs in rivers and estuaries have been used to understand the geochemical exchange between the crust and the ocean (Elderfield et al., 1988). The large-scale removal of light REEs occurs during estuarine mixing. Planktonic uptake, coprecipitation with non hydroxides, and salt-induced coagulation of colloids has been suggested as their removal mechanism (Martin et al., 1976; Feely et al., 1981; Hoyle et al., 1984; Sholkovitz, 1992).

These processes in a way, reduces the effective flux of REEs into the ocean (Martin et al., 1976). The major process that removes metals from water is adsorptive scavenging by sinking particles, which controls the distribution of many reactive elements in the ocean (Dorte and Yoshiyuki, 1998).

The elements Ce and Eu exhibit different oxidation states. Although Ce is well accommodated in the igneous rocks, oxidation of Ce^{3+} to Ce^{4+} proceeds in oxygenated systems. The Ce^{4+} hydrolyzes readily in seawater, but tends to be removed by scavenging. For this reason, Ce is often enriched in some authigenic minerals such as manganese nodules and phosphorites, while it remains depleted in seawater. Eu will be reduced to Eu^{2+} by magmatic processes, which is larger than other REEs (Sun and McDonough, 1989). Anomalous concentrations of Eu are not uncommon in igneous and sedimentary rocks. Eu enrichment has been observed in hydrothermal vents at mid-oceanic ridges (Debra and Peter, 1999). The Ce anomaly due to oxidation–reduction reactions can be evaluated relative to the trivalent neighbors (La and Pr) in the lanthanides series without significant influence of the other processes affecting their oceanic distributions (Grahamand Peter, 2001). In natural waters, the REEs exist in the trivalent state apart from Ce, which is the only REEs with redox transformations (Goldberg et al., 1963; Elderfield, 1988; Pernilla et al., 2008). However, the Ce (III) has a chemistry similar to its trivalent neighbors (La and Nd) and hence, its oxidation to Ce (IV) results in the formation of a less soluble form. The extent to which Ce is fractionated can be quantified by the Ce anomaly, which is a measure of the observed Ce abundance to that expected for trivalent Ce. A value of 1 means that all three REEs have a crust-like composition and that Ce is not fractionated from its trivalent neighbors. By definition, values between 0 and 1 are called negative anomalies while values above 1 are called positive anomalies. Large negative anomalies (0.1-0.5), typical of saturated water indicate the preferential removal of the less soluble Ce^{4+} (Elderfield, 1988; Piepgras and Jacobsen, 1992; Dubinin, 2006; Yoshitaka, 2008). This is an advantage of this element over other transition metals, which are individually affected by the oxidation states. The composition of rocks and minerals is extensively used as an indicator of evolution of the earth (Taylor and McLennan, 1985; Arifudin et al., 2007). The geochemical reactions fractionate REEs at low temperatures in sediment and water (Goldstein and Jacobsen, 1987; Braun et al., 1990; Johan et al., 2000).

Uranium and thorium coming under actinide series are found commonly in environment. In nature, uranium exists as U^{238} (99.284 %), U^{235} (0.711 %) and U^{234} (0.0058%). Uranium decays slowly by emitting an alpha particle. The half-life of uranium-238 is about 4.47 billion years and that of uranium-235 is 704 million years, which make them useful in estimating the age of the Earth (uranium-thorium dating, uranium-lead dating and uranium-uranium dating). Uranium in the ocean is an element which has a long oceanic residence time of more than one million years (Goldberg et al., 1971), probably due to the fact that U^{4+} forms a stable complex $UO_2CO_3^{4-}$ in oxic seawater (Garrels and Christ, 1965). On the other hand, U^{4+} under anoxic condition is unstable and probably exists in the form of hydroxides or oxide (uranite). This suggests that U has no definite sink in oxidizing environment, whereas coastal sediments act as a trap of U (Heye, 1969). Thorium is a natural radioactive metal and is about three times more abundant than U in rocks and soils. Thorium occurs in several minerals, the most common source being thorium phosphate mineral monazite. Th^{232} decays very slowly (its half-life is about three times the age of the earth), but other thorium isotopes occur in uranium's decay chains.

1.3 Previous studies

The continental shelf and coastal region are the most sensitive zone of any country and it is essential to initiate constant monitoring of the region. Metal pollution is one of the major threats to coastal zone worldly. Several studies are reported on the distribution, bioavailability and accumulation of metals in highly contaminated shelf areas and estuaries of temperate regions (Nolting, 1986; Bryan and Langston, 1992; Everaarts and Fischer, 1992), subtropical and tropical regions such as the Mediterranean Sea (Voutsinou-Taliadouri and Satsmadjis, 1983; Catsiki et al., 1991; den Das and Nolting, 1993), Java Sea and adjacent coastal zone (Everaarts, 1989), estuarine and coastal areas of the Gulf of Thailand (Windom et al., 1984; Hungspreugs et al., 1989; Everaarts et al., 1994; Censi et al., 2007), estuarine and coastal regions of China (Zhang and Wang, 2001; Zhang et al., 2002) etc. Studies on the sedimentary environment have established that most of the shale sediments are uniformly enriched in the light rare earth elements (LREEs) relative to the heavy rare earth elements (HREEs), when normalized to chondrite (Haskin and Gehl, 1962; Fleet, 1984). Haskin et al. (1966) and Sholkovitz (1990) reported that shale- normalized terrigenous inputs from land do not display significant Ce anomalies. McLennan (1989) studied about the influence of provenance and sedimentary processes on REEs in the sedimentary rocks. Murray et al. (1991) studied REEs in Japan Sea sediments along with Ce anomalies. Nath et al. (1992) studied REEs patterns of Central Indian basin sediment related to their lithology. Pattan et al. (1995) studied the distribution of major, trace and rare earth elements in surface sediments of the Wharton basin and observed that REEs in this sediment reflect a combination of surface water properties and diagenetic processes. Ross et al. (1995) studied the positive Eu anomalies along Manso

River by REEs normalisation. The REEs enrichment is associated with high pH, while the feldspars and their secondary products are the cause of Eu anomaly. There are environmental studies of similar nature from other regions as well (Araujo et al., 2002; Borrego et al., 2004; Michael and Kamber, 2006; Carman et al., 2007; Marmolejo et al., 2007; Kurian et al., 2008; Ergul et al., 2008).

The chemical oceanographic features of Arabian Sea have been exhaustively studied by Banse (1959), Reddy and Sankaranarayanan (1968), Sen Gupta et al. (1980), Naqvi et al. (1993; 2000), Naqvi and Jayakumar, (2000), Jyothibabu et al. (2008), Thresiamma et al. (2008), and Balachandran et al. (2008 a and 2008 b). The studies by Hashmi et al. (1981) revealed deposition of clay-sized sediments in the nearshore regions by the process of flocculation, which resulted in trapping of coarse particles in the Cochin-Kollam coast. Compared to cross shelf transport, along shelf transport appears to be the more dominant mechanism for sediment transport on the western continental shelf of India (Ramaswamy, 1987). Ramaswamy and Nair (1989) have reported that the anthropogenically-derived pollutants, associated with clay particles discharged from the coast, would tend to remain within the narrow confines of the inner continental shelf. The shoreline along Cochin has been classified under barrier beaches and the changes in morphology in response to different seasons are studied by Prasannakumar and Murthy (1987). Studies on the heavy-mineral suit of the coastal and river sediments of Kerala have the terrain constituted by opaques, horn-blende, hypersthene, tremolite/actinolite, pyroxene, epidote, zieron, silimite, Kyanite, staurolite, and alusite, monazite, rutile, spene, apatite and tourmaline (Reddy and Rao, 1992). They have observed differential wave activity together with static mud suspension at places in the nearshore region.

Recently, there are studies reporting the metal geochemistry in water and sediment in Arabian Sea (Prakash babu and Nath, 2005; Balakrishnan et al., 2005; Laluraj and Nair, 2006; Rejomon et al., 2008). Nath et al. (1997) studied the trace and rare earth elemental variation in Arabian Sea across the oxygen minimum zone (OMZ). They analyzed sediment samples beneath the intense OMZ and away from the OMZ and found that Ce anomaly showed not much significant differences between these two regions. However, earlier reports on geochemistry of sediments along the central southwest coast of India are limited to Murthy et al. (1973), Rao et al. (1974), Rajamani (1994), Nath et al. (2000), Balachandran et al. (2005) and Laluraj and Nair (2006) with only very few samples to represent the environment. The work of Nath et al. (2000) furnishes an insight to the provenance of rare-earth elements in the fluvial fraction (< 4 mm) that also date back to one set of sampling during 1981. Inadequacies in all the above studies have been their proper addressing of the influence of oceanographic and sedimentary processes to the metal geochemistry. Such studies require increased density of sampling covering seasonal signals, which play an important role when coastal regions are considered.

A number of multidisciplinary studies have been undertaken in the Cochin estuary during past several decades. The reduction in the carrying capacity of the backwaters, disruption in the life cycle of organisms, destruction of natural habitats, accumulation of pollutants, salt water intrusion, symptoms of eutrophication, over exploitation and dwindling of resources etc. stress the need for the conservation of the ecosystem. Some of the important works worth mentioning in this context (Ramamritham and Jayaraman, 1963; Murthy and Veerayya, 1972; Venugopal et al., 1980; Nair et al., 1990; Nair et al., 1994; Thresiamma et al., 1998; Sheeba, 2000;

Srinivas, 2000; Unnikrishnan and Nair, 2004; Balachandran et al., 2005; Laluraj et al., 2005; Geetha et al., 2006; Srinivas and Dinesh Kumar, 2006; Babu et al., 2006; Kalesh and Nair, 2006; Laluraj and Girish, 2006; Laluraj et al., 2006a). Partitioning of marine and estuarine sediments of this region has been carried out by Shibu et al. (1990); Nair, (1992), Rajamani, (1994), Shibu et al. (1995). The levels of trace metals in the water and particulate matter of Cochin estuary are reported by Nair et al. (1990, 1991), Suraj et al., (1996), Balachandran et al. (2005). Balachandran et al. (2006) has studied clay mineralogy of Periyar river sediments and their role in the uptake of metals. Nath et al. (2000) studied the provenance, weathering and distribution of rare earths, major and trace elements of the fine grained fraction of the bed load sediments from Cochin estuary and adjoining coastal region. They found salt induced adsoption/desoption mechanism for trace and rare-earth elements in Cochin estuary.

Being one of the largest sources of freshwater and continentally derived metals to the southeastern Arabian Sea, the Cochin estuary exhibits a range of hydrographical and geochemical properties, which modify the biogeochemical cycles of metals. The recent studies on the physical, sedimentological, biological, and chemical parameters have been discussed in detail about the different processes operating in the Cochin estuary (Laluraj et al., 2007; Narayana et al., 2007; Priju and Narayana, 2007; Renjith and Chandramohanakumar, 2007; Laluraj et al., 2008; Martin et al., 2008; Balachandran et al., 2008c; Padmalal et al., 2008).

1.4 Aim and scope of the present study

The basic requirement to characterise an environment is to synthesize systematic data at close grids of the region covering different seasons and to compare the results with existing processes in the region. An integrated study of this dimension has not been carried out so far along the southwest coast of India, which has been taken as the basic objective of this study. Eventhough information is available along the continental shelf of India, these data are collected from limited locations without considering the seasonal variability or frequency of more than one degree and well beyond in areas with depths > 30 meters. Considering the global demands of REEs as a mineral resource and its high abundance along the southwest coast of India, this region especially demands a comprehensive and systematic exploration to unravel the geochemical distribution of various elements. Similarly, the geochemical characteristics of the largest estuarine complex in the study region (Cochin estuary) will also compliment the above endeavor. With a view to delineate environmental changes and to evaluate the sediment geochemistry of the region, a detailed study on the non-transition, transition and rare-earth elements including uranium and thorium, and the parameters which affecting their adsorption/desorption mechanism have been undertaken along the continental shelf of Kerala and the Cochin estuarine system.

One of the greatest coincidence of the present study was that the two exhaustive sample collections were interspaced by a Catastrophe. It was during this period (December 2004) that the southern tip of Indonesia experienced a submarine earthquake (Mw 9.3) causing a tsunami, which was among the deadliest disasters in modem history (Laluraj et al., 2006b). This tsunami devastated the shores of Indonesia and several southeast Asian countries including India. Massive damage to the livings and non-living was inflicted along the coastal regions of Tamil Nadu, Andhra Pradesh and Orissa (east coast of India) and, Kamataka and Kerala (west coast of India) following the waves generated by the tsunami (Reddy et al., 2005). Cochin Estuary also experienced the ferocity of this tsunami (Laluraj et al., 2007). It has been estimated that the tsunami has caused high velocity waves (~ 700 km/hr) along the west coast of India, causing an elevation of about 2 m at Goa. Although there has been a different interpretation on the impact of tsunami on the oceanic realm, there were severe limitations in comparing the post tsunami scenario features with it previous conditions. The present study therefore, form an unambiguous analysis of the mineralogy and geochemistry of sediments along the southwest coast of India during the two periods of prior (July 2004) and after (March 2005) tsunami. A similar attempt was also possible to assess the impacts of tsunami on Cochin estuary. Hence, this study has gained invaluable significance as it can provide one of the realistic views on the impact that the tsunami has caused on the sedimentary environment along the southwest coast of India.

1.4.1 Objectives of the study

1. Study the seasonal variability of physio-chemical and sedimental characteristics along the shelf of Kerala and Cochin estuarine system.
2. Study the influence of seasonality and sediment texture on the geochemical distribution of elements along the shelf of Kerala and Cochin estuarine system.
3. Decipher the seasonal distribution of non-transition elements in sediments along the two environments.
4. Evaluate the geochemical index of transition elements in the two sub environments.
5. Study the seasonal variability of the rare earth elements along the coastal belt of Kerala in comparison to Cochin estuarine system.
6. Estimate the seasonal variations in the enrichment and excess of non-transition, transition and rare earth elements in sediments along the two environmental sections.

7. Estimation of the levels of metals such as Ga, Pr, Dy, Ho, Er and Tm in the Cochin estuary.
8. Study on the sedimentary geochemical interactions using statistical tool such as linear and multiple regressions.
9. Model representation on the geochemical distribution of transition metals along the shelf and estuary during different seasons.
10. Evaluate the impact of tsunami on the texture and composition of the sediments along the shelf of Kerala and Cochin Estuary.
11. Illustration of possible mechanisms on the accumulation of metals in sediments of the two environments.
12. Comparison of elemental enrichment in sediments along the shelf and Cochin Estuary.

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Chapter 2

Materials and Methods

Contents

2.1 Description of study area

The study region covers the continental shelf of the south east Arabian Sea and the Cochin estuarine system. The biogeochemical data from these regions were collected during different seasons. The western continental shelf of India, experiences intense upwelling and is also well known for the occurrence of mud banks during peak monsoon (Fieux, 1977; Nair et al., 1993; Balachandran, 2004). Since the Cochin estuary is moderately polluted due to increased anthropogenic activities, the export of materials is expected to influence the geochemical distribution of elements along the continental shelf of India (Balachandran et al., 2005). Thus, there is a need to identify the seasonal impact of estuary on the environmental changes of the continental shelf. It is to be mentioned here that west coast of India experienced a devastating Tsunami in December 2004. A significant change along the west coast of India has been reported following the tsunami (Reddy et al., 2005). Cochin Estuary has also experienced the ferocity of this tsunami (Laluraj et al., 2007). Hence, an attempt has been made here to assess the impacts of tsunami on the biogeochemical properties of sediments along the southwest coast of India and also in the Cochin Estuary.

2.1.1 Arabian Sea

The Arabian Sea covers an area of about 3,863,000 km^2 and is surrounded by arid landmasses to the west, north and east (India). The Arabian Sea has a negative water balance, since the evaporation far exceeds precipitation and run off. The Arabian Sea experiences extreme atmospheric forcing that leads to the observed seasonal variability, greater than in any other oceans. The seasonally reversing monsoon winds bring rain to the Indian subcontinent and cause upwelling along the continental margins (Fieux, 1977; Saher et al., 2007). As a consequence of the reversing winds, the surface circulation along the western and eastern costs of India also undergoes a reversal. Thus, surface currents are southerly from April to September, which weaken significantly after the peak monsoon rains. The southerly coastal current (Banse, 1968) of about 150 km wide is observed at 50 m depth along the continental shelf (Shetye et al., 1990; Shankar et al., 2005). Intense coastal upwelling occurs during the southwest monsoon to the south of 15°N. From November to February (northeast monsoon), the coastal current flows northward, when the currents reversed to northerly direction (Figure 2.1). However, an undercurrent of about 40 km wide at 100-250 m (Shetye et al., 1990) from the Bay of Bengal is found to prevail during both the SW and NE monsoons (Sarma et al., 1986; Pankajakshan and Rama Raju, 1987).

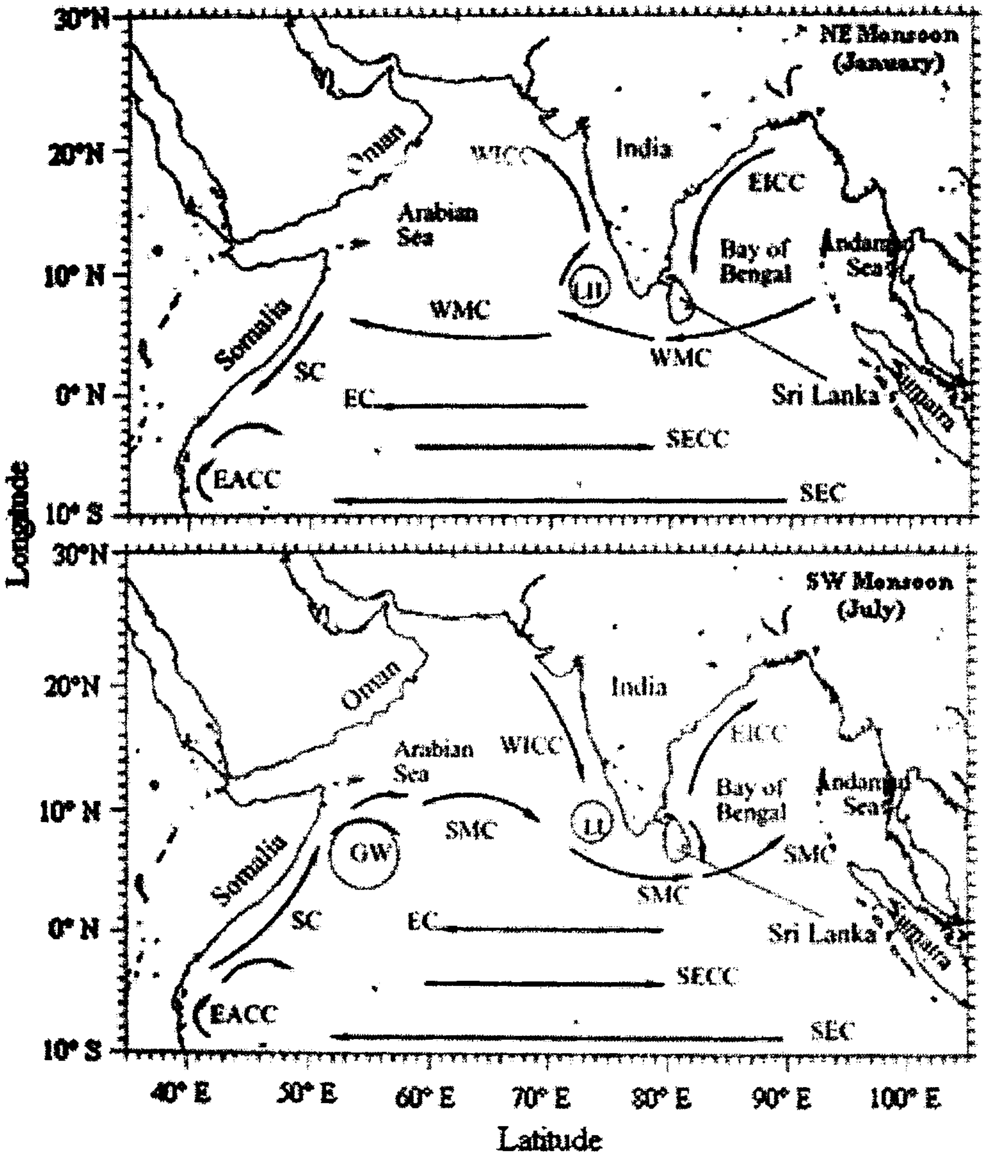

Figure 2.1. Surface circulation in the Northern Indian Ocean during NE and SW monsoon (Schematics from Shankar, et al., 2002).

2.1.2 Western continental shelf of India

The west coast of India has a wide continental shelf in the north, which becomes narrower towards south. The width of the continental shelf is about 130 km off Ratnagiri and narrows down to 80 km off Cochin (Rao and Rao, 1995). It is again wider (120 km) at the southern tip of India, off Cape Comorin. Accordingly, the inner shelf extends upto 60 m water depth in the northern part and narrows down to 30 m water depth in the southern part (off Cochin). The shelf break occurs at about 120 m in the northern part and at about 80 m in the southern part (Thamban, 1998).

2.1.3 Continental shelf of Kerala

Kerala is in the southernmost part of India bordered on the east by the Western Ghats and on the west by the Arabian Sea. The Kerala coast is known for the presence of lateritic cliffs, rocky promontories, offshore stacks, long beaches, dunes, estuaries, lagoons, spit bars and formation of mudbanks etc (Mathew and Baba, 1995; Soman, 2002). The sand ridges, extensive lagoons and barrier islands (700 km landlocked islands) are indicative of a dynamic coast. During the monsoon, the predominant approaching southwest wave results in northerly littoral drift with varying speed. The coastline seems to be highly unstable due to both emergence and submergence. Although 60% of the 720 km coastline is protected by seawall, the remaining coast is undergoing severe erosion. Maximum loss of material has been reported along the southern sections. Some parts of Kerala coast are known for rich heavy mineral deposits. The above characteristics of coastal geomorphology have provided an ecosystem, which supports fisheries.

The continental shelf of Kerala is fairly straight as a result of faulting during Late Pliocene (Krishnan, 1968). As many as 41 westearn-flowing streams cut across the coastal belt and flow to the sea through numerous lagoons and estuaries. The average annual rainfall exceeds 300 cm, most of which takes place during the south-west monsoon (Ananthakrishnan et al., 1979). During the SW monsoon (June-September) the rainfall is high and the rivers carry maximum sediment load to the continental shelf. Along the shelf between Mangalore and Quilon, the nature of bottom about 3.5 to 18 m depth is largely muddy. During monsoon, because of the wave actions and rip currents, the fine mud particles get churned up into a thick suspension (Udaya Varma and Kurup, 1969), in which, the wave energy gets consistently absorbed. This annually occurring feature has a semi-circular shape and is unique in many ways. Mudbanks, as they appear and disappear in the sea, have been considered as unique formations experienced only along Kerala coast. The coastal sediments of Kerala support mud suspensions, as they appear due to sediments brought by rivers, wave action, nearshore currents and considerable freshening of sea water. Mudbanks are well known for their fishery during the monsoon months. The recent finding that the formation of mud banks are closely linked to the subterranean flows from the adjacent Vembanad Lake (Cochin estuarine system) is quite invoking (Balachandran, 2004) and hence, further studies exploring the possible coupling between these regions have emerged great significance.

Two distinct sediment types occur on the continental shelf, modern elastic clays on the inner shelf and relict sandy sediments on the outer shelf. The continental slope is covered by silty clays dominant in terrigenous and biogenic components. The Holocene carbonate sands are seen between Saurashtra and Mangalore and terrigenous sands from Mangalore to Cochin (Nair and Pylee, 1968). The surficial sediments of this region can be further divided into terrigenous, biogenic and chemogenic sediments (Rao and

Wagle, 1997). Terrigenous sediments mostly occur as sands in the nearshore (upto 10-12 m water depth) followed by a zone of silty clays on the inner shelf between Saurashtra and Quillon. Biogenic sediments are again predominant on the continental shelf between Quillon and Cape Comorin (Thamban, 1998). Chemogenic sediments are phosphorites and authigenic green clays.

2.1.4 Cochin estuarine system

The Cochin estuarine system (9°30'–10°10'N and 76°15'–76°25'E), extending from Azhikode in the north to Alleppey in the south, form a complex system of shallow network of canals spread over more than 256 km^2 (Qasim, 2003). It has two openings to Arabian Sea, one at Cochin (width 450 m) and another at Azhikode.

The Cochin estuarine system (the seaward extension of Vembanad Lake) is the largest tropical estuarine system along the west coast of India. The total rainfall over the region is about 320 cm, of which, nearly 75% occurs during June to September. During peak monsoon (July/August), 4-5 cm of rainfall can occur within a few hours. The onset of southwest monsoon and its duration may, however, vary from year to year. Normally, it lasts from June to September, followed by winter monsoon (November-January) and premonsoon (February-May). Several rivers and tributaries are debouching into the Cochin estuary, which varies drastically with season. Of the total river discharge, about 33 % of the discharge into the Cochin estuary is from Periyar. Percentage contribution from Muvattupuzha, Achenkovil, Pampa, Meenachil and Manimala rivers were 24.2, 5.8, 19.7, 8.3 and 8.8 respectively (Srinivas, 2000). During the lean period January to May, Muvattupuzha River maintains a constant flow probably due to tailrace water from the Idukki hydroelectric power station.

The tides in the estuary is of a mixed predominantly semi-diurnal with a maximum range of about 1 m and the tidal influence is felt upto the entire length of the estuary (Qasim, 2003). The salinity gradient is in agreement with stratification in the estuary. During monsoon, the stratification is observed in the lower estuary, which progressively changes to partly mixed (postmonsoon) and completely mixed (premonsoon). During monsoon, heavy silting occurs in the estuary due to the supply of finer materials. The estuarine sediments are comprised of terrigenous matter brought from the rivers as well as the materials imported from the sea during the post and premonsoon through tidal currents.

The peculiar topography (oxbow shape) of the estuary has a strong bearing on the tidal modulations and flushing characteristics, which make this estuary unique in its water balance. During southwest monsoon (June-September), the estuary receives enhanced transport of alluvium which is accumulated to bed sediment during winter monsoon (November-January). The remaining period favors silting, modified by tidal activity. Due to heavy industrialization, the northern part of the estuary has been identified as severely polluted with respect to trace metals (Nair et al., 1990). The hinterland is composed of Archean crystalline rocks, tertiary sediments, and rocks with laterite capping where the sediments experience extreme chemical weathering (Mallik et al., 1987; Nath et al., 2000). The basement of the limnetic and coastal terrains are made up of charnokite, underlined by a thick succession of Tertiary and Quaternary sediments comprised of sand, silt, clay, peat and shell beds (Nair and Rao, 1980). The estuarine sediments are mostly a mixture of clay, silt and sand. The northern part of the lake is covered with clayey sand and silty sand, the central part with clayey sand

and sandy silt, and the southern part are covered with silty sand and clayey silt (Narayana et al., 2002; Laluraj et al., 2008).

2.2 Sampling

The present study focuses on the southwestern continental shelf of India in the Arabian Sea between 8.5°-13°N and 73.8°-77°E and the Cochin estuarine system, one of the largest wetland ecosystems along the west coast of India. The sample collections from these regions were carried out during same period to understand the impact of the anthropogenically polluted estuary on the southwestern continental shelf. The geochemical samples from the continental shelf region were collected during two cruises under the project "Studies on the nearshore dynamics of southwest coast of India". The samples from the Cochin estuary were also collected during the same period under the programme "Ecosystem modeling of Cochin backwaters". The southwest coast of India experiences strong upwelling during summer monsoon period along with the formation of mud banks. This period also brings in a lot of biogeochemical changes at the coastal and continental shelf induced by the rivers. Accordingly, the strategy followed was to evaluate the geochemical composition of elements distributed over the environments during summer monsoon followed by their re-distribution during the premonsoon season.

The surface sediment samples from the western Indian continental shelf and Cochin Estuary were collected during monsoon (July, 2004) and premonsoon (March, 2005) periods. The details of sampling location are given in Table 2.1. For shelf studies, surface sediments were collected from 8 transects along the continental shelf of Kerala between Thiruvananthapuram and Mangalore (Figure 2.2). Bottom water samples collected from each station using onboard CTD probe Niskin samplers and were analyzed for dissolved oxygen following standard procedure (Grasshoff, 1983). The temperature and salinity data were collected from the CTD probe records. For the estuarine studies, nine samples were collected from different regions of Cochin Estuary; representing three stations each from northern, central and southern zones during both seasons (Table 2.1; Figure 2.3).

Table 2.1. Sampling locations and selected depths for the present study.

Continental shelf of Kerala				
Transect	Latitude (°N)	Longitude range (°E)	Sampling depths (m)	Location zone
Manglore	13°00′	74°40′24″ – 73°55′52″	20,50,100,200	Northern
Kannoore	12°00′	75°05′56″ – 74°25′23″	20,50,100,200	Northern
Baypore	11°10′01″	75°40′33″ – 74°59′06″	20,50,75,100,150,200	Northern
Ponnani	11°00′	75°45′00″ – 75°07′05″	20,50,100,200	Northern
Cochin	10°00′	76°02′20″ – 75°35′24″	20,50,75,100,150,200	Southern
Alleppy	09°19′59″	76°14′49″ – 75°50′24″	20,50,75,100,150,200	Southern
Kollam	09°00′	76°25′19″ – 75°56′34″	20,50,100,200	Southern
Trivandrum	08°30′	76°48′14″ – 76°21′07″	20,50,100,200	Southern

Cochin estuarine system				
Stations	Latitude (°N)	Longitude (°E)	Station depth (m)	Location zone
1	9°58′05″	76°14′05″	3.0	Central
2	10°01′00″	76°15′11″	4.5	Northern
3	10°03′05″	76°15′12″	2.5	Northern
4	10°02′15″	76°15′01″	ND	Northern
5	9°55′06″	76°18′06″	1.5	Central
6	9°52′01″	76°19′07″	ND	Central
7	9°47′13″	76°21′09″	5.5	Southern
8	9°45′03″	76°22′11″	4.0	Southern
9	9°40′16″	76°23′12″	8.5	Southern

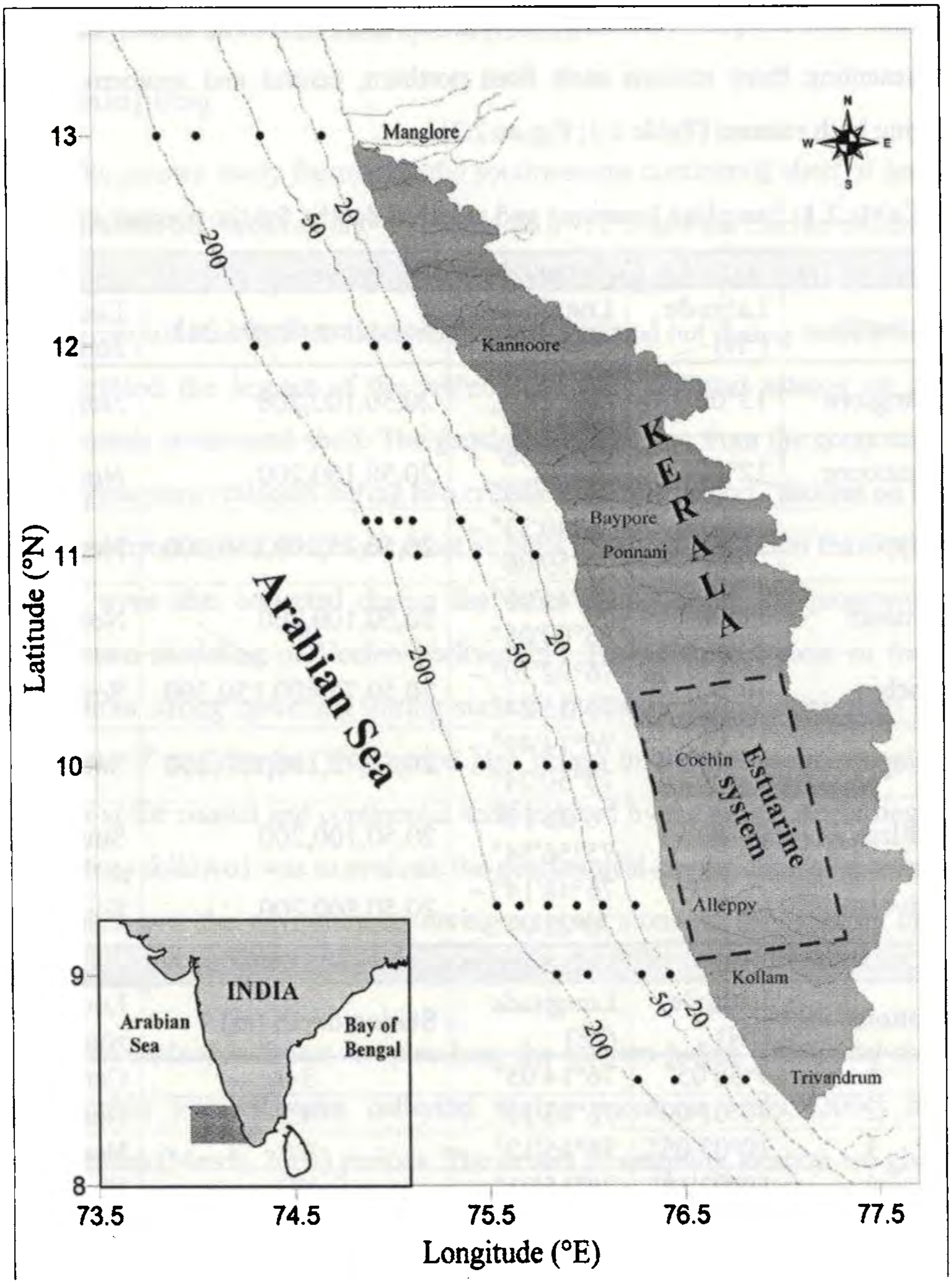

Figure 2.2. Study area showing station locations along the continental shelf of Kerala. (Bathymetric depths given in meters)

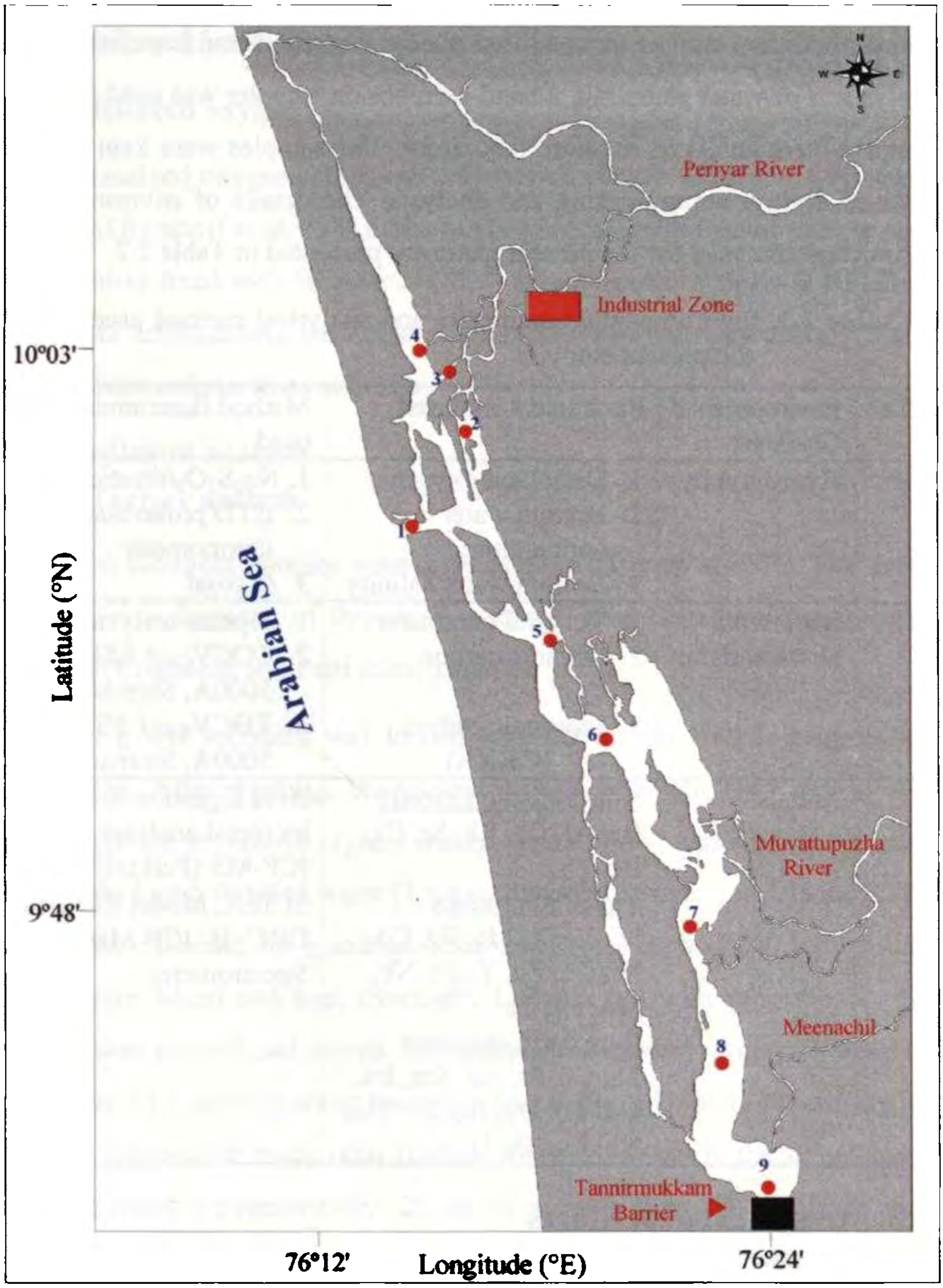

Figure 2.3. Study area showing station locations in the Cochin estuary.

The sediments were collected using Van Veen Grab and the undisturbed portion was scooped into plastic containers and kept frozen till analysis. For water sampling, a hand-own Niskin sampler was used and the samples were analyzed in shore laboratory. The samples were kept frozen prior to drying, homogenizing and analysis. The details of environmental parameters analysed for the present study are presented in Table 2.2.

Table 2.2. Environmental parameters and analytical method used for the present study.

Sl.no	Environmental Character	Parameters analysed	Method /Instrument used
1	Hydrography	1. Dissolved oxygen 2. Bottom water temperature 3. Bottom water salinity	1. $Na_2S_2O_3$/titration 2. CTD probe/bucket thermometer 3. Autosal
2	Sediment characteristic	1. Textural parameter 2. Organic carbon 3. Inorganic carbon ($CaCO_3$)	1. Pipette analysis 2. TOCV$_{CHS}$(SSM-5000A, Shimadzu) 3. TOCV$_{CHS}$ (SSM-5000A, Shimadzu)
3	Metals	Non-transition metals Be, Al, Ga, Rb, Sr, Cs, Ba, Pb Transition metals Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Hf, Ta Rare earth elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U	Acid digestion followed by metal analysis using ICP-MS (PerkinElmer SCIEX, Model ELAN® DRC- II- ICP-Mass Spectrometer

2.3 Analytical procedures

2.3.1 Salinity and temperature

Salinity and bottom temperature from shelf zone were analysed using the Conductivity-Temperature- Depth profiler (CTD, Seabird Electronics, accuracy ± 0.001°C) available onboard the research vessel. Salinity from estuary was estimated using a pre calibrated Autosal by standard sea water.

2.3.2 Dissolved oxygen

Dissolved oxygen estimation was carried out by Winkler's titrimetric method (Grasshoff et.al, 1983). The oxygen present in the water sample was immediately fixed with Winkler A (Mn^{2+} solution) and Winkler-B (alkaline KI). After acidification, the iodine released was estimated by using sodium thiosulphate and starch as indicator.

2.3.3 Sediment analysis

2.3.3.1 Texture analysis

The sediment samples were dried in a hot air oven at 95°C. The sand, silt and clay fractions of this dried material were determined by pipette analysis (Krumbein and Petti John, 1938).

40 g wet sediment was treated with 10 ml 1N HCl to remove all carbonates. After washing, the residue was treated with H_2O_2 (15%) and kept overnight to remove organic matter. The solution was slightly warmed and washed with distilled water (3 times) and kept in oven for drying. To 10 g of dried sediment, 7.5 g sodium hexa metaphosphate and 200 ml distilled water were added and kept overnight. Using a rod with rubber cork, the sample was pressed and stirred. The sample was passed through a sieve of mesh size 63 μ pouring water through a funnel into a 1000 ml measuring jar and the volume was made upto 1000ml. The residue left in the sieve (sand) was estimated gravimetrically. 20 ml of sample from 10 cm depth was pipetted out, dried and weighed as clay. The balance in the fraction after subtracting the sand and clay was taken as silt. After oven drying, the

weight of material in the beaker was calculated. The percentages of sand, clay and silt were calculated using the formula:

$$\text{Sand (\%)} = \frac{\text{(Final wt.of dish - Initial wt. of dish)}}{10} \times 100$$

$$\text{Clay (\%)} = \frac{\text{(Final wt.of beaker - Initial wt. of beaker- 0.15)}}{20 \times 10} \times 1000 \times 100$$

$$\text{Silt (\%)} = 100\text{- (sand \% + clay \%).}$$

The precision of the analysis was calculated by duplicate measurement.

2.3.3.2 Inorganic carbon ($CaCO_3$) and organic carbon analysis

The sediment samples were dried in a hot oven (60°C) and powdered using a mortar. The analysis was carried out using total organic carbon analyser (TOC-V series SSM-5000A from Shimadzu) at National Centre for Antarctic and Ocean Research (NCAOR), Goa. Glucose and sodium carbonate were used as the organic carbon and $CaCO_3$ standards respectively. For the measurement of organic carbon, each sediment sample was treated with 2M hydrochloric acid to remove inorganic fraction, dried in oven and powdered well. About 100 mg of the treated sample was placed in a ceramic sample boat which was then transferred into a 900°C catalytic (mixture of cobalt oxide and platinum) combustion chamber inside the SSM-5000A and oxidized into CO_2 in presence of oxygen. The CO_2 was then carried by O_2 carrier gas into a short cell of a non-dispersive infrared (NDIR) detector in the $TOCV_{CSH}$ and measured. For measurement of $CaCO_3$, each untreated sediment sample (about 100 mg) was placed in a ceramic sample boat, 0.5 ml 85% phosphoric acid was added to the sample using a dispenser before the sample boat was transferred into a 200°C combustion chamber, to produce CO_2 from carbonates, which was measured using the NDIR detector in the $TOCV_{CSH}$. For each standard and sample, the measurements were repeated at least two times to achieve coefficient of variation less than 2% or standard deviation of 0.1. The average results, % coefficient variation and standard deviation were calculated.

2.3.3.3 Analysis of metals

The metals analyzed during the present study are classified into three groups such as non-transition, transition and rare earth elements. The details of elements studied are given in Table 2.2. The sediment samples were dried in a hot air oven at 60°C. These powdered samples were measured for the metal contents after acid digestion and subsequent analysis in Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at National Geophysical Research Institute (NGRI), Hyderabad, India.

ICP-MS system outline

ICP-MS instrument consists of 3 basic units and they are:-

1. Conventional argon ICP operating at temperature 6000-9000K with nebulizer, spray chamber, work coil and associated power supplies.
2. A conventional quadrupole mass spectrometer and data collection electronics, which permit rapid scanning of selected mass range between 0-300 amu.
3. An interface unit consisting of two water coiled nickel cones, each containing a small orifice at the centre, which allow sampling of plasma gases and transfer ion beam into the small spectrometer.

Samples in the form of solution are introduced through the peristaltic pump at a rate of about 1ml/min into the central region of the plasma at atmospheric pressure with the help of a nebulizer and water-cooled spray chamber system. The sample is heated to 9000K in plasma, resulting in a series of processes involving de-solvation, vaporization, dissociation, atomization and ionization, in analytical zone of ICP (Figure 2.4). At this temperature chemical interference effects are insignificant.

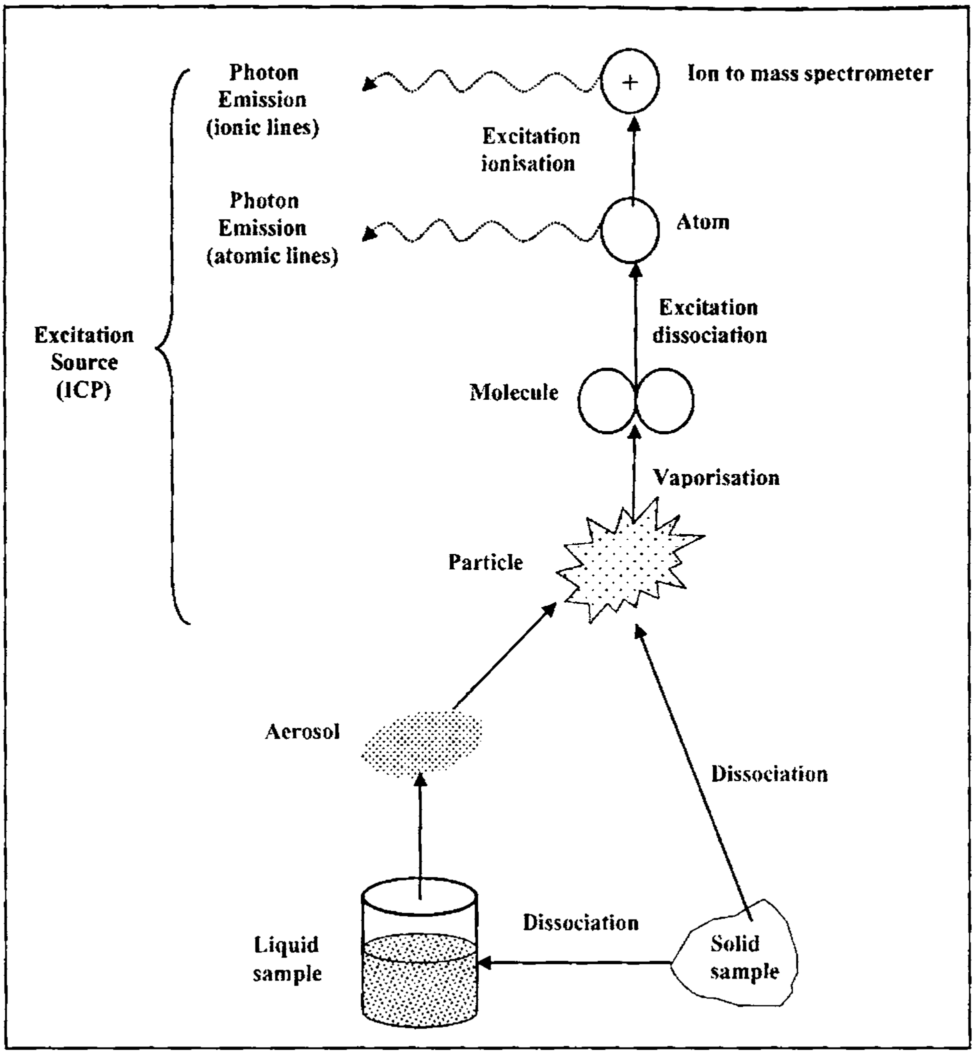

Figure 2.4. Schematic representation of sequence of sample introduction to the formation of ions in ICP-MS.

54 elements are expected to ionize with an efficiency of 90% or more. A fraction of positively charged ions produced in plasma is transported through a narrow aperture of samples empanels at supersonic by skimmer cone.

Sample digestion and internal standard rhodium

Standard and sediment samples were dissolved following acid dissolution procedure (Balaram and Rao, 2002). In this procedure, 10 ml of acid mixture containing (6:3:1) parts of HF, HNO_3 and $HClO_4$ was added to a 50 mg of samples and standards in the clean dry teflon beakers and evaporated to dryness in the fuming hood. After 30 minutes, 2ml of concentrated HCl was added to remove any black particles, if present in the sample. The addition of acid mixture was repeated to ensure the complete dissolution of samples, and was kept on sand bath till it was evaporated to dryness. After cooling, 5 ml of 1 ppm Rh solution and 20 of ml 1:1 HNO_3 were added and made upto 250 ml. In all cases, clear solutions were obtained. The solutions were then analyzed in an ICP-MS for multi elemental analysis. A total of 105 sediment samples in triplicate were analyzed along with equal number of blanks and certified marine standards.

Accuracy and reproducibility

Certified Marine Reference Material (MAG-1) obtained from the US Geological Survey was used for calibrating the geochemical analyses. Analysis of standard has yielded very good results in comparison with the certified values for MAG-1. The elements Ba, Ce, Co, Cu, Cs, Dy, Eu, Fe, Ga, Ho, La, Lu, Mn, Nb, Ni, Pr, Rb, Sm, Sr, Ta, Th, Tm, V, Yb and U showed excellent results with accuracy better than 99% (Table 2.3). The elements such as Cr, Er, Hf, Gd, Pb, Sc, Tb and Zr showed an accuracy of > 98% and Be &Al showed accuracy > 95% (Table 2.3). The reproducibility of the analysis was checked by analysing three MAG-1 sediments and the values are given in Table 2.3.

Table 2.3. Percentage accuracy of the metals analysis and PAAS values [(all in ppm, except Al, Mn and Fe (% dry weight)].

Metal	STD	Mean	% variation	Analysis-1	Analysis-2	Analysis-3	PAAS
Be	3.20	3.4	5.0	3.22	3.26	3.60	----
Al (%)	16.4	16.7	2.2	16.66	16.72	16.86	10.0
Sc	17.2	16.9	1.6	17.29	16.99	16.47	16
V	140	141.5	1.0	140.96	137.86	145.68	150
Cr	97	99.3	2.3	98.35	99.54	99.91	110
Mn(%)	0.10	0.10	0.0	0.10	0.10	0.10	0.085
Fe(%)	6.8	6.86	0.9	6.78	6.86	6.96	4.55
Co	20.4	20.4	0.0	20.20	20.78	20.17	23
Ni	53	53.3	0.1	52.95	52.87	54.00	55
Cu	30	30.1	0.3	30.12	30.18	29.97	50
Zn	130	129.9	0.1	130.04	129.46	130.07	85
Ga	20.4	20.4	0.0	20.57	20.68	19.96	20
Rb	149	149.1	0.0	149.57	149.63	147.92	160
Sr	146	145.1	0.6	146.07	145.04	144.10	200
Y	28	27.9	0.0	28.06	28.16	27.75	----
Zr	126	124.4	1.3	125.21	124.52	123.34	210
Nb	12	11.9	1.0	11.94	11.81	11.89	19
Mo	1.6	1.57	1.8	1.64	1.53	1.53	1
Cs	8.6	8.6	0.1	8.57	8.54	8.65	15
Ba	479	481.0	0.4	481.49	473.57	488.00	650
La	43	43.1	0.1	42.97	43.23	42.94	38.2
Ce	88	87.9	0.2	88.19	87.58	87.77	79.6
Pr	9.3	9.31	0.1	9.29	9.38	9.26	8.83
Nd	38	38.1	0.2	38.26	37.62	38.32	33.9
Sm	7.5	7.51	0.0	7.51	7.53	7.46	5.55
Eu	1.55	1.55	0.0	1.55	1.54	1.55	1.08
Gd	5.8	5.91	1.9	5.85	5.95	5.95	4.66
Tb	0.96	0.96	0.0	0.95	0.95	0.98	0.774
Dy	5.2	5.19	0.2	5.17	5.15	5.24	4.68
Ho	1.02	1.02	0.0	1.02	1.00	1.05	0.991
Er	3.0	2.95	1.6	2.97	2.90	2.97	2.85
Tm	0.43	0.43	0.0	0.43	0.43	0.43	0.405
Yb	2.6	2.59	0.4	2.59	2.58	2.59	2.82
Lu	0.40	0.40	0.0	0.40	0.40	0.41	0.433
Hf	3.7	3.64	1.6	3.74	3.60	3.60	5
Ta	1.1	1.09	0.9	1.11	1.08	1.08	-----
Pb	24	24.4	1.7	24.31	24.31	24.57	20
Th	11.9	12.1	1.4	11.82	12.60	11.79	14.6
U	2.7	2.70	0.0	2.71	2.68	2.71	3.1

2.4 Data analysis

The environmental data collected from the present study were used to differentiate the seasonal changes of different parameters along the study region. This was mainly achieved using different environmental techniques such as elemental normalisation, enrichment factor, elemental excess, cerium and europium anomalies and authigenic uranium. The details of each parameters and their significance are given below.

2.4.1 Elemental normalisation

The significance of this normalization is to check the similarity of pattern for many elements supporting homogeneity (Taylor and McLennan, 1985), which is caused by mixing of materials derived from different sources, with different age and rock types, during weathering, transport and deposition (McLennan 1989; Dupre et. al, 1996; Nath et.al, 2000). Elements are normalized with Past Archean Australian Shale Reference Material values (PAAS) for plotting shale normalized patterns. The values of PAAS are presented in Table 2.3. Normalization means the concentration of each element in the sample is divided by the concentration of the same element in the reference material. The plot is usually given as logarithm of the normalized abundance versus atomic number. The chondrite values are taken to represent cosmic abundance of the rare earths, while shale values are taken to represent crustal abundances (Gromet et al., 1984).

2.4.2 Enrichment factor

Enrichment factor is used for the determination of level of contamination of sediments. Several methods for normalization are possible, ranging from the use of simple metal/normalizer ratios to more complex methods based on regression analysis (Rowlatt and Lovell, 1994). The present study normalizes metal concentration as ratios to another constituent of the sediment. The constituent chosen for normalization should be associated with finer particles (related to grain size) and its concentration should not be anthropogenically altered (Ackerman, 1980). Aluminium is a conservative element and a major constituent of clay minerals (Rubio et. al, 2000). Iron is the next most consistent element and has been used as a grain size proxy by number of authors working on marine and estuarine sediments (Ackerman, 1980, Lee et al, 1998, Rubio et al, 2000). The enrichment factor is calculated using the formula

$$\mathrm{EF} = \frac{[\text{Concentration of metal/Aluminium}]\text{ in sediments}}{[\text{Concentration of metal/Aluminium}]\text{ in PAAS}} \quad \text{and}$$

$$\mathrm{EF} = \frac{[\text{Concentration of metal/iron}]\text{ in sediments}}{[\text{Concentration of metal/iron}]\text{ in PAAS}}$$

2.4.3 Elemental excess

Aluminum or titanium normalization is generally used to correct for terrestrial influence in marine sediments (Bischoff et al., 1979; Nath et al., 1989, Murray et al., 1993). In the present study, elemental concentration in excess (El_{ex}), which can be supplied through shale like terrigenous particles are determined using the formula

$$\mathrm{El}_{ex} = \mathrm{El}_{total} - [\mathrm{Al}_{sample} \times (\mathrm{El/Al})_{PAAS}]$$

This equation subtracts the amount of an element that has structurally bound to detrital component from the total concentration of that element in the sediment. (Murray et al., 1993).

2.4.4 Ce and Eu anomalies

Eu and Ce anomaly, if present, can also be detected from this normalization plot. Hence, it is important to normalize the REEs patterns either with chondrite or average shale values. Ce anomaly is represented as Ce/Ce*, where Ce is the concentration of Ce in the sediment normalized with shale value ($Ce_{sediment}/Ce_{PAAS}$) and Ce* is a predicted value obtained by linear interpolation of La/ La* and Pr/Pr*.

$$Ce^* = \frac{[(La_{sediment}/La_{PAAS}) + (Pr_{sediment}/Pr_{PAAS})]}{2}$$

The values above 1 indicate positive Ce anomaly and values less than 1 indicate a negative Ce anomaly. Value close to 1 indicates no anomaly ie, Ce is not fractionated relative to the crustal composition.

Similarly, Eu anomaly is represented as Eu/Eu*, where Eu is the concentration in sediments normalized with shale value ($Eu_{sediment}/Eu_{PAAS}$) and Eu* is a predicted value obtained by linear interpolation of Sm/Sm* and Gd/Gd*.

$$Eu^* = \frac{[(Sm_{sediment}/Sm_{PAAS}) + (Gd_{sediment}/Gd_{PAAS})]}{2}$$

Value greater than 1 and less than 1 indicate positive and negative anomalies respectively. A value of one indicated no anomaly.

2.4.5 Authigenic uranium

Authigenic uranium, a parameter based on U and Th concentrations has been suggested as an index of bottom water anoxia and ancient sedimentary sequences (Nath et al, 1997; Wignall and Myers, 1988). It is calculated using the formula,

authigenic U= [Total (U)- Th/3].

Nath et al, (1997) and Wignal and Myers, (1988) placed the boundary between oxic and dysoxic environments at 2 ppm authigenic U.

2.4.6 Statistical analysis

To study the dependence of metals on each of the variables and their relative importance in the prediction equation, multiple regression analysis was employed. Goodness of fit of the regression was tested using ANOVA and the percentage of variability explained by the fitted regression measured using r^2. Similar analysis was done separately for season wise along the continental shelf and estuarine system. In addition, Pearson correlation coefficients also were calculated for metal association along the study region.

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Chapter 3

General hydrography and sediment characteristics along the continental shelf of Kerala and Cochin Estuary

Contents

3.1 Introduction

Coastal waters form a multi-dimensional system where the dynamic processes are rarely in equilibrium. Compared to the open ocean systems, the coastal region exhibits environmental gradients spatially and temporally on micro or macro-scale. Once materials get discharged into the sea, they are rapidly associated with particulates and deposited to the sediments. With the increase in the human settlement along the coast, the coastal marine areas are receiving close attention especially with respect to environmental changes, biological production and other resource distribution. The health of an environment is commonly expressed in terms of water quality (temperature, salinity, dissolved oxygen, nutrients etc.) and sediment characteristics such as (texture, trace metals, organic carbon etc). The variability of metals in sediments is controlled by overlying hydrography, which transports these elements for an ultimate sink in sediments (Marcus, 1996; Graf et al., 1991; Thomas and Maynard, 2008). The study of sedimentological aspects provides background information necessary for the understanding of the oceanographic processes, which regulate the adsorption/dispersion mechanism in a region.

Arabian Sea is a semi-enclosed sea bordered on the northern, eastern and western sides by the land-masses of Asia and Africa. The width of the continental shelf along the southwest coast of India varies from place to place. It is narrow on south and gets widened towards the north. Arabian Sea is an area of negative water balance, where evaporation exceeds precipitation and run off, which lead to the formation of high salinity water masses (Venkateswaran, 1956). The maximum primary production was reported nearer to the coasts, with in 50 m depths and gradually decreases towards the open ocean (Nair et al., 1973). An outstanding feature of the Arabian Sea is the occurrence of a permanent oxygen minimum zone at mid depth. The mid-depth oxygen deficiency in the Arabian Sea is perhaps the most severally observed anywhere in the ocean, as the concentrations within 150–1000 m are <0.2 ml/L) in a large part of Arabian Sea, which intensify towards north (Naqvi and Jayakumar, 2000; Lothar et al., 2008). The high photosynthetic activity in the Arabian Sea often leads to a greater flux of sinking organic particles, which consume oxygen during decomposition (Sen Gupta et al., 1976). The supply of oxygen to the waters below the euphotic zone gets restricted by the strong density gradient and poor horizontal advection, which results in severe depletion of oxygen below the thermo cline (Naqvi and Qasim, 1983). The high organic carbon content (2–6%) in the western continental shelf of Arabian Sea (Prakashbabu et al., 1999) has also enhanced the oxygen deficiency in the water column.

The coastal currents along the westcoast of India are southerly from April to September and northerly from November to February. The coastal zone of western India experiences upwelling during summer monsoon (Banse, 1959; Purushan and Rao, 1974; Naqvi et al,. 2000; Rajesh et al., 2008). The high overlying productivity and sluggish intermediate water moments during northeast monsoon (December–February) lead to higher consumption of oxygen and more intense suboxic and denitrifying conditions in Arabian Sea (De'Souza et al., 1996; Madhupratap et al., 1996; Naqvi et al., 2006). Hence, the change in winds, reversing currents, coastal upwelling and the intense suboxic condition are the major factors which influence the biogeochemical cycling of trace metals in the sediments of western continental shelf of India.

The Cochin estuary (Vembanad Lake) is one of the largest tropical estuarine systems in India, extending to about 90 km, as it acts as a major depocentre for Quaternary deposits brought from the Western Ghats (Narayana et al., 2002). The sediment flux from catchments is about 32 x 10^6 tons.y^{-1} (Thomson, 2002) and the consequent siltation has caused the shrinkage of the estuarine area considerably. The average tide in the Cochin Estuary is ~ 1 m (Srinivas et al., 2003). The currents are weak (~15 cm/s) during October–December, which increase to 45 cm/s during February–May (Srinivas et al., 2004). During southwest monsoon (June–October), the estuary receives enhanced transport of alluvium, which is accumulated as bed sediment. During this season, the estuary gets flooded and discharges sizeable quantities of sediments into the sea, whereas during other periods, seawater enters into the estuary to modify sediment deposition. Following an increase in the human interference, the estuary has changed into moderately polluted (Balachandran et al., 2005; Laluraj et al., 2007). The hinterland is composed of archaean crystalline rocks, tertiary sediments, and rocks with laterite capping (Mallik et al., 1987). In the south Vembanad region, the swampy areas (Kari lands) with black peaty soil has a high proportion of carbonaceous wood, representing the areas that were dense mangroves in the past. Although textural characteristics of sediments from various parts of Vembanad Lake are available (Mallik, 1975; Veerayya and Varadachari, 1975; Padmalal and Seralathan, 1994; Laluraj et al, 2008), a proper interpretation linking the hydrodynamics, geomorphology, and coastline changes to this estuary has not been completed.

3.2 Hydrogeographical parameters

3.2.1 Temperature and salinity

The hydrographical features along the eastern Arabian Sea and the Cochin estuary are given in the Figures 3.1 to 3.3. The bottom water temperature was almost uniform in estuarine stations during both seasons whereas, it gradually decreased from coastal to offshore region (Figure 3.1 a & b). In Cochin estuary, the maximum temperature (32°C) was observed during premonsoon and minimum (26°C) during monsoon (Figure 3.1c) due to the fresh water influx through rivers (Martin et. al., 2008). The southern stations were warmer than northern stations. In shelf region, the water was relatively warm (29.5°-6°C) during premonsoon (Figure 3.1 b). Almost all off shore stations (>150 m) were cooler (< 12°C) during premonsoon, but were slightly warmed (13.5°-18.1°C) during monsoon (Figure 3.1 a) due to the effect of coastal upwelling (Banse, 1959; De Sousa, et al., 1996; Rajesh et al., 2008). The temperature decreased from south to north, but the coastal stations were warmer.

The upwelling phenomenon observed along the west coast of India during June-September persists upto October (Shankar, 2000), as evidenced by cooler (25 to 28°C) waters in the offshore region.

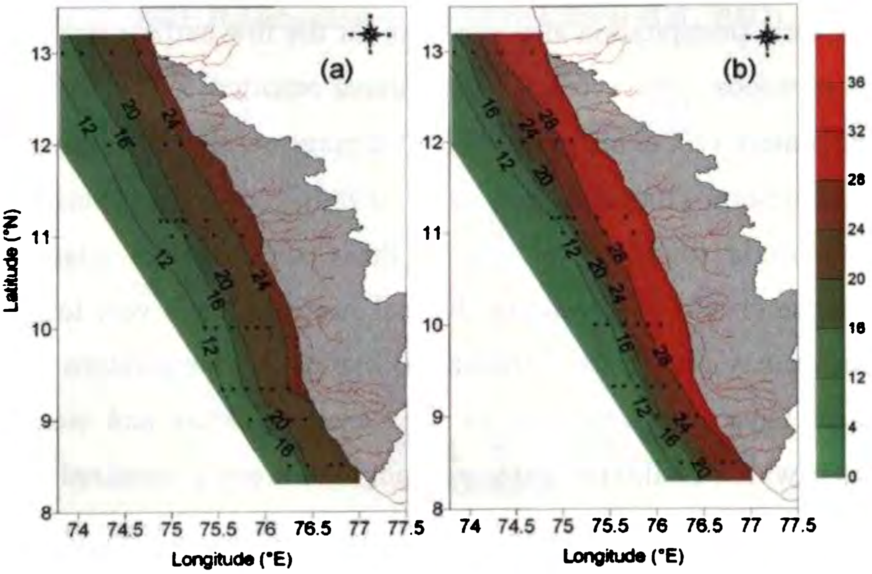

Figure 3.1 a&b. Distribution of bottom temperature along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

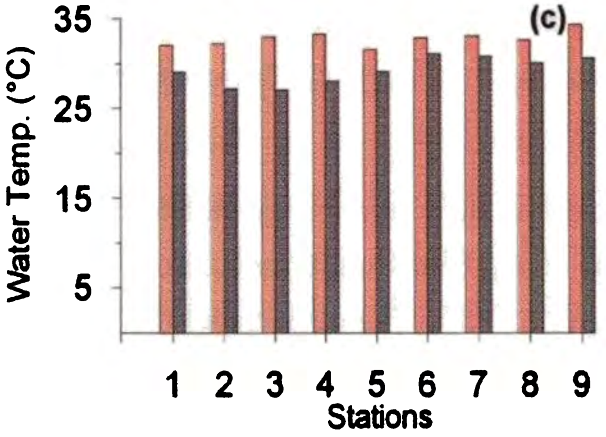

Figure 3.1 c. Distribution of bottom temperature in the Cochin estuary during premonsoon (red) and monsoon (black).

Thermal stratification of 2 to 4°C was observed, which increased to deeper stations. The cold waters in the bottom during October may be related to the upwelling in the region (Banse, 1959; Purushan and Rao, 1974; Rajesh et al., 2008). In addition, the combined effect of land run-off and local precipitation also accounts for the low surface temperature during monsoon. The average temperatures reported earlier for inshore surface waters of Cochin were 30.5°C during pre-monsoon and 27.0°C during monsoon (Balachandran et al., 1989). The annual variation in temperature is found to be less in the Cochin estuary. Qasim and Gopinathan (1969) observed that thermal stratification is very low in the Cochin estuary due to its shallowness. Increase in temperature towards upstream have been attributed to their shallow nature and weak tidal forcings, which facilitates water exchange weakening localized thermal excursions (Saraladevi et al., 1979). The influx of fresh water has profound influence on the distribution of temperature in Cochin Estuary. Ramamritham and Rao (1973) also observed similar feature in Cochin Estuary and along the west coast of India. The temperature distribution from January to May has been reported to be uniform throughout the estuary with maximum in April (Sankaranarayanan and Qasim, 1969; Martin et al., 2008).

Salinity did not show any marked difference between coastal and offshore stations during both seasons (premonsoon average 34.5 PSU and monsoon average 33.3 PSU). The variation of salinity and temperature were also found to be similar. However, during monsoon, the temperature of the coastal waters was cooler, due to the persistent upwelling (Figure 3.1a). The salinity in the estuary showed drastic difference between stations and seasons (Figure 3.2 a). During monsoon, the entire estuary remained fresh water dominant except at barmouth (5 PSU), whereas it was high saline during premonsoon. The high salinity at the barmouth gradually decreased towards the northern and southern ends, behaving as a typical estuary. The salinity intrusion in the estuary has a major role in metal adsorption/desoption mechanism (Richard et al., 1981; Balachandran et al., 2005; Laluraj et al., 2007).

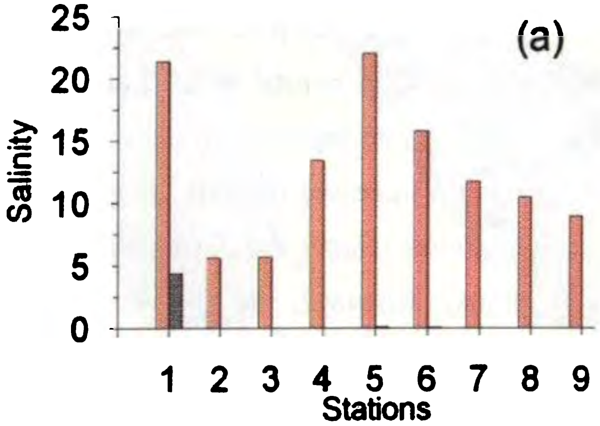

Figure 3.2 a. Distribution of bottom salinity in the Cochin estuary during premonsoon (red) and monsoon (black).

The results of the present study are comparable with the observations made by several workers in this estuary and other estuaries along the southwest coast of India. Wide variability in salinity of Cochin estuary is known to be due to the extreme conditions of monsoons modifying its flushing characteristics (Haridas et al., 1973; Martin et al., 2008). Saraladevi (1986) and Nair et. al. (1988) observed wide ranges of salinity variation (0.24 to 31 psu) in this estuary and attributed the feature to the shallow nature, monsoonal flow and the tidal forcing. Sankaranarayanan et al. (1986) have observed salinity intrusion beyond 21 km in the Periyar river estuary during premonsoon and upto 5 km during the monsoon. Nair et al. (1983) observed a distinct seasonal pattern of salinity in the Ashtamudy estuary with highest values during premonsoon. Jose (1993) observed well-mixed (26 psu salinity) estuarine conditions upto 15 km upstream in Chaliyar river estuary.

3.2.2 Dissolved oxygen

The distributions of bottom dissolved oxygen concentrations during premonsoon and monsoon seasons are presented in Figure 3.3 a & b. The dissolved oxygen decreased from coastal to offshore waters. The values were close to anoxic condition during premonsoon due to the calm sea and low mixing. The low values increased towards the northern region as also reported by the earlier studies (Naqvi and Jayakumar, 2000; Naqvi et al., 2000; Naqvi et al., 2006). However, the entire region along the shelf received oxygen deficient waters during monsoon. The variation in the dissolved oxygen during premonsoon may be due to the biochemical and other processes by which, the oxygen is transported through water column. But the major factor causing the depletion of oxygen might be the oxidation of organic matter. The geochemical characteristics of redox sensitive metals in surface sediments are associated with the oxygen concentration of the overlying water column (Laluraj and Nair, 2006). The estuarine stations showed a marked difference in oxygen concentration, ranged between 3 ml/L to 6 ml/L, but during monsoon, the dissolved oxygen in the estuary ranged between 4.4 ml/L to 5 ml/L (Figure 3.3 c). The northern stations showed low dissolved oxygen compared to the southern stations, which may be due to the very high organic load from the industrial zone situated near the bank of Periyar River (Balachandran et al., 2005).

The sub-pycnocline oxygen depletion over the western Indian shelf, especially during the southwest monsoon, similar to other environments off Namibia (Calvert and Price, 1971) and Peru (Codispoti and Packard, 1980), has been attributed primarily of natural origin because the nutrient enrichment occurs mainly through upwelling. These conditions start developing in June, intensity by September-October and dissipate by December.

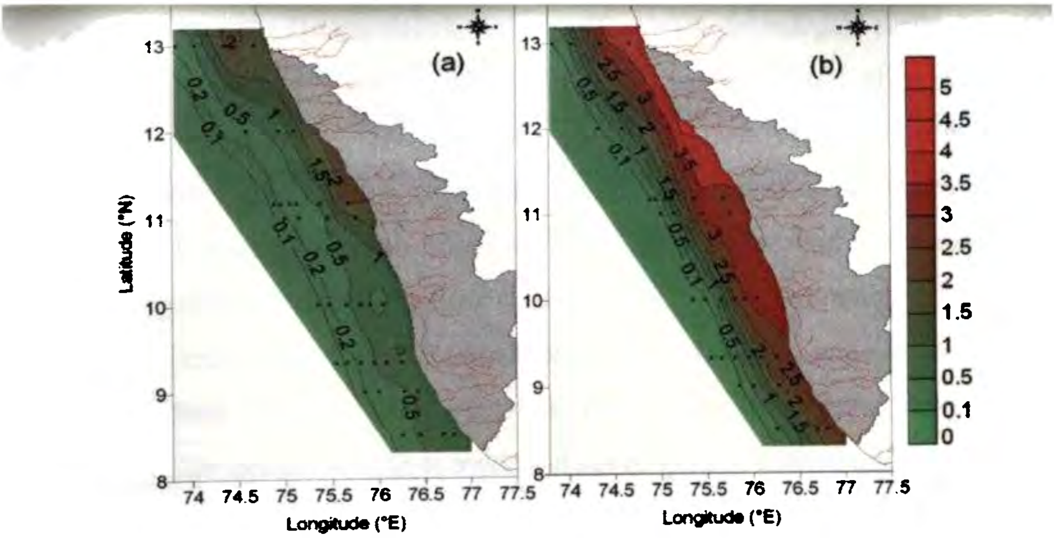

Figure 3.3 a&b. Distribution of bottom dissolved oxygen (μM) along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

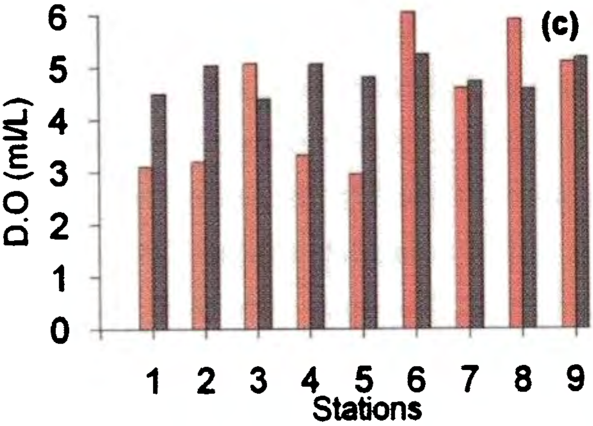

Figure 3.3 c. Distribution of bottom dissolved oxygen in the Cochin estuary during premonsoon (red) and monsoon (black).

This shallow, seasonal suboxic zone is distinct from the deeper, perennial suboxic layer of the central Arabian Sea (Naqvi, 1987; Naqvi and Jayakumar, 2000). The seasonal hypoxic zone on the Indian shelf is separated from the perennial suboxic zone of the central Arabian Sea by an undercurrent that transport waters with higher oxygen contents northward off the continental slope

(Naqvi, 1987; Naqvi et al., 2006). The oxygen deficiency off western India was first noticed in 1950's (Banse, 1959; 1968; Carruthers, 1959) based on limited measurements in the inner shelf. From May through September, during the southwest monsoon period, the surface circulation is southward. Upwelling of the Arabian Sea high saline water (> 35 psu) is the dominant process during this period (Johannessen et al., 1987). This is evidenced that the lifting of the halocline, shoaling and sharpening of the thermocline, and the penetration of the low oxygen water (< 0.5 ml/l) over the entire shelf. Another feature is the lowering of the surface salinity in the nearshore region associated with the land runoff.

3.2.3 Textural characteristics

The seasonal changes in the slit, clay and sand contents along the shelf and Cochin Estuary are presented in Table 3.1. The entire shelf was dominated by sand during both seasons. The average sand, slit and clay contents along the shelf region was 68.2, 20.9 and 10.9 % during monsoon, whereas it was 67.4, 21.7 and 10.9 during premonsoon (Table 3.1). The northern and southern zones showed drastic changes in texture during both seasons. The seasonal average of sand along the 20, 50, 100 and 200 m depths were 39, 83, 63 and 74 %, whereas slit was 36, 10.5, 28 and 18 %. Clay showed very low values and the seasonal averages were 25, 6, 9 and 8 % along the 20, 50, 100 and 200 m. Along the 20 m contour, the northern zone was dominated by slit and clay, whereas southern was dominated by sand. Along 50 m stations, sand dominated over slit and clay. Along the 100 m, slit and clay contents were high in shallow regions, while the southern zone exhibited high clay content. In Cochin estuary, the textural properties changed drastically between seasons. The average sand, slit and clay contents were 52.1, 10.3 and 37.6% during premonsoon, whereas they were 43.8, 9.6 and 46.6% during monsoon (Table 3.1).

Table 3.1. Grain-size distribution (% dry weight) of the sediment along the study region.

Coastal region							
Station		Monsoon			Premonsoon		
Transects	Depth	Silt %	Clay %	Sand %	Silt %	Clay %	Sand %
Manglore	20	74.1	25.0	0.9	69.1	20.1	10.8
	50	13.7	15.5	70.8	17.4	17.3	65.3
	100	48.0	18.2	33.8	47.7	20.2	32.1
	200	6.9	6.6	86.5	7.6	6.2	86.2
Kannoore	20	53.6	46.4	0.0	54.6	40.1	5.3
	50	10.7	7.9	81.4	11.6	5.2	83.2
	100	82.8	4.4	12.8	81.6	8.2	10.2
	200	30.4	2.8	66.8	32.1	5.3	62.5
Baypore	20	50.7	48.9	0.5	42.3	52.1	5.6
	50	5.0	7.9	87.1	14.4	5.4	80.3
	75	9.3	5.5	85.3	11.9	4.5	83.6
	100	14.7	2.0	83.4	18.6	1.3	80.1
	150	4.6	3.5	91.9	6.3	2.5	91.2
	200	49.6	5.7	44.8	48.9	8.9	42.2
Ponnani	20	42.5	56.3	1.2	40.5	56.2	3.3
	50	27.9	1.4	70.8	23.1	6.5	70.5
	100	17.9	6.8	75.3	25.2	2.5	72.3
	200	16.1	4.6	79.3	22.2	2.5	75.4
Cochin	20	1.2	4.6	94.2	3.4	3.1	93.5
	50	14.9	6.3	78.8	14.5	7.3	78.2
	75	19.4	3.5	77.1	21.6	4.3	74.2
	100	20.0	3.5	76.6	25.9	2.8	71.3
	150	2.1	2.8	95.1	1.2	3.8	95.0
	200	6.0	1.2	92.8	7.3	2.5	90.3
Alleppy	20	13.3	0.2	86.5	13.5	1.3	85.2
	50	5.9	7.5	86.5	8.6	7.2	84.2
	75	7.8	7.9	84.3	6.2	8.5	85.3
	100	6.3	11.6	82.2	6.8	12.0	81.2
	150	8.9	3.4	87.7	12.9	4.5	82.6
	200	19.2	6.7	74.1	18.3	8.2	73.5
Kollam	20	68.6	16.1	15.2	58.6	21.2	20.2
	50	1.2	1.6	97.3	3.0	0.7	96.4
	100	7.4	2.6	90.1	9.8	1.0	89.2
	200	7.5	33.0	59.5	6.4	33.3	60.3
Trivandrum	20	2.3	3.8	93.9	1.7	4.1	94.3
	50	2.5	2.0	95.5	2.8	2.0	95.2
	100	18.2	24.0	57.8	23.6	20.1	56.3
	200	1.4	1.7	97.0	3.6	1.1	95.2
Estuarine region							
Station		Monsoon			Premonsoon		
St.No	Depth	Silt %	Clay %	Sand %	Silt %	Clay %	Sand %
1	3.0	0.3	21.5	78.2	28.3	37.5	34.2
2	4.5	28.1	63.0	8.9	0.8	50.5	48.8
3	2.5	0.8	45.5	53.7	25.1	23.0	51.9
4	ND	31.1	60.0	9.0	31.5	46.0	22.5
5	1.5	0.6	30.5	68.9	0.5	24.5	75.0
6	ND	21.7	78.0	0.3	1.7	98.0	0.4
7	5.5	0.5	20.0	79.5	0.6	15.5	83.9
8	4.0	2.9	27.0	70.1	3.8	22.5	73.7
9	8.5	0.2	74.0	25.8	0.6	20.5	78.9

The difference in sand and clay content between seasons might be due to the sediment transport by rivers during monsoon (Laluraj et al., 2008). The entire region was dominated by clay and sand during both seasons except stations 1, 3 and 4 during premonsoon and at stations 2, 4 and 6 during monsoon, where slit was higher than clay.

The sediment distribution is influenced by the input source, channel morphology, weathering, abrasion, corrosion of grains, sorting, and deposition. Different hydrodynamic subdivisions facilitate a depositional environment. The grain-size distribution provides a measure of energy conditions during deposition. The sorting of sediments with respect to hydrodynamic energy conditions are given (Figure 3.4 a-d) as a ternary diagram, as proposed by Prejup (1988) and Flemming (2000).

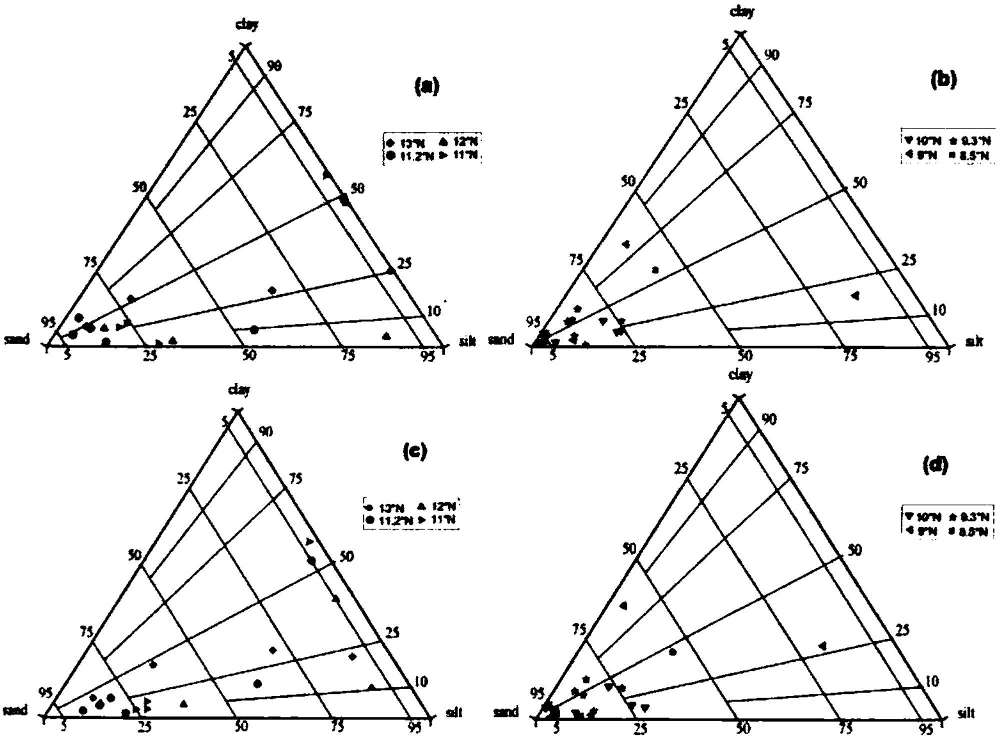

Figure 3.4 a-d. Ternary diagrams showing the textural trend along the continental shelf of Kerala (monsoon a & b; premonsoon c & d).

The energy condition was evaluated, by following the classification made by Prejup (1988), and their textural classification was made according to Flemming (2000) and is presented in Table 3.2.

The sediments generally showed a range of textural facies such as clayey slightly sandy mud, very clayey sand, clayey-sand etc. (Table 3.1). Sand and slit were generally high along the shelf during monsoon due to the high-energy conditions that prevailed over the region. Along the continental margin, a narrow band of sand was found in the inner shelf and outer shelf respectively. The sediment distribution pattern between Manglore and Cochin showed a deviation from the southern parts with dominance of slit over clay. The shelf sediment near Kollam was almost sandy except at coastal stations. The slit contents along the coastal stations of Ponnani and Alleppy might be due to the presence of mud banks, whereas in the Cochin estuary, the texture was sandy-clay during all seasons. The southern and northern limbs of the estuary showed a very high sand content, indicating their fluvial supply. This can also be seen in the trilinear diagram, indicating the textural changes in the region from monsoon to post-monsoon (Figure 3.4 e).

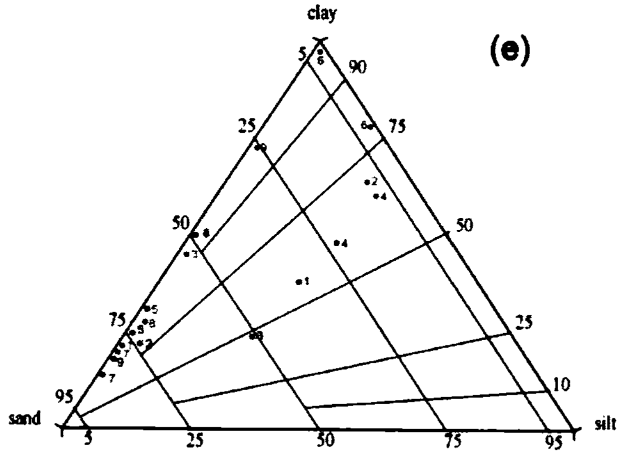

Figure 3.4 e. Ternary diagrams showing the textural trend along the Cochin estuary during postmonsoon (blue solid circles) and monsoon (red solid circles).

Table 3.2. Textural classification and hydrodynamic subdivisions of the study region (based on Fleming, 2000).

Shelf					
		Premonsoon		Monsoon	
Transect	Depth	Code Fleming, 2000	Textural classification	Code Fleming, 2000	Textural classification
Manglore	20	D-II	Very silty slightly sandy mud	E-II	Slightly clayey silt
	50	B-II	Silty sand	B-III	Clayey sand
	100	C-III	Silty sandy mud	C-III	Silty sandy mud
	200	A-II	slightly clayey sand	A-II	slightly clayey sand
Kannore	20	D-III	Silty slightly sandy mud	E-III	Clayey silt
	50	A-II	slightly clayey sand	A-I	Slightly silty sand
	100	D-II	Very silty slightly sandy mud	D-I	Extremely silty slightly sandy mud
	200	B-I	Very silty sand	B-I	Very silty sand
Baypore	20	C-II	Very silty sandy mud	E-III	Clayey silt
	50	A-I	Slightly silty sand	A-II	slightly clayey sand
	75	A-I	Slightly silty sand	A-I	Slightly silty sand
	100	A-I	Slightly silty sand	A-I	Slightly silty sand
	150	A-I	Slightly silty sand	A-I	Slightly silty sand
	200	D-III	Silty slightly sandy mud	C-I	Extremely silty sandy mud
Ponnani	20	E-IV	Silty clay	E-IV	Silty clay
	50	B-I	Very silty sand	B-I	Very silty sand
	100	B-I	Very silty sand	A-I	Slightly silty sand
	200	A-I	Slightly silty sand	A-I	Slightly silty sand
Cochin	20	A-I	Slightly silty sand	S	Sand
	50	A-I	Slightly silty sand	A-I	Slightly silty sand
	75	B-I	Very silty sand	A-I	Slightly silty sand
	100	B-I	Very silty sand	A-I	Slightly silty sand
	150	S	Sand	S	Sand
	200	A-I	Slightly silty sand	A-I	Slightly silty sand
Alleppy	20	A-I	Slightly silty sand	A-I	Slightly silty sand
	50	A-I	Slightly silty sand	A-II	slightly clayey sand
	75	A-II	slightly clayey sand	A-II	slightly clayey sand
	100	A-II	slightly clayey sand	A-II	slightly clayey sand
	150	A-I	Slightly silty sand	A-I	Slightly silty sand
	200	B-II	Silty sand	B-II	Silty sand
Kollam	20	D-III	Silty slightly sandy mud	D-II	Very silty slightly sandy mud
	50	S	Sand	S	Sand
	100	A-I	Slightly silty sand	A-I	Slightly silty sand
	200	C-IV	Clayey sandy mud	B-II	Silty sand
Trivandrum	20	A-II	slightly clayey sand	A-II	slightly clayey sand
	50	A-I	Slightly silty sand	S	Sand
	100	B-II	Silty sand	B-III	Clayey sand
	200	A-I	Slightly silty sand	S	Sand
Cochin Estuary					
1	3.0	A-II	slightly clayey sand	C-IV	Clayey sandy mud
2	4.5	D-IV	Clayey slightly sandy mud	D-IV	Clayey slightly sandy mud
3	2.5	B-IV	Very clayey sand	B-II	Silty sand
4	ND	D-IV	Clayey slightly sandy mud	D-IV	Clayey slightly sandy mud
5	1.5	B-IV	Very clayey sand	B-IV	Very clayey sand
6	ND	E-V	Slightly silty clay	E-VI	Clay
7	5.5	A-II	slightly clayey sand	A-II	slightly clayey sand
8	4.0	B-IV	Very clayey sand	C-VI	Extremely clayey sandy mud
9	8.5	C-VI	Extremely clayey sandy mud	A-II	slightly clayey sand

During monsoon, the river mouth remained highly energetic and rich in suspended sediments, which gradually decreased during premonsoon. This was reflected in a shift in the sediment texture towards the clay axis during premonsoon because the sediment supply has reduced as the result of the decreased river flow. The low-energy condition favored the deposition of clay during premonsoon (Flemming, 2000). However, there was no appreciable variation in energy condition at the central part of the estuary as the tidal activity at the convergence of two channels encouraged swift flow in the region. Textural characteristics in the estuarine system are mainly controlled by the progressive sorting of sediments under tidal currents and monsoonal influx from rivers (Laluraj et al., 2008).

3.2.4 Organic carbon

The quantity and nature of the organic matter accumulation in sediments depend on the environmental conditions. Over the shelf, organic carbon was high along the 20 – 200 m zone. The seasonal distribution of organic carbon along the shelf region are presented in Figure 3.5 a & b. The monsoon distribution showed high values compared to premonsoon. However, along the coast (20 m), high values were observed during premonsoon compared to monsoon. The northern continental shelf (north of 10°N) showed high organic carbon compared to southern zone during both seasons. The average concentrations were 1.9% and 1.4% along the northern and southern zones during monsoon, whereas they were 1.4 % and 1.2% during premonsoon. The northern zone behaved almost uniformly during both season, whereas along the southern zone, Kollam transect showed high organic carbon compared to other transects during both season. The maximum (average 3%) concentration was along the 200 m, whereas the minimum (0.25 %) was along the 50 m (Figure 3.5 a & b). In Cochin estuary, the northern zone showed high organic carbon compared to the central and southern zones during both seasons (Figure 3.5 c).

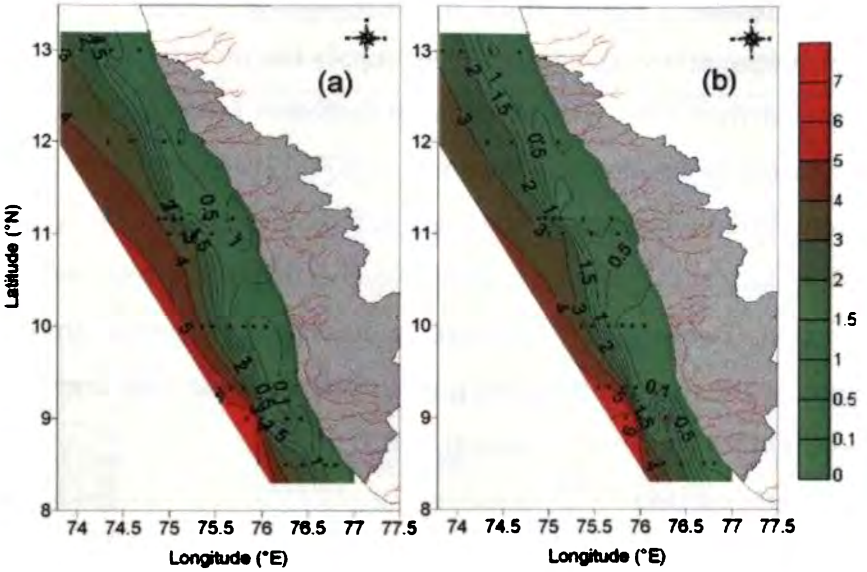

Figure 3.5. Distribution of organic carbon (% dry weight) along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

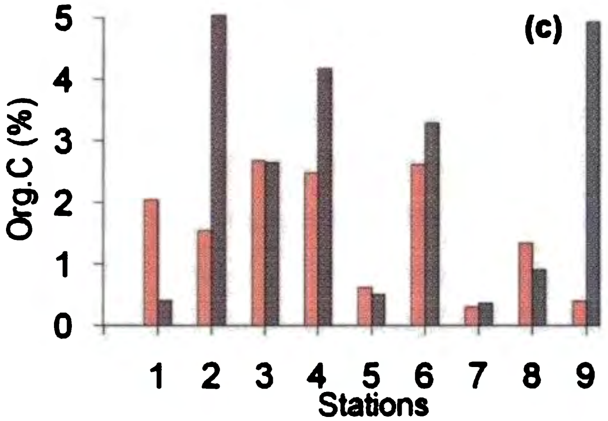

Figure 3.5. Distribution of organic carbon in the Cochin estuary during premonsoon (red) and monsoon (black).

The average concentrations were 4, 1.4 and 2% along the northern, central and southern zones respectively during monsoon, whereas they were 2.2, 1.8 and 0.7% during premonsoon. However, station near to Thannirmukkam barrier (station no. 9) showed high concentration (3.9%) during monsoon, which may be due to the high input of organic matter through Thannirmukkam barrage. It showed a monsoonal enrichment (average 2.5%) compared to the premonsoon (average 1.5%). The enrichment of organic matter along the inner shelf of Ponnani, Kochi and Alleppy transects may be due to the fact that the modern sediments are heavily laden with organic detritus (Saraladevi et al., 1972), which are carried southward by the alongshore currents (Kumar et al., 1985). These currents prevent the sediments from reaching the outer shelf, resulting in their preservation in sediments along the region.

The factors that contribute to the biogenic depositions are the quality of organic matter, the rate of deposition, coastal currents, primary production, bottom oxygen concentration and texture of the sediments. Moreover, Cochin estuarine system, oriented parallel to the southwest coast of India is fed by various rivers which originate in the Western Ghats having dense vegetation. This estuarine system seems to be augmented by substantial amount of industrial and domestic sewage, etc. Therefore, the organic accumulation along the inner shelf sediments may be the result of out flow of the Cochin estuary laden heavily with terrestrial organic detritus. Many authors have reported the variation in organic carbon content of sediments along the western continental shelf and along the Indian margin (Paropkari et al., 1992, 1993; Calvert et al., 1995). Comparing the sediment organic carbon in these regions, the maximum values (>4%) were reported along the western continental shelf of India especially from Mumbai to

Cochin (Paropkari et al., 1992). The debate on whether productivity or bottom water anoxia is the controlling factor for preservation of organic carbon is going on (Paropkari et al, 1992, 1993, Calvert et al., 1995, Prakash Babu et al., 1999; Rajesh et al., 2008). Paropkari et al (1992) emphasized that the productivity is not an ultimate control of organic matter preservation in bottom sediments, instead, a combination of bottom water anoxia and other depositional parameters. Calvert et al. (1995) suggested that the distribution of organic matter on the western continental margin is controlled by the supply of particulate matter, texture of sediments and their sorting by other processes. Cowie et al. (1995) has found that along with productivity and anoxia, water depth, sedimentation, sediment mineralogy, texture, winnowing, biological interaction and irrigation also contribute to the preservation of organic carbon. Increased rates of terrigenous inputs (biogenic), which are resistant to oxidation due to the fine nature of the sediments, are controlling the preservation of organic carbon along the western continental shelf of India (Paropkari et. al., 1987). The distribution of organic carbon in the study region is mainly controlled by the texture of sediments in conjunction with detrital supply, productivity of the overlying waters, energy condition and the low oxygen levels in bottom waters.

3.2.5 Inorganic carbon ($CaCO_3$)

The $CaCO_3$ concentration in shelf sediments increased from the coastal to seaward stations in all transects during both seasons (Figure 3.6 a & b). The average concentrations of $CaCO_3$ along the northern and southern zones were uniform through out seasons. The average carbonate concentrations along the northern and southern zones were 5.4 % (premonsoon) and 5.7% (monsoon). The outer shelves of Ponnani, Cochin and Alleppy showed high concentrations compared to the other transects, especially during monsoon.

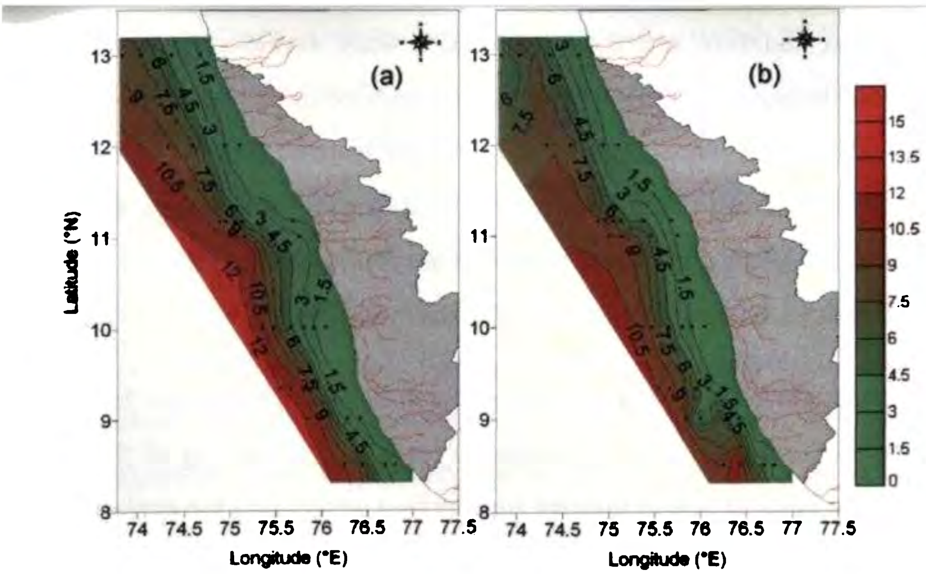

Figure 3.6. Distribution of $CaCO_3$ (% dry weight) along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

The 100 m contours showed maximum concentration (8.4%), whereas minimum (1.1%) was showed along the 20 m during both seasons (Figure 3.6 a & b). The seasonal averages were almost similar during both seasons (5.5%). In Cochin estuary, it varied between 3.2 to 20.4% during premonsoon and between 3.1 to 18.3% during monsoon (Figure 3.6 c).

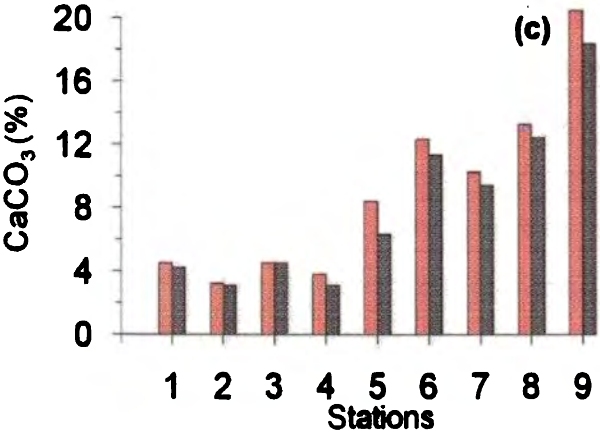

Figure 3.6. Distribution of $CaCO_3$ in the Cochin estuary during premonsoon (red) and monsoon (black).

The northern and southern zones showed a wide variation in distribution during both seasons. The northern zone contained an average carbonate of 3.7 and 4 % during monsoon and premonsoon respectively, whereas it was 11.5 and 13 % along the southern zone during monsoon and premonsoon respectively. Maximum concentration was found at the station near to Thannirmukkam barrier (station 9) during both seasons.

The sediment traps studies in the Arabian Sea have suggested that higher wind speeds during SW and NE monsoon leads to a deepening of the mixed layer and the introduction of nutrient rich surface waters into the euphotic zone results in high productivity in the area (Nair et.al., 1989). They have also reported that carbonate is the main component in the total flux (~65%), supporting the fact that productivity controls the carbonate distribution in the Arabian Sea. By studying the $CaCO_3$ content in the sediment cores from the Arabian Sea, Divakar (1991) and Rajesh et al. (2008) also emphasized that $CaCO_3$ content in the sediment is directly related to the productivity of overlying waters. The principal sources of carbonate in marine sediments are a) residual carbonate resulting from weathering of lime stone rock on the sea floor b) authigenic carbonate resulting from inorganic chemical precipitation c) terrestrial carbonate resulting from river and winds and d) biogenic carbonate accumulated on the skeletal parts of marine animals and plants (Nair and Pylee, 1968). Among these, biogenic carbonates are dominant in recent marine sediments. Nair and Pylee (1968) studied $CaCO_3$ content and size distribution of the western continental shelf sediments and found high percentage in the off shore regions compared to the coastal regions. In this study also, the carbonate content of the sediment increased towards offshore and maximum values were reported at 100 m, where sand was also high. This may be due to the presence of relict carbonate sand along the margins. Stewart et al. (1965) studied the sediments of northern Arabian Sea and observed a band of $CaCO_3$ rich sediment (up to 86%) on the outer shelf. In several continental shelves, foraminifera dominate the carbonate fraction and others are probably wind blown grains of lime stone or dolomite. Molluscs are also reported in the carbonate-rich sand. Murty et al. (1980) reported that texturally, the inner shelf of western continental shelf of India up to 70 m is covered by fine-grained sediments of terrigenous origin (clays, silty-clay and clayey-silt) with low $CaCO_3$ content, while the outer shelf (70 m to shelf break) is carpeted by coarse grained sediments (sand, clayey sand, silty sands) with high $CaCO_3$ content. The present observation also supported the above findings.

3.3 Summary

1. During monsoon, the southwest continental shelf of India experienced strong upwelling, where oxygen deficient waters prevailed over the region indicating the intensity of upwelling.
2. The Cochin estuary was fresh water dominated during monsoon, but was progressively influenced by seawater intrusion during post and premonsoon seasons, indicating the changing influence of river discharge and tides
3. The textural characteristics of surficial sediments in the Cochin estuary was controlled by the tidal currents and fresh water flow, whereas the high energy conditions along the shelf retained an almost consistent sandy substrate.
4. The oxygen deficient conditions (<0.5 ml/L) was restricted to the outer shelf during premonsoon, whereas the oxygen deficient waters were found to spread along the entire coastal and offshore environment during summer monsoon. This was due to the influence of the coastal upwelling along the southwest cost of India.

5. The outer shelf sediment showed high organic accumulation (average 3%) than coastal stations (0.25%) during both seasons, where the southern region especially contained high organic contents. The sediments in the Cochin estuary were very rich in organic carbon during monsoon, especially along the northern zone. Along the continental shelf, the high values may be due to high productivity of overlying waters and bottom water anoxia, whereas the organic enrichment in the Cochin estuarine sediment is due to the eutrophic characteristics shown by the estuary.
6. The outer shelf sediments were mostly sandy and rich in carbonate fraction compared to the coastal sediments during both seasons. The sandy substrates are normally rich in carbonate contents, but relict in elemental accumulation due to calcareous deposition. In the Cochin estuary, the carbonate content was high in the southern zone, possibly due to the presence of calcareous shells in the southern estuary.
7. The results of premonsoon and monsoon data revealed that tsunami has no effect on the physiochemical and sedimentary characteristic along the shelf and estuary.

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Chapter 4

Chemical composition of non-transition elements along the shelf of Kerala and Cochin estuarine system

Contents

4.1 Introduction

The S and P block elements in the periodic table are included in the non-transition elements. Possessing an outer electronic configuration of $n\mathrm{s}^{(1\text{-}2)}$ and $n\mathrm{s}^2$ $n\mathrm{p}^{(1\text{-}6)}$, these metals are distributed in the marine environment according to: conservative, nutrient-like, scavenging and redox-controlled (Chester, 2003). The conservative elements (halogens, alkali and alkaline earth) are present in seawater at relatively high concentrations. The 's' block elements are chemically more reactive and hence, their behaviors are more diverse.The major elements in rocks (Si, Al) are sparingly soluble, so they are transported as solid particles (e.g, sand and clay) through rivers or as dust particles. The non-transition metals in the present study are specific in their abundance and reactivity in marine environment. These include the conservative elements (Rb, Cs, Sr), nutrient and scavenging type (Ba, Be, Ga, etc.), reactive and scavenging like (Al, Pb) and, redox sensitive type (Pb). The details are given in (Annexure I).

Sediments are the ultimate burial grounds for metals in the hydrological cycle because metals are adsorbed onto particles during their interaction with surrounding waters. Coastal and estuarine regions are also important sinks for many toxic elements as they accumulate in bottom sediments (Szefer et al., 1995). Thus, geochemical characteristics of the sediments can be used to infer the provenance and fate of elements in aquatic environment (Förstner and Salomons, 1980; Fedo et al., 1999; Nath et al., 2000; Yang et al., 2004; Huntsman et al., 2005; Selvaraj and Chen, 2006). Suspended sediments are deposited on the margins of the continents under varying environmental conditions that range from oxic to anoxic in character. These sediments include gravels, sands, silt and muds, and are composed of mixtures of terrigenous, authigenic and organic compounds, which are deposited under reducing conditions (Chester, 1990). Because of their large surface area, sediments represent a major repository for metals and a record of the temporal changes in contamination.

Metals are introduced into the sea through river runoff, winds, hydrothermal venting, diffusion and anthropogenic activities. Rivers are major sources of particulate and dissolved metals, which are mobilized during weathering of granitic and basaltic crust. Some of the particulate metals are present as cations adsorbed onto the surface of clay minerals. The increase in ionic strength (via seawater) during estuarine mixing leads to desorption of certain metals. The increase in ionic strength causes the dissolved metals to precipitate as oxyhydroxides and organometalic colloids. These include nutrient-like elements (Be, Zn) and conservative like

(Rb, Cs). The nutrient type metals play an important role in enzymatic reactions and their biochemical cycles are controlled by redox reactions.

The chemical characteristics of shallow marine sediments are closely related to the regional climate and geology of adjacent land areas. Elemental distributions in sediments and rocks are diagnostic of various geological processes. As a consequence, the sedimentological study can provide valuable information on the regional hydrodynamics, particle transport and deposition. The western continental shelf of India is one of the most studied marine environments. The present study estimates the seasonal distribution of selected non-transition elements along with texture (sand, silt & clay), carbonate and organic matter in sediments of western continental shelf of India and from Cochin estuarine system in order to understand the geological and oceanographic processes controlling the depositional and post depositional changes.

4.2 Results

4.2.1 Elemental distribution

The seasonal variations of non-transition elements along the shelf as well as estuarine regions are given in Figures 4.1 to 4.8. The variations of each element are explained below:

Beryllium

Beryllium is a moderately rare element, present principally as beryl (beryllium aluminium silicate). Its compounds of chloride, fluoride, nitrate, phosphate and sulphate are soluble, whereas other compounds are either insoluble or sparingly soluble. The chemistry of beryllium is analogous to Al or Zn (Bohn, 1972; Drury et al., 1978). Beryllium gets fixed in sediments and share common sorption sites. The oxides and hydroxides of Be are insoluble and hence, are not leached during weathering.

Beryllium showed near shore enrichment (Figure 4.1 a & b) and varied from 1.71 ppm to 0.29 ppm during premonsoon and from 2.24 to 0.21 ppm during monsoon.

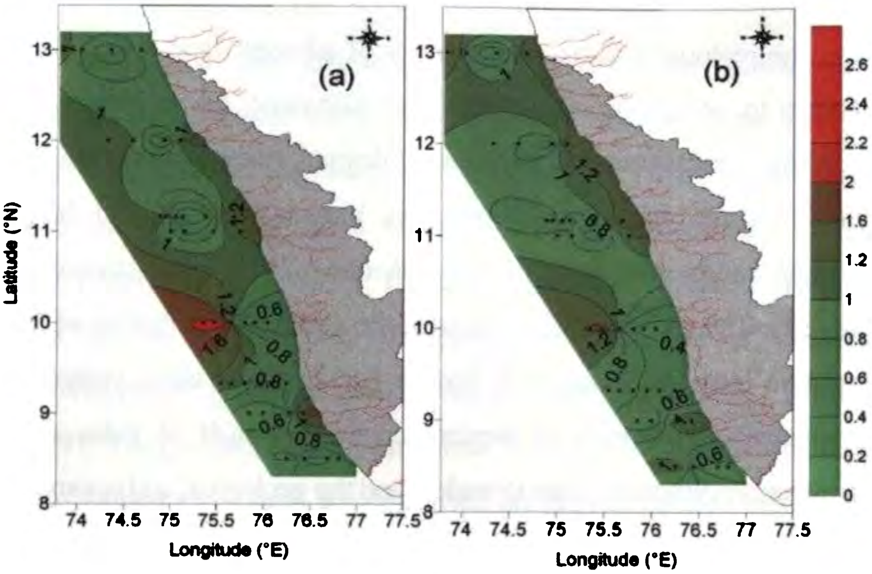

Figure 4.1 a&b. Distribution of beryllium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

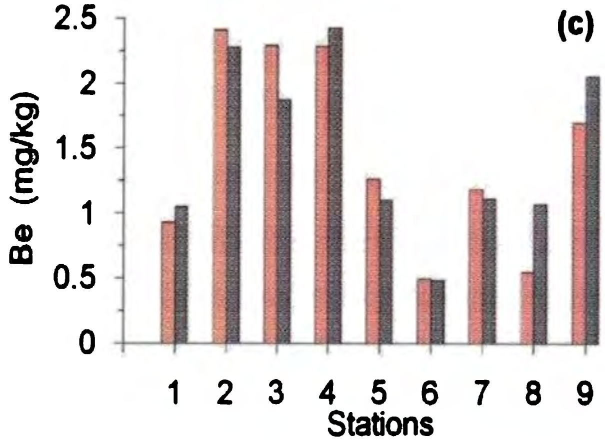

Figure 4.1 c. Distribution of beryllium in the Cochin estuary during premonsoon (red) and monsoon (black).

In almost all transects, a coastal enrichment is striking. A slight enrichment was also observed along the outer stations of Cochin. Beryllium showed almost similar distribution in the estuary during both seasons, except the high values in the southern estuary during monsoon (Figure 4.1c). The average concentrations were 1.45 and 1.49 ppm during premonsoon and monsoon periods respectively. The distribution generally reveals the inputs carried by the major rivers. Out of 9600 metric tons of Be annually added to ocean, approximately 0.00002 % is being retained (Schroedev, 1974), as the residence time of beryllium is a few hundred years (Merrill et al., 1960; Drury et al., 1978).

Aluminium

Aluminium is the third most abundant element in the earth's crust after oxygen and silicon and, occurs in nature as free metal. Aluminium is a trivalent metal with a strong tendency to hydrolyze in seawater to form $Al(OH)^{3-}$ and $Al(OH)^{4-}$ (Orians and Merrin, 2001). Al is sparingly soluble in seawater and has a short residence time compared to the oceanic mixing time of about 1000 years (Orians and Merrin, 2001; Hajime et al., 2004). The distribution depends on their relative strength in sources and sinks in the ocean.

The nearshore region accumulates very high aluminium (10%) especially in northern and Kollam transects, whereas the deeper regions showed normal values irrespective of seasons (Figure 4.2 a & b). The accumulation during monsoon suggests their origin from landmass. The concentration of aluminium decreased from nearshore to offshore stations during monsoon.

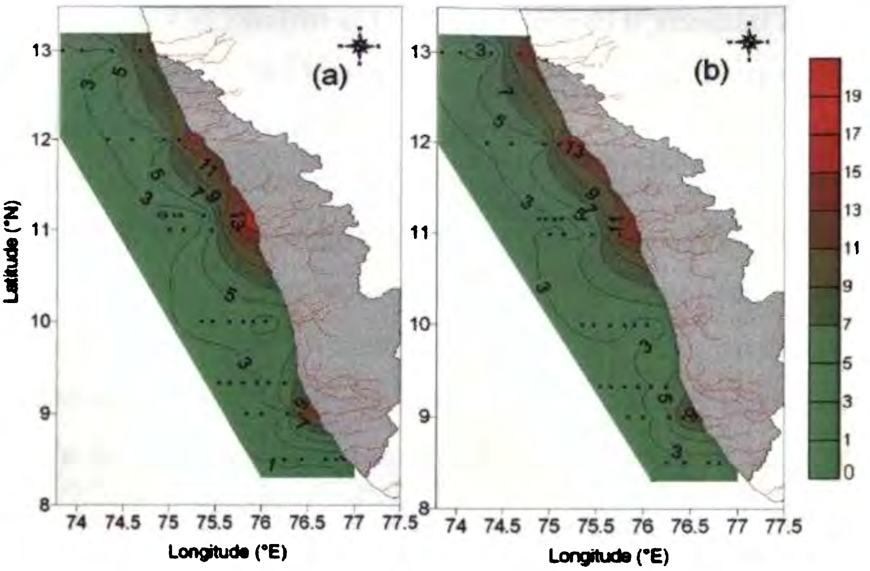

Figure 4.2 a&b. Distribution of aluminum (% dry weight) along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

The depletion in the middle transects (Cochin and Alleppey) could be due to the coastal currents. In the estuary, aluminium was uniformly distributed during monsoon compared to premonsoon (Figure 4.2c).

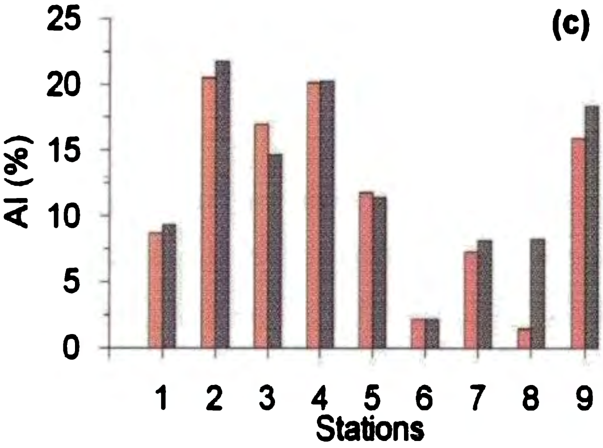

Figure 4.2 c. Distribution of aluminum in the Cochin estuary during premonsoon (red) and monsoon (black).

Higher values were in the north and the southernmost part of the estuary. The average concentrations during premonsoon were 19.2, 7.6 and 8.2 % in the northern, central and southern estuary respectively, whereas it was 18.9, 7.6 and 11.6 % during monsoon. The high values in the northern estuary indicate the industrial activities in the Periyar River and that in the south estuary was due to the three major rivers.

Al has a primary source of terrigenous material and is among the most particle reactive element in seawater (Orians and Bruland, 1986; Li, 1991; Van den Berg et al., 1994). Accordingly, geochemists have traditionally assumed that Al in marine sediment is affiliated with terrigenous minerals. The removal of particulate and dissolved Al occurs in continental margins and estuaries. In the open ocean, where terrigenous input is insignificant and dominantly eolian in origin.

Gallium

Gallium is chemically similar to aluminium, though less reactive (Orians and Bruland, 1988). Ga is delivered to the ocean primarily through atmosphere and can be described in conjunction with studies of other elements. Ga competes with iron in binding with siderophores, and transporting to cells because the high dissolved Ga overlaps with low dissolved Fe. Also, since Fe availability is found to limit primary production in some parts of the ocean (Martin et al., 1991), Ga has potential to competitively interact with Fe uptake.

Ga was distributed almost uniformly in almost all transects (Figure 4.3 a & b). The average concentration of Ga during premonsoon was 4.89 ppm and during monsoon was 4.59 ppm. Ga showed consistent pattern in the Cochin estuary during all seasons (Figure 4.3 c).

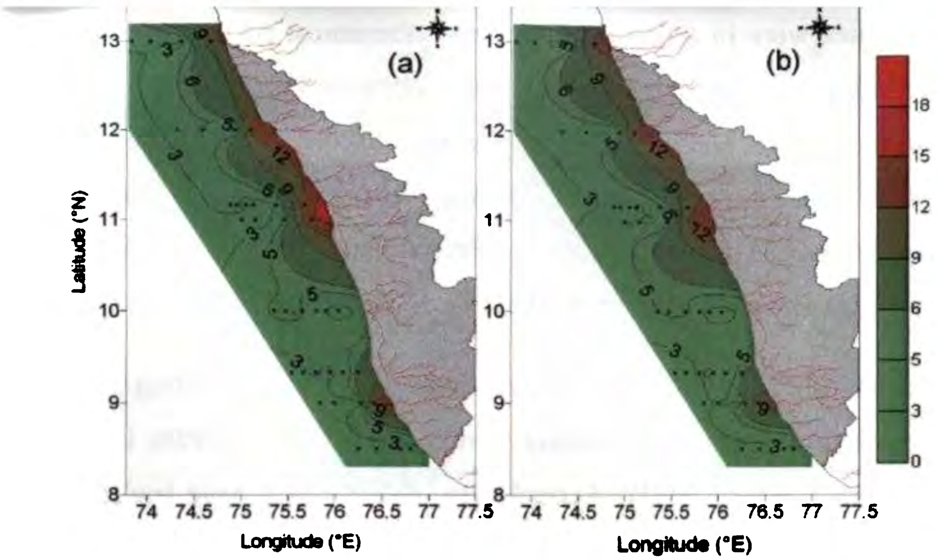

Figure 4.3 a&b. Distribution of gallium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

The average concentration of Ga during monsoon was 14.72 ppm, whereas it was 13.54 ppm during premonsoon. The northern side of the estuary showed very high values during both seasons.

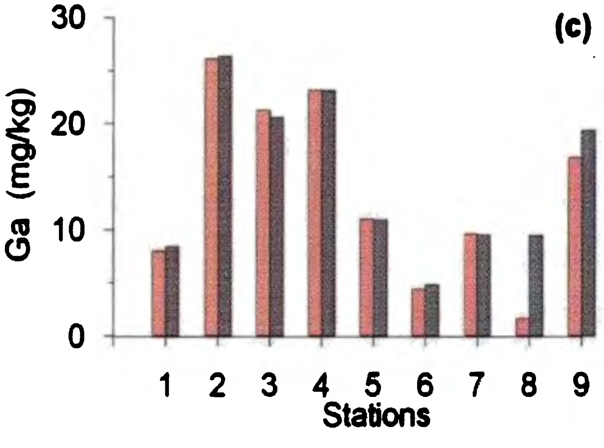

Figure 4.3 c. Distribution of gallium in the Cochin estuary during premonsoon (red) and monsoon (black).

The average concentration was 23.51 ppm in the northern zone, 7.79 ppm in the central zone and 9.34 ppm in the southern zone during premonsoon, whereas during monsoon they were 23.33 ppm, 8.07 ppm and 10.8 ppm respectively.

Rubidium

Rubidium is a chemically reactive, silvery-white and one of the most electropositive alkaline element. Rubidium is considered to be the 16th most abundant element in the earth's crust. It is very similar to potassium and there are no environments where it is seen as a threat. Rubidium has no known biological role but has a slight stimulatory effect on metabolise, probably because it is like potassium (Hans and Astrid, 1994).

Rubidium was high in the nearshore stations and it decreased towards offshore (Figure 4.4 a & b). The concentrations generally ranged between 44.82 to 4.39 ppm during monsoon, whereas it was between 46.98 and 2.91 ppm during premonsoon. The nearshore sediments (20 m) contained on an average 31.7 and 30.3 ppm during monsoon and premonsoon seasons respectively. The northern transects (north of 10°N) showed higher values than the southern transects and the pattern of distribution was more or less similar during both seasons. In the estuary, Rb showed a uniform distribution during both seasons with an average of 46.5 ppm during premonsoon and 50.3 ppm during monsoon (Figure 4.4 c). The distribution of this element in the estuary generally indicates the influence of high river flux at both zones.

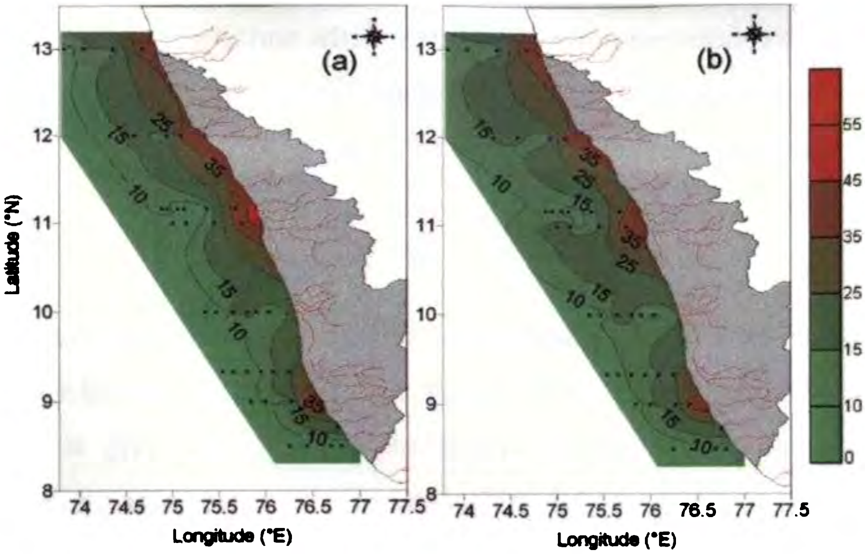

Figure 4.4 a&b. Distribution of rubidium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

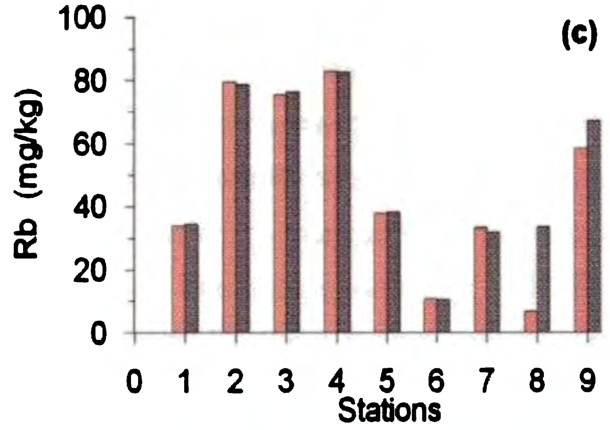

Figure 4.4 c. Distribution of rubidium in the Cochin estuary during premonsoon (red) and monsoon (black).

Strontium

Strontium commonly occurs in nature, forming about 0.034% of all igneous rock. It also occurs as sulphate mineral celestite ($SrSO_4$) and the carbonate strontianite ($SrCO_3$). Strontium is mainly present in the dissolved form and is not fractionated by any natural chemical or biologic process (Hans and Astrid, 1994).

Sr showed nearshore depletion and deeper enrichment along all transects during both seasons (Figure 4.5 a & b).

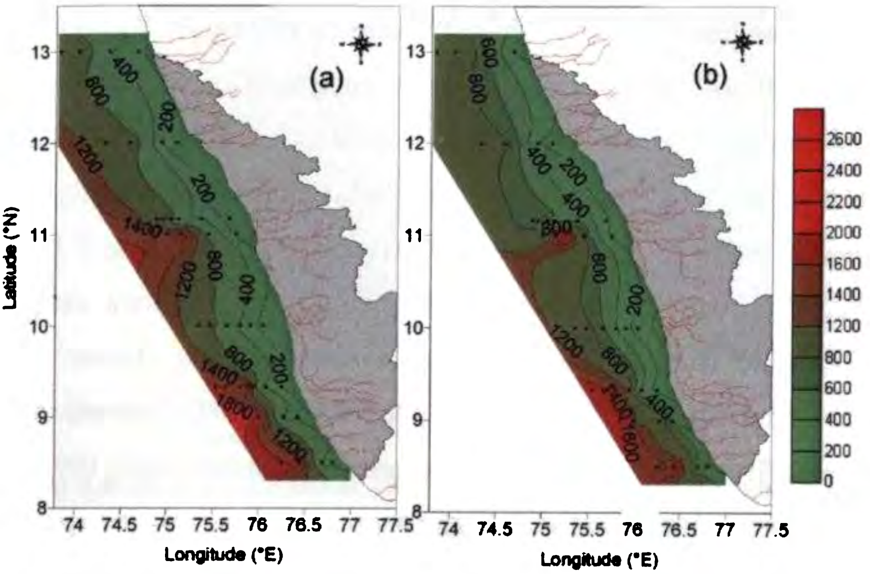

Figure 4.5 a&b. Distribution of strontium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

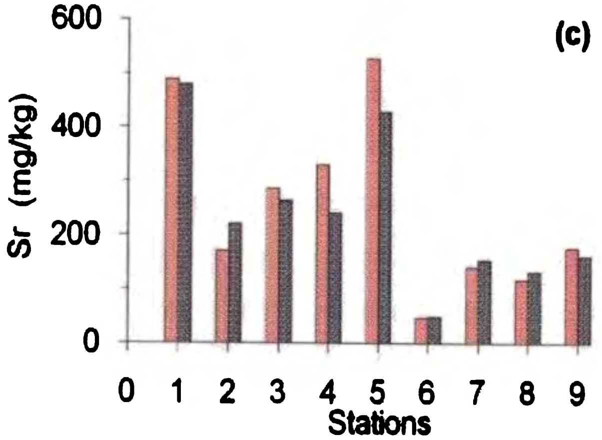

Figure 4.5c. Distribution of strontium in the Cochin estuary during premonsoon (red) and monsoon (black).

The average concentration of strontium during premonsoon was 808.1 ppm, whereas it was 823.5 ppm during monsoon. Sr concentrations were high in Alleppy transect compared to other transects during both season. The high concentration towards deeper stations revealed its lithogenic origin and the less anthropogenic influence. In estuary, strontium showed high accumulation in the central zone compared to other zones. The average concentrations of strontium were 240.8, 318.4 and 148.2 ppm, along the northern, central and southern zones respectively during monsoon whereas during premonsoon it was 261.5, 353.3 and 143 ppm respectively (Figure 4.5c). Studies have suggested that regional differences in Sr isotopic composition are possible on timescales shorter than its residence time (Stoll and Schrag, 1998; de Villiers, 1999). Non-conservative behavior of Sr has been observed in estuaries (Andersson et al., 1994; Wang et al., 2001), in which various dynamic processes modify its transport to the oceans. The non-conservative behavior of Sr in estuaries is quite essential to interpret more on oceanic Sr archives.

Cesium

The pollution by cesium in the ocean is dominated by atmospheric fallout and fluvial run-off (Simon, 1996). Cesium is a relatively rare element and has a large ionic radius of 174 pm in 8–fold co-ordination, which renders it incompatible with many of the silicate minerals (Simon, 1996). It will however, make a limited substitution for K in mica and K-feldspar, which contain most of the Cs in the earth's crust. It has relatively less applications and hence, is not often encountered as an anthropogenic contaminant in industrial or manufacturing sources.

Cesium showed nearshore enrichment, but decreased towards offshore (200 m). Cs showed a wide variation of 2.78 - 0.06 ppm (monsoon) and 2.92 - 0.12 ppm (premonsoon). The seasonal variation was insignificant (Figure 4.6 a & b).

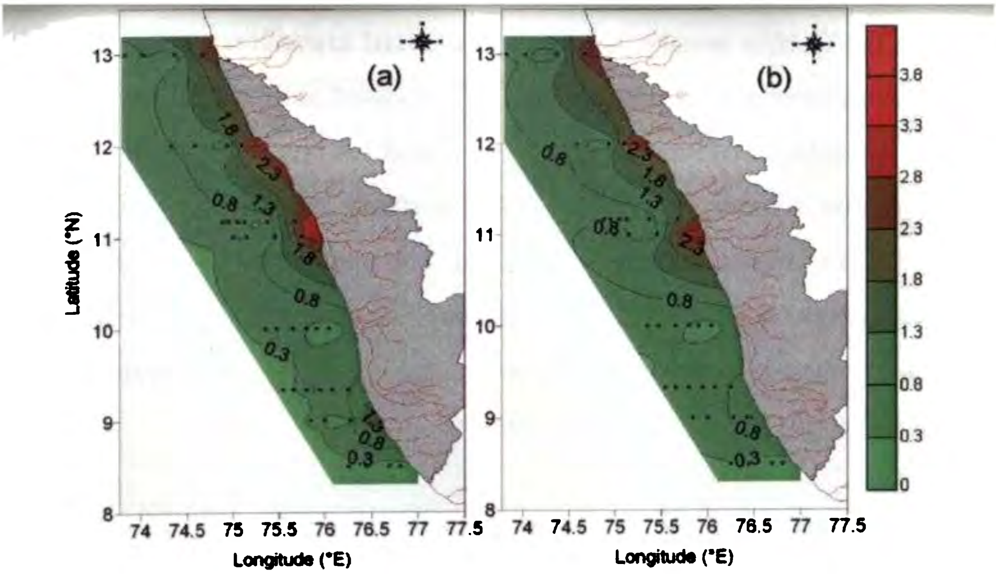

Figure 4.6 a&b. Distribution of cesium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

The maximum concentration of Cs was observed along Ponnani transect during both seasons. It must be noted that beyond 20 m depth, Cs was very low (>1ppm) during all seasons. There was an enrichment towards north (north off 10°N) along the shelf.

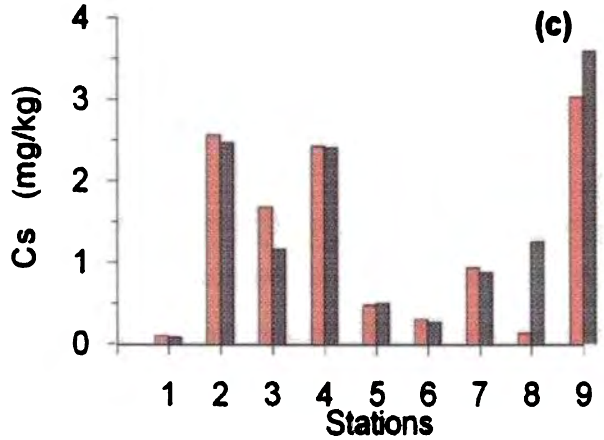

Figure 4.6 c. Distribution of cesium in the Cochin estuary during premonsoon (red) and monsoon (black).

In the Cochin estuary, Cs was accumulated towards northern zone and the southern most station (Figure 4.6 c). Cs showed an identical distribution pattern irrespective of seasons (average 1.3 and 1.4 ppm during premonsoon and monsoon seasons respectively). The northern zone showed an average of 2.01 ppm, whereas it was 0.28 and 1.9 ppm along the central and southern zones respectivily during monsoon. They were 2.21, 0.29 and 1.36 ppm respectively during premonsoon, the highest concentration was recurred towards south during both seasons.

Barium

The growing interest in barium in oceanic systems resides in its general link between barite and ocean productivity (Bishop, 1988). More specifically, Ba in suspended barite has the potential to trace export production and water column mineralization (van Beek et al., 2003).

The Ba concentrations varied between 31 and 394.8 ppm during monsoon and, 38.7 and 578.3 ppm during premonsoon. The average concentration was 120.8 ppm during monsoon and 165.9 ppm during premonsoon. It showed a marked increase (Figure 4.7 a & b) towards the southern transects (south off 10°N) than the northern transects. The concentration was high in the nearshore compared to deeper region. The region between Cochin and Kollam is marked as rich in primary productivity during both seasons (Thresiamma et al., 2008). Goldberg and Arrhenius (1958) proposed the use of barium as a proxy for productivity based studies in sediment. The limitation was in the productive nearshore and anoxic sediments depleted in Ba (remobilization). It was demonstrated by Brumsack and Gieskes (1983) and Brumsack (1989) in the Gulf of California marginal sediments due to sulphate reduction by bacteria. The average concentration of barium in the Cochin estuary during monsoon was 744.9 and 750.8 during premonsoon (Figure 4.7c).

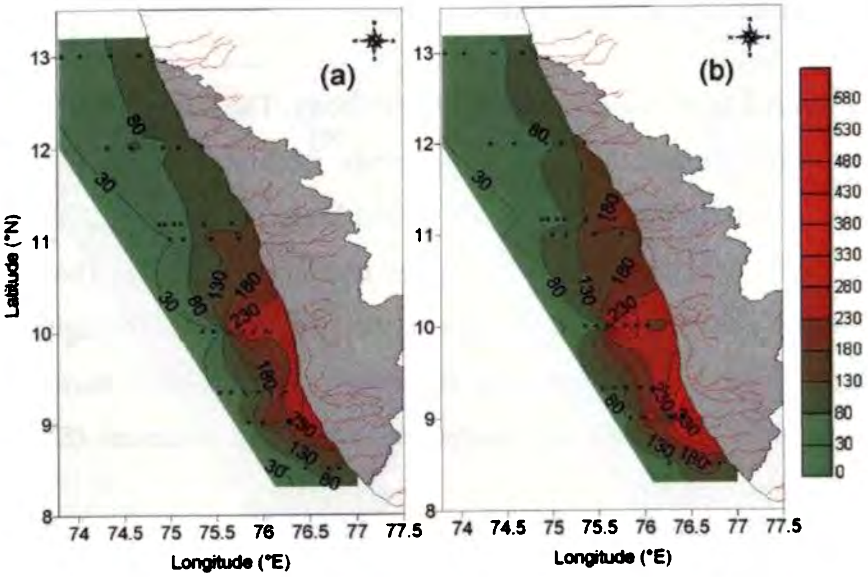

Figure 4.7 a&b. Distribution of barium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

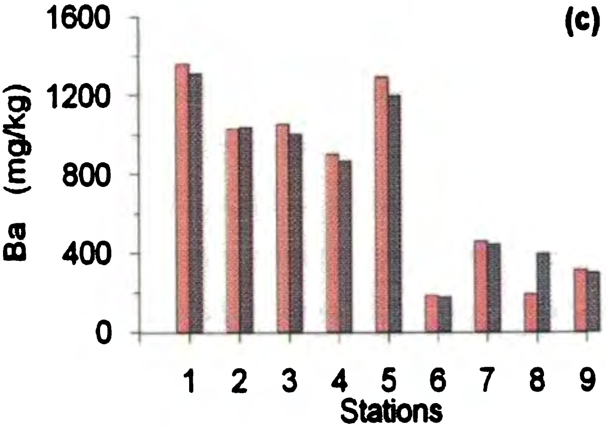

Figure 4.7 c. Distribution of barium Cochin estuary during premonsoon (red) and monsoon (black).

Ba showed high accumulation in the northern estuary irrespective of seasons. The average concentrations along northern, central and southern zones during monsoon were 966.1, 892.3 and 376.6 ppm, whereas they were 991.5, 942.6 and 318.4 ppm respectively during premonsoon.

Lead

Lead is a cumulative poison to human body. The large affinity of Pb^{2+} for thiol and phosphate containing ligands inhibits the biosynthesis of haeme and thereby affects kidney, liver and brain. The aerosol is the main source of Pb into the oceans (Praxedes and Marco, 2003). The natural source of Pb is weathering, volcanic activity and forest fires (Nriagu, 1989), the other sources being aerosols emitted from fossil-fuel burning and industrial activity, which are transported over long distances (Shen and Boyle; 1988).

Pb showed nearshore enrichment followed by a decrease and an increase towards deep in almost all transects (Figure 4.8 a & b). It generally shows nearshore enrichment through out the seasons. The average concentration of Pb in nearshore stations during monsoon was 18.4 ppm, whereas it was 9.5 ppm during premonsoon. High concentrations of Pb were observed in the southern region compared to northern side. There is an impoverishment of lead towards the deep, except the deeper stations south of 10°N during monsoon which was high. The very high values of Pb observed along the nearshore stations during monsoon compared to premonsoon indicate the nearshore inputs. During monsoon, lead concentrations in estuary were < 26 ppm, except in the industrial belt (Figure 4.8c; 70 ppm).

But during premonsoon, lead showed enrichment especially in the industrial area (average 558 ppm) and at Thevara (201 ppm). The average concentration of lead during premonsoon was 105.5 ppm, whereas it reduced to 20.5 ppm during monsoon. These drastic changes indicate that the metal is accumulated during premonsoon due to the restricted flow in the estuary.

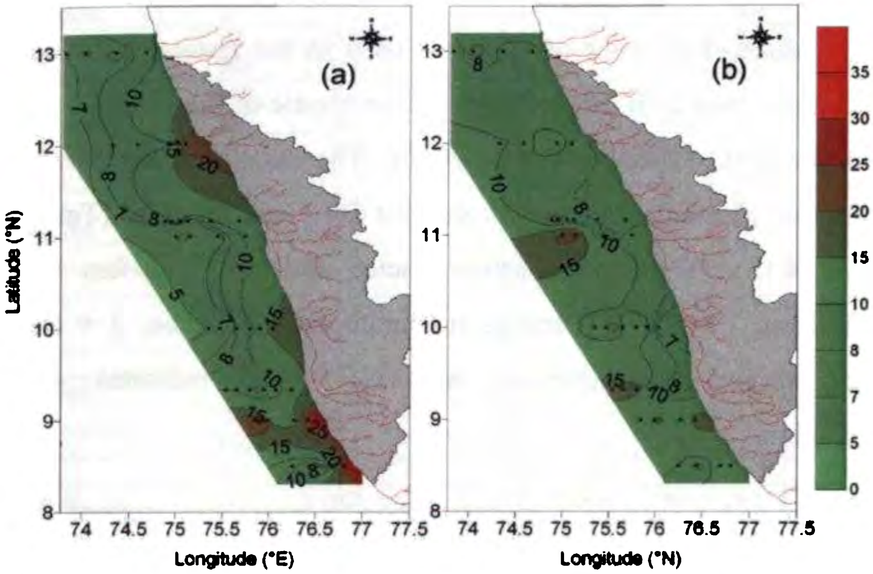

Figure 4.8 a&b. Distribution of lead [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

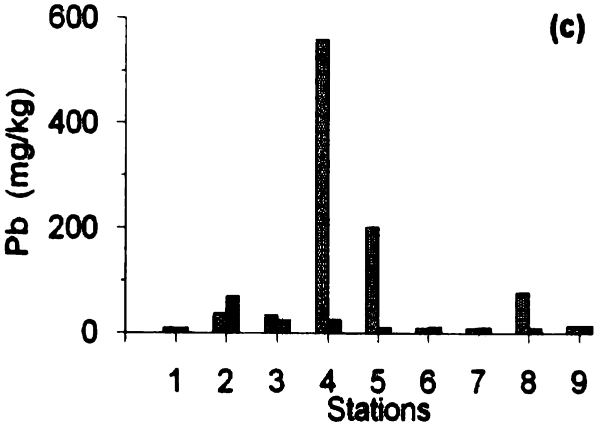

Figure 4.8 c. Distribution of lead in the Cochin estuary during premonsoon (red) and monsoon (black).

4.2.2 Normalisation of non-transition elements

Geochemical normalization of an element is the fraction of the particular element in the sample to the concentration of the same element in the global shale. The order of elements used in the normalized diagrams generally decreased with respect to primitive mantle of the earth (Hofmann, 1988; Dupre et al., 1996; Nath et al., 2000). The shale normalised values of non-transition elements during both seasons are given in tables (Table 4.1a & Table 4.1b). The normalisation factor (NF) < 1 refers to low contamination, $1 < NF < 3$ means moderate contamination, $3 < NF < 6$ indicates severe contamination, and $NF > 6$ indicates extreme contamination.

Al showed a moderate contamination in nearshore stations (20 m) along north of 10° N and Kollam transect during both seasons. Pb showed moderate contamination along the nearshore stations (20 m) off Kannore and Trivandrum, nearshore and deeper stations (200 m) of Kollam during monsoon. Sr showed high values in seaward stations along all transects, where the southern zone had better normalisation than the northern zone. All other metals showed low contamination during both seasons. Al, Ga, Ba, Sr and Pb showed moderate contamination along northern estuary during both seasons, indicating an increased deposition. The severe contamination for Pb was observed at stations 4 and 5 (27.9 and 10.1) during premonsoon.

Table 4.1a. Shale normalised values of non-transition elements along the study region during premonsoon.

Shelf

Transects	Depth (m)	Al	Rb	Sr	Cs	Ba	Pb	Ga
Manglore	20	1.3	0.3	1.0	0.2	0.2	0.4	0.7
	50	0.2	0.1	3.2	0.0	0.1	0.4	0.1
	100	0.3	0.1	5.6	0.1	0.1	0.3	0.2
	200	0.4	0.1	5.3	0.1	0.1	0.4	0.2
Kannoore	20	1.3	0.3	0.9	0.2	0.2	0.4	0.7
	50	0.2	0.1	0.9	0.0	0.1	0.6	0.1
	100	0.4	0.1	4.5	0.1	0.1	0.4	0.2
	200	0.4	0.1	4.7	0.1	0.1	0.5	0.2
Baypore	20	1.1	0.2	1.2	0.1	0.3	0.4	0.5
	50	0.4	0.1	2.9	0.0	0.2	0.4	0.2
	75	0.2	0.0	2.4	0.0	0.1	0.4	0.1
	100	0.3	0.1	3.8	0.0	0.1	0.5	0.2
	150	0.3	0.1	6.1	0.0	0.1	0.7	0.2
	200	0.2	0.1	2.7	0.0	0.1	0.2	0.1
Ponnani	20	1.4	0.3	0.7	0.2	0.2	0.4	0.7
	50	0.3	0.1	3.4	0.0	0.3	0.3	0.2
	100	0.2	0.1	11.1	0.0	0.1	0.9	0.1
	200	0.5	0.1	5.4	0.1	0.2	1.3	0.3
Cochin	20	0.2	0.1	0.5	0.0	0.3	0.2	0.1
	50	0.3	0.1	2.0	0.0	0.6	0.8	0.2
	75	0.4	0.2	2.9	0.0	0.9	0.6	0.3
	100	0.5	0.2	3.5	0.0	0.8	0.4	0.3
	150	0.4	0.0	4.6	0.0	0.1	0.3	0.3
	200	0.4	0.1	3.7	0.0	0.1	0.3	0.3
Alleppy	20	0.5	0.2	0.9	0.1	0.4	0.4	0.3
	50	0.3	0.1	1.8	0.0	0.3	0.4	0.2
	75	0.3	0.1	4.4	0.0	0.3	0.4	0.2
	100	0.2	0.1	7.0	0.0	0.3	0.5	0.1
	150	0.3	0.1	7.4	0.0	0.2	0.6	0.2
	200	0.3	0.1	7.6	0.0	0.2	0.9	0.2
Kollam	20	1.0	0.3	1.9	0.1	0.9	0.9	0.6
	50	0.4	0.1	6.1	0.1	0.1	0.4	0.2
	100	0.3	0.1	4.9	0.0	0.5	0.9	0.3
	200	0.2	0.1	8.7	0.0	0.2	0.5	0.1
Trivandrum	20	0.1	0.0	2.2	0.0	0.2	0.6	0.1
	50	0.2	0.1	1.3	0.0	0.4	0.6	0.2
	100	0.2	0.1	9.9	0.0	0.2	0.3	0.1
	200	0.2	0.0	6.7	0.0	0.1	0.5	0.1

Estuary

St.no	Depth (m)	Al	Ga	Rb	Sr	Cs	Ba	Pb
1	3.0	0.9	0.4	0.2	2.4	0.0	2.1	0.5
2	4.5	2.0	1.3	0.5	0.8	0.2	1.6	1.8
3	2.5	1.7	1.1	0.5	1.4	0.1	1.6	1.7
4	ND	2.0	1.2	0.5	1.6	0.2	1.4	27.9
5	1.5	1.2	0.5	0.2	2.6	0.0	2.0	10.1
6	ND	0.2	0.2	0.1	0.2	0.0	0.3	0.5
7	5.5	0.7	0.5	0.2	0.7	0.1	0.7	0.5
8	4.0	0.1	0.1	0.0	0.6	0.0	0.3	3.9
9	8.5	1.6	0.8	0.4	0.9	0.2	0.5	0.7

Table 4.1b. Shale normalised values of non-transition elements along the study region during monsoon.

Shelf								
Transects	**Depth (m)**	**Al**	**Ga**	**Rb**	**Sr**	**Cs**	**Ba**	**Pb**
Manglore	20	1.1	0.6	0.3	1.2	0.2	0.2	0.5
	50	0.2	0.1	0.1	2.0	0.0	0.1	0.3
	100	0.3	0.2	0.1	5.6	0.1	0.1	0.4
	200	0.3	0.2	0.1	4.7	0.0	0.1	0.4
Kannoore	20	1.3	0.7	0.3	0.3	0.2	0.2	1.2
	50	0.2	0.1	0.1	0.7	0.0	0.1	0.4
	100	0.5	0.3	0.1	5.5	0.1	0.1	0.5
	200	0.4	0.2	0.1	5.2	0.1	0.1	0.4
Baypore	20	1.4	0.7	0.3	0.7	0.2	0.2	0.7
	50	0.3	0.1	0.0	1.9	0.0	0.2	0.5
	75	0.2	0.1	0.0	1.9	0.0	0.1	0.3
	100	0.2	0.1	0.0	3.3	0.0	0.1	0.4
	150	0.1	0.1	0.0	9.0	0.0	0.1	1.0
	200	0.4	0.2	0.1	4.1	0.1	0.1	0.3
Ponnani	20	1.4	0.7	0.3	0.7	0.2	0.2	0.5
	50	0.4	0.2	0.1	3.2	0.0	0.3	0.3
	100	0.2	0.1	0.0	9.4	0.0	0.1	0.3
	200	0.2	0.1	0.0	7.7	0.0	0.0	0.4
Cochin	20	0.2	0.1	0.1	0.7	0.0	0.3	0.9
	50	0.4	0.2	0.1	1.9	0.0	0.5	0.4
	75	0.3	0.2	0.1	2.3	0.0	0.3	0.5
	100	0.5	0.3	0.1	3.3	0.0	0.6	0.5
	150	0.5	0.3	0.1	3.9	0.0	0.1	0.3
	200	0.5	0.3	0.1	3.4	0.0	0.1	0.3
Alleppy	20	0.6	0.4	0.2	1.0	0.1	0.4	0.6
	50	0.3	0.2	0.1	1.5	0.0	0.2	0.4
	75	0.3	0.2	0.1	4.2	0.0	0.2	0.4
	100	0.1	0.1	0.0	12.6	0.0	0.1	0.3
	150	0.3	0.2	0.0	6.0	0.0	0.1	0.4
	200	0.3	0.2	0.1	6.9	0.0	0.1	0.5
Kollam	20	1.3	0.7	0.3	2.0	0.1	0.5	1.5
	50	0.2	0.1	0.1	1.2	0.0	0.2	0.5
	100	0.3	0.1	0.1	9.2	0.0	0.3	0.5
	200	0.2	0.1	0.1	9.2	0.0	0.1	1.4
Trivandrum	20	0.1	0.1	0.0	1.9	0.0	0.1	1.5
	50	0.2	0.1	0.1	1.1	0.0	0.2	0.4
	100	0.1	0.1	0.0	9.4	0.0	0.1	0.3
	200	0.2	0.1	0.0	7.8	0.0	0.1	0.4

Estuary								
St. No	**Depth (m)**	**Al**	**Ga**	**Rb**	**Sr**	**Cs**	**Ba**	**Pb**
1	3	0.9	0.4	0.2	2.4	0.0	2.0	0.4
2	5	2.2	1.3	0.5	1.1	0.2	1.6	3.5
3	3	1.5	1.0	0.5	1.3	0.1	1.5	1.2
4	ND	2.0	1.2	0.5	1.2	0.2	1.3	1.3
5	2	1.1	0.5	0.2	2.1	0.0	1.8	0.6
6	ND	0.2	0.2	0.1	0.2	0.0	0.3	0.6
7	6	0.8	0.5	0.2	0.8	0.1	0.7	0.6
8	4	0.8	0.5	0.2	0.7	0.1	0.6	0.4
9	9	1.8	1.0	0.4	0.8	0.2	0.5	0.6

4.2.3 Enrichment factor (EF)

Elemental enrichment factor is used for the determination of level of contamination in sediments. The enrichment factor is calculated with respect to Al and Fe (Table 4.2a & Table 4.2b and Table 4.3a & Table 4.3b). It is evident that the southern zone (south of 10°N) showed higher enrichment factor for all non-transition elements during both seasons. Similar to the normalisation factor, the enrichment factor (EF) < 1 refers to low contamination, $1 < \text{EF} < 3$ means moderate contamination, $3 < \text{EF} < 6$ indicates severe contamination, and $\text{EF} > 6$ indicates extreme contamination.

4.2.3.1 Enrichment with respect to aluminium

Strontium showed very high enrichment among the non-transition elements, which increased seaward during both seasons. Lead showed high accumulation along the southern transects, especially along Kollam and Trivandrum transects during both seasons. However, it was very high in the estuary at stations 4, 5 and 8 during premonsoon and at stations 2 and 6 during monsoon. The premonsoon elemental deposition was slightly higher than that during monsoon.

4.2.3.2 Enrichment with respect to iron

Enrichment factor with respect to iron was low compared to that of Al during both seasons, but the pattern was similar. Southern zone showed very high enrichment as compared to the northern zone. Among non-transition elements, Sr and Pb showed high enrichment compared to others. Whereas the Fe enrichment was slightly higher than Al enrichment in estuary, the pattern was similar. It showed a seasonal upsurge, monsoon showed comparatively high values than premonsoon. The observed enrichments for Rb, Sr and Cs indicate their lithogenic origin, whereas for Pb is of anthropogenic origin.

Table 4.2a. Enrichment factors of non-transition elements with respect aluminium along the study region during premonsoon.

Shelf

Transects	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
Manglore	20	1.0	0.5	0.1	0.1	0.3	0.5
	50	1.3	9.7	0.2	0.3	2.1	0.5
	100	1.4	10.8	0.2	0.3	1.0	0.6
	200	0.9	8.1	0.1	0.2	1.1	0.6
Kannoore	20	0.9	0.4	0.1	0.1	0.3	0.5
	50	1.0	2.3	0.1	0.3	2.5	0.6
	100	1.2	6.7	0.2	0.3	1.1	0.5
	200	1.2	7.3	0.2	0.3	1.3	0.6
Baypore	20	0.8	0.7	0.1	0.3	0.4	0.5
	50	0.8	4.0	0.1	0.5	0.9	0.5
	75	0.9	5.8	0.1	0.5	1.6	0.5
	100	0.9	7.2	0.1	0.3	1.6	0.5
	150	1.0	11.8	0.1	0.3	2.4	0.6
	200	1.3	7.6	0.2	0.3	0.9	0.7
Ponnani	20	0.9	0.3	0.1	0.2	0.3	0.5
	50	1.1	6.0	0.1	0.8	0.9	0.5
	100	1.1	31.0	0.2	0.6	4.2	0.6
	200	1.3	7.0	0.2	0.4	2.7	0.6
Cochin	20	1.4	1.7	0.1	1.8	1.4	0.6
	50	1.3	3.9	0.1	1.8	2.6	0.5
	75	1.9	4.3	0.1	2.1	1.5	0.7
	100	1.3	4.0	0.1	1.5	0.7	0.5
	150	0.6	7.7	0.1	0.3	0.8	0.7
	200	0.7	5.6	0.1	0.3	0.9	0.7
Alleppy	20	1.3	1.0	0.1	0.8	0.7	0.6
	50	1.4	4.1	0.1	1.2	1.6	0.6
	75	1.7	9.7	0.1	1.1	1.3	0.6
	100	1.7	24.8	0.1	1.7	2.8	0.7
	150	1.2	15.8	0.1	0.8	2.0	0.6
	200	1.2	16.7	0.1	0.8	3.2	0.6
Kollam	20	1.2	1.1	0.1	0.9	0.9	0.6
	50	1.1	9.8	0.2	0.3	1.2	0.6
	100	1.6	11.0	0.0	1.8	3.3	1.0
	200	1.4	25.8	0.2	0.8	2.5	0.6
Trivandrum	20	1.1	11.5	0.1	1.4	5.4	1.0
	50	1.8	4.5	0.1	2.2	3.7	0.9
	100	1.4	35.2	0.1	1.2	1.8	0.6
	200	0.8	18.0	0.1	0.5	2.2	0.6

Estuary

St.No	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
1	3.0	0.9	10.0	0.0	8.6	1.9	1.6
2	4.5	0.2	0.4	0.0	0.7	0.8	0.6
3	2.5	0.2	0.6	0.0	0.6	0.7	0.4
4	ND	0.2	0.7	0.0	0.6	12.3	0.5
5	1.5	0.4	4.9	0.0	3.7	18.8	1.0
6	ND	0.2	0.6	0.0	0.7	1.3	0.6
7	5.5	0.2	0.8	0.0	0.8	0.5	0.5
8	4.0	0.3	3.7	0.0	1.9	25.1	0.5
9	8.5	0.2	0.5	0.0	0.3	0.4	0.5

Table 4.2b. Enrichment factors of non-transition elements with respect aluminium along the study region during monsoon.

Shelf

Transects	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
Manglore	20	1.1	0.7	0.2	0.2	0.4	0.5
	50	1.7	5.6	0.1	0.6	1.5	0.6
	100	1.4	10.8	0.2	0.3	1.4	0.6
	200	0.9	10.3	0.1	0.2	1.3	0.7
Kannoore	20	0.9	0.1	0.1	0.1	1.0	0.6
	50	1.2	2.1	0.1	0.4	2.3	0.6
	100	1.3	6.8	0.2	0.3	1.0	0.6
	200	1.1	8.8	0.2	0.2	1.2	0.6
Baypore	20	0.9	0.3	0.1	0.1	0.5	0.5
	50	0.8	4.1	0.1	0.6	1.7	0.5
	75	1.0	5.8	0.1	0.5	1.3	0.5
	100	1.1	9.3	0.1	0.5	1.8	0.6
	150	1.1	42.0	0.2	0.4	7.9	0.6
	200	1.1	6.5	0.2	0.2	0.8	0.6
Ponnani	20	0.9	0.3	0.1	0.1	0.4	0.5
	50	1.0	4.6	0.1	0.6	0.7	0.5
	100	1.1	31.3	0.2	0.3	1.5	0.5
	200	0.7	30.8	0.1	0.3	2.7	0.6
Cochin	20	1.5	2.4	0.0	1.9	4.8	0.5
	50	1.3	2.8	0.1	1.3	1.0	0.5
	75	1.4	4.8	0.1	1.1	1.5	0.7
	100	1.3	3.8	0.1	1.2	0.9	0.5
	150	0.6	5.0	0.1	0.2	0.6	0.6
	200	0.6	4.3	0.1	0.2	0.7	0.6
Alleppy	20	1.2	1.0	0.1	0.6	1.0	0.6
	50	1.2	3.4	0.1	0.9	1.6	0.6
	75	1.2	9.0	0.1	0.7	1.5	0.5
	100	1.0	60.3	0.1	0.8	2.7	0.6
	150	0.8	14.2	0.1	0.4	1.4	0.6
	200	0.9	13.7	0.1	0.4	1.5	0.6
Kollam	20	1.0	0.9	0.1	0.4	1.1	0.5
	50	1.4	4.3	0.1	1.4	3.2	0.5
	100	1.4	21.0	0.1	1.2	1.9	0.5
	200	1.2	26.5	0.1	0.6	6.5	0.5
Trivandrum	20	0.8	10.6	0.1	1.3	14.2	0.9
	50	1.4	3.8	0.1	1.4	1.9	0.7
	100	1.1	53.6	0.1	0.8	3.2	0.5
	200	0.7	22.9	0.1	0.3	1.8	0.6

Estuary

St.No	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
1	3.0	1.1	1.6	0.0	2.2	0.5	0.5
2	4.5	1.0	0.3	0.1	0.7	1.6	0.6
3	2.5	1.5	0.5	0.1	1.1	0.8	0.7
4	ND	1.2	0.4	0.1	0.7	0.6	0.6
5	1.5	1.0	1.1	0.0	1.6	0.5	0.5
6	ND	1.4	0.7	0.1	1.2	2.8	1.1
7	5.5	1.1	0.6	0.1	0.8	0.7	0.6
8	4.0	1.2	0.5	0.1	0.7	0.5	0.6
9	8.5	1.0	0.3	0.1	0.2	0.3	0.5

Table 4.3a. Enrichment factors of non-transition elements with respect iron along the study region during premonsoon.

Shelf

Transects	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
Manglore	20	0.2	0.7	0.0	0.1	0.3	0.4
	50	0.1	7.8	0.0	0.2	1.0	0.3
	100	0.1	4.6	0.0	0.1	0.2	0.2
	200	0.0	2.8	0.0	0.0	0.2	0.1
Kannoore	20	0.2	0.6	0.0	0.1	0.3	0.5
	50	0.1	2.3	0.0	0.2	1.5	0.3
	100	0.1	6.5	0.0	0.2	0.6	0.3
	200	0.1	4.2	0.0	0.1	0.5	0.2
Baypore	20	0.2	1.1	0.0	0.3	0.3	0.5
	50	0.1	4.2	0.0	0.3	0.6	0.3
	75	0.1	5.2	0.0	0.3	0.9	0.3
	100	0.1	4.2	0.0	0.1	0.6	0.2
	150	0.0	3.3	0.0	0.1	0.4	0.1
	200	0.1	2.4	0.0	0.1	0.2	0.1
Ponnani	20	0.2	0.4	0.0	0.1	0.3	0.5
	50	0.1	5.3	0.0	0.5	0.5	0.3
	100	0.1	12.2	0.0	0.1	1.0	0.1
	200	0.1	3.1	0.0	0.1	0.7	0.2
Cochin	20	0.2	2.2	0.0	1.4	1.1	0.5
	50	0.3	7.1	0.0	1.9	2.8	0.6
	75	0.2	3.9	0.0	1.2	0.8	0.4
	100	0.2	5.0	0.0	1.1	0.6	0.4
	150	0.0	2.1	0.0	0.0	0.1	0.1
	200	0.0	1.5	0.0	0.0	0.1	0.1
Alleppy	20	0.2	1.3	0.0	0.7	0.6	0.5
	50	0.2	3.8	0.0	0.7	0.9	0.3
	75	0.2	9.3	0.0	0.7	0.8	0.4
	100	0.2	17.6	0.0	0.7	1.2	0.3
	150	0.1	9.2	0.0	0.3	0.7	0.2
	200	0.1	10.0	0.0	0.3	1.2	0.2
Kollam	20	0.2	1.7	0.0	0.8	0.8	0.5
	50	0.1	3.9	0.0	0.1	0.3	0.2
	100	0.1	6.2	0.0	0.6	1.1	0.3
	200	0.1	20.3	0.0	0.4	1.2	0.3
Trivandrum	20	0.1	5.2	0.0	0.4	1.5	0.3
	50	0.2	3.7	0.0	1.1	1.8	0.5
	100	0.2	28.7	0.0	0.6	0.9	0.3
	200	0.0	3.9	0.0	0.1	0.3	0.1

Estuary

St.No	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
1	3.0	1.1	1.7	0.0	2.4	0.5	0.5
2	4.5	1.1	0.3	0.1	0.8	0.9	0.6
3	2.5	1.3	0.5	0.1	1.0	1.0	0.6
4	ND	1.2	0.5	0.1	0.7	13.9	0.6
5	1.5	0.9	1.4	0.0	1.7	8.6	0.5
6	ND	1.4	0.6	0.1	1.3	2.2	1.0
7	5.5	1.3	0.6	0.1	1.0	0.7	0.7
8	4.0	1.3	2.4	0.1	2.0	26.7	0.6
9	8.5	1.0	0.3	0.1	0.3	0.4	0.5

Table 4.3b. Enrichment factors of non-transition elements with respect iron along the study region during monsoon.

Shelf

Transects	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
Manglore	20	0.2	0.9	0.0	0.1	0.4	0.5
	50	0.2	4.7	0.0	0.3	0.8	0.3
	100	0.1	4.4	0.0	0.1	0.3	0.1
	200	0.0	2.9	0.0	0.0	0.2	0.1
Kannoore	20	0.2	0.2	0.0	0.1	0.9	0.5
	50	0.2	2.5	0.0	0.3	1.6	0.4
	100	0.2	7.1	0.0	0.2	0.6	0.3
	200	0.1	4.3	0.0	0.1	0.3	0.2
Baypore	20	0.2	0.5	0.0	0.1	0.4	0.5
	50	0.1	5.3	0.0	0.4	1.3	0.4
	75	0.1	5.4	0.0	0.3	0.7	0.3
	100	0.1	6.8	0.0	0.2	0.8	0.3
	150	0.0	13.6	0.0	0.1	1.6	0.1
	200	0.1	2.7	0.0	0.1	0.2	0.2
Ponnani	20	0.2	0.4	0.0	0.1	0.3	0.5
	50	0.1	4.2	0.0	0.3	0.4	0.3
	100	0.1	14.5	0.0	0.1	0.4	0.2
	200	0.0	7.1	0.0	0.0	0.4	0.1
Cochin	20	0.4	4.3	0.0	2.1	5.2	0.6
	50	0.3	4.2	0.0	1.2	0.9	0.5
	75	0.1	3.1	0.0	0.4	0.6	0.3
	100	0.2	5.1	0.0	0.9	0.7	0.4
	150	0.0	1.6	0.0	0.0	0.1	0.1
	200	0.0	1.3	0.0	0.0	0.1	0.1
Alleppy	20	0.2	1.3	0.0	0.5	0.8	0.5
	50	0.1	3.1	0.0	0.5	0.9	0.3
	75	0.1	8.5	0.0	0.4	0.8	0.3
	100	0.1	30.5	0.0	0.2	0.8	0.2
	150	0.0	5.6	0.0	0.1	0.3	0.1
	200	0.1	6.4	0.0	0.1	0.4	0.2
Kollam	20	0.2	1.3	0.0	0.3	0.9	0.4
	50	0.2	5.1	0.0	1.0	2.3	0.4
	100	0.2	21.7	0.0	0.8	1.2	0.3
	200	0.1	19.7	0.0	0.3	2.9	0.2
Trivandrum	20	0.0	4.0	0.0	0.3	3.2	0.2
	50	0.2	3.3	0.0	0.7	1.0	0.4
	100	0.1	31.3	0.0	0.3	1.1	0.2
	200	0.0	6.4	0.0	0.1	0.3	0.1

Estuary

St.No	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
1	3.0	3.4	38.1	0.0	32.1	7.1	6.7
2	4.5	0.9	2.1	0.0	3.0	6.5	2.5
3	2.5	0.9	2.6	0.0	3.0	2.3	2.0
4	ND	1.0	2.4	0.0	2.7	2.5	2.3
5	1.5	1.8	16.4	0.0	14.1	4.4	4.2
6	ND	0.8	2.9	0.0	3.1	7.0	2.9
7	5.5	1.0	3.9	0.0	3.5	2.9	2.4
8	4.0	0.9	2.9	0.0	2.7	2.0	2.1
9	8.5	1.0	1.8	0.0	1.0	1.4	2.2

4.2.4 Elemental excess

The elemental concentration, in excess of its supply from global shale like terrigenous particles, is called the elemental excess (El_{ex}). This represents the structurally bound detrital component to the total concentration of that element in the sediment. The high elemental excess generally indicates alternate source of that element other than Post Archaean Australian Shale (PAAS). The elemental excess along the study region showed negative values for some of the samples (Table 4.4a & Table 4.4b).

Along the shelf, premonsoon season was normally characterised by higher values than monsoon. All stations, except at nearshore depths (20 m) showed positive El_{ex} for Sr, which was 50-60 % of the total metal concentration. Pb showed positive values along the southern transects, whereas barium showed positive values along the mid-depth of southern zone. Sr showed strong positive correlation with $CaCO_3$ reflecting the well known association of Sr with calcite in the carbonate phase (Table 4.5 & Table 4.6).

It is thought that Sr is present mainly in the calcareous shells of organisms. Foraminifers and coccoliths are known to contain Sr up to 1750 ppm, part of which, are diagenetically added (Turekian, 1964; Ramalingam et al., 2005). Acantharid skeletons made up of celestite ($SrSO_4$) are also important contributors of Sr to marine sediments (Turekian, 1977). In Cochin estuary, almost all metals (except Pb) showed mostly negative or very low values in El_{ex}. Lead showed positive values in the central zone and at station 8 during premonsoon and at stations 2 & 6 during monsoon. Gallium showed positive values at stations 4, 5, 6 & 8 during premonsoon.

Table 4.4a. Elemental excess (non-transition elements) along the study region during premonsoon.

Shelf

Transects	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
Manglore	20	0.2	0.9	0.0	0.1	0.4	0.5
	50	0.2	4.7	0.0	0.3	0.8	0.3
	100	0.1	4.4	0.0	0.1	0.3	0.1
	200	0.0	2.9	0.0	0.0	0.2	0.1
Kannoore	20	0.2	0.2	0.0	0.1	0.9	0.5
	50	0.2	2.5	0.0	0.3	1.6	0.4
	100	0.2	7.1	0.0	0.2	0.6	0.3
	200	0.1	4.3	0.0	0.1	0.3	0.2
Baypore	20	0.2	0.5	0.0	0.1	0.4	0.5
	50	0.1	5.3	0.0	0.4	1.3	0.4
	75	0.1	5.4	0.0	0.3	0.7	0.3
	100	0.1	6.8	0.0	0.2	0.8	0.3
	150	0.0	13.6	0.0	0.1	1.6	0.1
	200	0.1	2.7	0.0	0.1	0.2	0.2
Ponnani	20	0.2	0.4	0.0	0.1	0.3	0.5
	50	0.1	4.2	0.0	0.3	0.4	0.3
	100	0.1	14.5	0.0	0.1	0.4	0.2
	200	0.0	7.1	0.0	0.0	0.4	0.1
Cochin	20	0.4	4.3	0.0	2.1	5.2	0.6
	50	0.3	4.2	0.0	1.2	0.9	0.5
	75	0.1	3.1	0.0	0.4	0.6	0.3
	100	0.2	5.1	0.0	0.9	0.7	0.4
	150	0.0	1.6	0.0	0.0	0.1	0.1
	200	0.0	1.3	0.0	0.0	0.1	0.1
Alleppy	20	0.2	1.3	0.0	0.5	0.8	0.5
	50	0.1	3.1	0.0	0.5	0.9	0.3
	75	0.1	8.5	0.0	0.4	0.8	0.3
	100	0.1	30.5	0.0	0.2	0.8	0.2
	150	0.0	5.6	0.0	0.1	0.3	0.1
	200	0.1	6.4	0.0	0.1	0.4	0.2
Kollam	20	0.2	1.3	0.0	0.3	0.9	0.4
	50	0.2	5.1	0.0	1.0	2.3	0.4
	100	0.2	21.7	0.0	0.8	1.2	0.3
	200	0.1	19.7	0.0	0.3	2.9	0.2
Trivandrum	20	0.0	4.0	0.0	0.3	3.2	0.2
	50	0.2	3.3	0.0	0.7	1.0	0.4
	100	0.1	31.3	0.0	0.3	1.1	0.2
	200	0.0	6.4	0.0	0.1	0.3	0.1

Estuary

St.No	Depth (m)	Rb	Sr	Cs	Ba	Pb	Ga
1	3.0	3.4	38.1	0.0	32.1	7.1	6.7
2	4.5	0.9	2.1	0.0	3.0	6.5	2.5
3	2.5	0.9	2.6	0.0	3.0	2.3	2.0
4	ND	1.0	2.4	0.0	2.7	2.5	2.3
5	1.5	1.8	16.4	0.0	14.1	4.4	4.2
6	ND	0.8	2.9	0.0	3.1	7.0	2.9
7	5.5	1.0	3.9	0.0	3.5	2.9	2.4
8	4.0	0.9	2.9	0.0	2.7	2.0	2.1
9	8.5	1.0	1.8	0.0	1.0	1.4	2.2

Table 4.4b. Elemental excess (non-transition elements) along the study region during monsoon.

Shelf							
Transects	**Depth (m)**	**Ga**	**Rb**	**Sr**	**Cs**	**Ba**	**Pb**
Manglore	20	-9.70	-129.31	16.69	-13.55	-586.85	-12.23
	50	-1.86	-21.18	354.31	-2.79	-60.76	2.10
	100	-2.62	-34.64	1048.15	-3.76	-145.17	2.18
	200	-1.78	-35.86	893.69	-3.63	-144.48	1.68
Kannoore	20	-11.33	-161.24	-194.90	-16.34	-706.27	-0.82
	50	-1.59	-22.98	96.22	-2.50	-71.26	4.91
	100	-4.30	-55.57	994.14	-5.97	-224.60	-0.29
	200	-2.98	-42.57	964.59	-4.47	-174.62	1.33
Baypore	20	-13.37	-175.88	-127.19	-17.73	-761.34	-14.09
	50	-2.83	-37.92	329.65	-3.99	-80.18	4.07
	75	-1.84	-25.58	347.80	-2.72	-62.57	1.22
	100	-1.82	-25.85	607.94	-2.77	-71.70	3.20
	150	-1.14	-15.97	1776.46	-1.64	-46.84	18.02
	200	-2.86	-45.63	736.50	-4.74	-194.43	-1.28
Ponnani	20	-14.01	-186.26	-152.96	-18.71	-804.69	-17.97
	50	-4.21	-54.09	558.00	-5.75	-115.44	-2.52
	100	-1.63	-21.99	1835.30	-2.29	-76.70	1.87
	200	-1.26	-20.56	1513.92	-2.04	-67.70	5.23
Cochin	20	-1.79	-19.46	108.28	-2.70	105.26	13.97
	50	-3.95	-45.77	293.17	-5.67	81.91	0.33
	75	-1.76	-33.03	408.44	-4.08	21.30	3.21
	100	-4.91	-60.50	557.35	-7.37	54.00	-1.29
	150	-3.60	-66.38	691.46	-6.64	-242.51	-3.34
	200	-3.49	-66.24	576.86	-6.64	-238.13	-3.08
Alleppy	20	-5.23	-73.22	86.02	-8.41	-148.04	-0.04
	50	-2.44	-32.55	247.34	-3.75	-17.91	3.07
	75	-2.57	-33.81	784.90	-3.85	-60.15	2.61
	100	-1.04	-15.76	2501.22	-1.70	-15.95	4.25
	150	-2.08	-34.22	1156.23	-3.56	-97.64	2.11
	200	-2.64	-39.57	1314.93	-4.17	-109.78	2.97
Kollam	20	-12.81	-159.78	141.61	-17.30	-528.87	3.62
	50	-1.56	-18.70	201.53	-2.37	45.06	7.41
	100	-2.44	-29.56	1790.03	-3.71	35.02	5.00
	200	-1.91	-24.84	1793.60	-2.73	-54.77	23.23
Trivandrum	20	-0.31	-14.14	352.51	-1.49	21.08	28.20
	50	-0.93	-19.92	188.06	-2.56	44.12	3.40
	100	-0.95	-12.92	1852.39	-1.44	-12.49	4.57
	200	-1.78	-27.95	1510.35	-2.84	-88.99	3.22

Shelf							
St.No	**Depth (m)**	**Ga**	**Rb**	**Sr**	**Cs**	**Ba**	**Pb**
1	3.0	-10.17	-114.30	293.09	-13.87	704.72	-9.71
2	4.5	-17.12	-268.76	-214.63	-30.11	-377.19	26.12
3	2.5	-8.68	-157.87	-29.78	-20.80	48.12	-5.10
4	ND	-17.38	-241.16	-164.94	-27.94	-450.70	-15.10
5	1.5	-11.83	-143.76	199.56	-16.57	454.45	-11.43
6	ND	0.55	-23.92	5.79	-2.97	33.58	7.66
7	5.5	-6.80	-98.43	-10.49	-11.33	-87.79	-5.01
8	4.0	-7.06	-98.49	-33.40	-11.13	-142.69	-7.53
9	8.5	-17.35	-226.45	-206.45	-23.96	-897.93	-23.97

4.3 Discussion

Metals are delivered to sediments in the form of detritus, clay and hydrogenous precipitates. Upon reaching the seafloor, metals are subjected to physical and chemical changes, collectively called diagenesis. Most of the non-transition elements are lithophilic (affinity for silicates) in nature. These elements readily form ions constituting 8-electrons in their outermost shell. Goldschmidt (1954) pointed out some marked correlation between geochemical character and atomic volume. If the atomic volume of the elements is plotted against atomic number, the resulting curve shows maxima and minima, where the lithophile elements are located from the maxima to the declining sections of the curve.

Beryllium exists in ocean at low concentration compared to other non-transition elements. The levels in estuary however, are substantially high. Assuming that the element behaves conservatively during estuarine mixing and gets transported to ocean, the average residence time of the element is 800 years. The shorter residence time and high reactivity makes the geochemistry of this element so complex. The enrichments of Be along coastal belt of Kerala and in estuarine sediments indicates its major input from anthropogenic activity. The enrichment of Be in basins receiving a high fluvial flux can be better explained from the low $^{10}Be/^{9}Be$ ratios reported for molluscan carbonate in the Mediterranean (Kaufman et al., 1983). However, Be is scavenged onto particulates implying that fluvial Be is remobilized from the particles during estuarine mixing. The southwards increase of Be concentrations indicate its efficient and rapid cycling in the shelf.

Aluminium in marine sediments is principally derived from alumino-silicate, which are generally detrital (Kolla et al., 1976; McMurtry and Yeh, 1981; Pattan, 2002). It is also derived from the alteration of marine volcanic rocks, hydrothermal exhalations and authigenic growth (Cronan, 1980; Pattan and Shane, 1999; Nameroff et al., 2002; Iyer et al., 2007). Hence, Al is used as one of the best indicator of terrigenous inputs to marine sediments. The low salinity and high Al along the nearshore region suggests a lateral input from fluvial sources, probably from Kerala coast. This implies that the lateral transport may have a significant contribution to these metals in the nearshore region. The advection from fluvial and weathering sources over the eolian source for these metals depends upon their mean residence time. It strongly suggests that coastal influence is the primary source for Al in this region. The Al concentrations decreased towards the deep suggesting that this metal is released from coastal input. In addition, the thermal gradient between nearshore and deeper region (6°–28°C) may have significant influence on the strongly hydrolyzed metals such as Al. At higher temperature (25 °C), the hydrolysis is also higher than at 5°C (Byrne et al., 1988). Hydrolyzed species [Al $(OH)^{4-}$] will be more soluble at higher temperature. The study brings out the importance of input fluxes, particle scavenging and mixing of water masses which regulate the distribution of elements in the estuarine, coastal and shelf regions. The estuarine metal distribution is additionally controlled by fluvial input (Nath, 2000) and industrial activities (Shibu et al., 1995).

Gallium behaves conservatively over the space and time scales. However, rivers might be the source of Ga to this area. Ga has substantially higher fluvial as well as coastal concentrations than in the ocean. Laboratory experiments by Moran and Moore (1991) showed that resuspended sediments could act as a source of dissolved Al causing depletion in a high energy boundary area. Given the geochemical similarity of Ga and Al, it is expected to have low concentration of Ga at high energy zones. The high coastal accumulation of Al than Ga is due to its preferential input from land masses. Sources of Ga include rivers and anthropogenic input associated with coal burning (Bertine and Goldberg, 1971). However, the residence time of gallium is longer, implying a decoupling of the processes that remove Ga from waters by siderophore (Emery and Hoffer, 1980), whereas Al is primarily incorporated into diatoms (Stoffyn, 1979). Various workers have shown that Al is rapidly removed by the biota from productive waters (Hydes, 1989), indicating greater reactivity of Al as compared to Ga.

The present study observed the high concentration of rubidium along nearshore stations along shelf indicating its anthropogenic or geographical nature. However, the low estuarine levels show its insignificant contribution from anthropogenic activities. Biscaye and Dasch (1971) reported that Rb in marine sediments increase with decrease in particle size, the highest contents being in the clay-size fractions. This element probably occupies crystalline sites in illite (Horstman, 1957) and could be the reason for its high concentrations in the mud compared to sand (Table 4.5 and Table 4.6).

Based on data from this study, the Sr in shelf sediments was higher than that in the estuary. Fine-grained particles deposited in nearshore regions represent another source of Sr to the oceans (Yingfeng and Franco, 2004). This indicates its very conservative nature and its lithogenic origin. The high Sr stored in the shelf sediment are as ion-exchangeable and reducible components, which are remobilized under elevated ion-strength seawater and increase the hypoxic/anoxic conditions (Roberta et al., 2001). Our study observed that the seasonal effect has a less impact on the abundance of Sr. However, seasonal changes in the environment (temperature, salinity) induces episodic biologic (bioturbation, anoxia, storms, submarine slumps and slides) release of Sr from the surface sediments (Wang et al., 2001).

The moderately high concentration of cesium along nearshore station and in estuary reveals its origin from Western Ghats, which are transported by rivers. Cesium released to river water by weathering of rocks and minerals is rapidly adsorbed by soil, especially clay (Kabata-Pendias, 2001) and therefore, tend to remain in sediment. Sand generally contains less Cs than finer sediments. Hirst (1962) and Vincent et al. (2005) reports values of 1–3.2 ppm for modern marine sand and 7.9-3 ppm in modern marine clay. Cesium has a strong tendency to bind with clay, because their finer grain size supports more exchange sites.

Barium showed a very high accumulation along the southern shelf compared to the northern shelf indicating its relation to productivity. The particulate barium fluxes in the water column and sediments highlight the relation between barite and primary production and provide quantitative information on the (paleo)-productivity of the oceans (Dehairs et al., 1980; Paytan et al., 1996; Jeandel et al., 2000; Moreno et al., 2004; Plewa et al., 2006). The settling of biogenic detritus with associated barite to the deep sea and the sediments explains the relationship between barite accumulation in the sediments and biological production in overlying surface waters observed originally by Turekian and Tausch (1964). During monsoon, the excess-Ba along the shelf (without a lithogenic component) indicates its coincidence with the phytoplankton bloom (Thresiamma et al., 2008). Additionally, the elevated concentration of barium excess along the southern shelf appears to be due to the presence of relict terrigenous sands. Very high sand content along this zone support this assumption (Table 3. 1 a & b). Calvert and Price (1983) have also observed slightly higher barium values for nearshore sediments of Namibia and ascribed it to be the presence of feldspars. The estuarine sediments contain higher organic matter (Figure 3.5c), which was however, depleted in Ba. This is probably because the high sedimentation in these areas has shallow sulphate reduction zones which may induce the diagenetic changes in Ba and obscure the productivity signals.

Lead also showed nearshore enrichment, but the variation is not significant. However, the high concentrations are found in the southern shelf compared to the northern zone, probably due to the input from estuaries, which are entraining to Arabian Sea and associated coastal process. The scavenging of Pb during upwelling (Salamanca, 1993) was estimated through ^{210}Pb distribution as it crosses the shelf. On the other hand, large amount of sinking particles following the high primary productivity (Bauer et al., 1991; Prassanna kumar et al., 2000) allows a rapid net flux into the sediments and hence, a short residence time of Pb in the water column. In anoxic waters, it is removed rapidly as insoluble PbS, commonly as an independent sulphide rather than in solid as pyrite (Morse and Luther, 1999) causes an increase towards deeper stations. Lead is easily removed from the water column by adsorption to mineral particles and subsequent scavenging by Fe-Mn hydroxide precipitate. Also, Pb is rapidly scavenged to the anoxic sediments; it has a short residence time in the water column, preventing its sedimentation. These could be the reason for observed high levels of normalisation factor, enrichment factor and metal excess for lead along the southern zone. Several studies reported Pb concentration in the range 17.9 to 80.9 ppm along the Kerala coast, which are comparable with the present study (Rajamaniamma, 1994; Siby, 2004; Balachandran et al., 2005). The mild fluctuations in Pb concentrations indicate that anthropogenic inputs were of minor importance, in contrast to other areas around the world. The anthropogenic input of lead into this estuary seems to be significant, as very high concentrations are encountered at certain stations along northern and central estuary. The estuarine enrichment can be attributed to the sedimentation of metal associated suspended solids and to flocculation due to increasing salinity. The residual fractions of lead in middle region are found to be an order of magnitude higher than those at less saline regions; even though the carbonate bound lead is uniformly present (Nair et al., 1991). Additionally, the high Pb concentration observed in the estuary could be due to the recent anthropogenic influence. Pb deposited in sediments can be modified by bio-turbation, re-suspension and redistribution of particles and pollutants. Salamanca (1989) observed that the bioturbation is an order of magnitude higher in the first 10 cm of the sediment column, which probably control lead accumulation in Cochin estuarine system.

The textural and organic characteristics of coastal and estuarine sediments were reflected in their geochemical properties (Table 4.5 and Table 4.6). The distribution of elements in the estuary indicates a point-source either by industrial/river transported during weathering of rocks. The Cochin estuarine sediments are known to contain Kaolinite depositions (Nath et al., 2000; Laluraj et al., 2006), which is mostly related to chemical weathering. The sediment traverses through lateritic terrains during which, it is subjected to intense chemical weathering under a humid, tropical climate (Nath et al., 2000). Under these conditions, alkali and alkaline earth elements are leached to produce Kaolinite (Weaver, 1989). The difference in weathering pattern of alkali and alkaline earth metals was noted by Nesbitt et al. (1980). They examined the distribution of alkali and alkaline earth elements in a weathering profile on granodiorite and noted that larger cations (Rb, Cs) were fixed in weathering profile owing to ion exchange processes; whereas smaller cations were lost in solution.

Table 4.5. Pearson correlation for non-transition elements with biogeochemical parameters along the shelf sediments during monsoon and premonsoon (metals are in ppm).

Premonsoon

	Be	Rb	Sr	Cs	Ba	Pb	Ga	Al (%)	Fe (%)	Silt %	Clay %	Sand %	DO (ml/l)	Temp (°C)	Org.C %	$CaCO_3$ %
Be	1															
Rb	0.45	1														
Sr	-0.05	-0.45	1													
Cs	0.61	0.87	-0.35	1												
Ba	-0.19	0.44	-0.28	-0.05	1											
Pb	-0.06	0.06	0.25	-0.04	0.25	1										
Ga	0.63	0.94	-0.46	0.91	0.25	0.01	1									
Al (%)	0.62	0.94	-0.46	0.94	0.21	-0.04	0.99	1								
Fe(%)	0.88	0.24	0.08	0.43	-0.29	0.02	0.44	0.39	1							
Silt %	0.30	0.66	-0.20	0.67	0.08	-0.06	0.59	0.63	0.12	1						
Clay %	0.26	0.63	-0.19	0.70	0.00	-0.18	0.66	0.71	0.08	0.48	1					
Sand %	-0.33	-0.75	0.23	-0.79	-0.06	0.13	-0.72	-0.77	-0.12	-0.91	-0.80	1				
DO(ml/l)	-0.04	0.45	-0.67	0.42	0.17	-0.21	0.44	0.49	-0.27	0.20	0.40	-0.33	1			
Temp(°C)	-0.18	0.43	-0.65	0.32	0.30	-0.18	0.37	0.42	-0.42	0.21	0.34	-0.30	0.94	1		
Org.C %	0.17	-0.20	0.74	0.01	-0.41	0.18	-0.20	-0.18	0.25	0.05	0.08	-0.07	-0.56	-0.66	1	
$CaCO_3$ %	0.02	-0.49	0.84	-0.31	-0.43	0.01	-0.49	-0.46	0.19	-0.07	-0.25	0.17	-0.65	-0.67	0.70	1

Monsoon

	Be	Ga	Rb	Sr	Cs	Ba	Pb	Fe (%)	Al (%)	Silt %	Clay %	Sand %	DO (ml/l)	W.T.B	Org.C %	$CaCO_3$ %
Be	1															
Ga	0.65	1														
Rb	0.50	0.96	1													
Sr	-0.17	-0.45	-0.45	1												
Cs	0.52	0.95	0.93	-0.36	1											
Ba	0.05	0.23	0.37	-0.34	0.04	1										
Pb	0.06	0.25	0.27	-0.07	0.23	0.20	1									
Fe(%)	0.93	0.58	0.40	-0.06	0.50	-0.21	-0.05	1								
Al (%)	0.61	0.99	0.96	-0.43	0.95	0.26	0.26	0.53	1							
Silt %	0.40	0.70	0.77	-0.18	0.81	0.04	0.12	0.37	0.70	1						
Clay %	0.23	0.72	0.68	-0.20	0.77	-0.05	0.33	0.26	0.74	0.47	1					
Sand %	-0.39	-0.82	-0.85	0.21	-0.92	-0.01	-0.24	-0.38	-0.83	-0.92	-0.78	1				
DO(ml/l)	0.12	0.59	0.61	-0.47	0.60	0.09	0.09	0.09	0.60	0.34	0.63	-0.52	1			
W.T.B	-0.14	0.46	0.55	-0.66	0.44	0.41	0.20	-0.27	0.49	0.28	0.42	-0.39	0.64	1		
Org.C %	0.09	-0.12	-0.15	0.74	0.00	-0.41	0.19	0.19	-0.12	0.16	0.12	-0.16	-0.33	-0.62	1	
$CaCO_3$ %	-0.04	-0.42	-0.47	0.93	-0.33	-0.43	-0.17	0.10	-0.42	-0.15	-0.19	0.19	-0.51	-0.79	0.80	1

Table 4.6. Pearson correlation for non-transition elements with biogeochemical parameters along the estuarine sediments during monsoon and premonsoon (metals are in ppm).

Premonsoon

	Be	Ga	Rb	Sr	Cs	Ba	Pb	Fe (%)	Al (%)	Silt %	Clay %	Sand %	D.O (ml/l)	Sal	Org.C %	CaCO$_3$ %
Be	1															
Ga	0.99	1														
Rb	0.99	0.99	1													
Sr	0.17	0.14	0.23	1												
Cs	0.84	0.86	0.84	-0.16	1											
Ba	0.44	0.43	0.48	0.87	0.01	1										
Pb	0.37	0.36	0.41	0.34	0.26	0.23	1									
Fe(%)	0.96	0.96	0.95	-0.06	0.88	0.22	0.30	1								
Al (%)	0.97	0.98	0.98	0.30	0.85	0.52	0.42	0.90	1							
Silt %	0.34	0.30	0.42	0.49	0.05	0.51	0.48	0.29	0.34	1						
Clay %	-0.21	-0.10	-0.18	-0.32	-0.14	-0.19	0.03	-0.11	-0.19	-0.03	1					
Sand %	0.03	-0.06	-0.04	0.05	0.10	-0.07	-0.25	-0.04	0.01	-0.45	-0.88	1				
D.O(ml/l)	-0.45	-0.48	-0.50	-0.77	-0.18	-0.86	-0.42	-0.21	-0.58	-0.32	0.18	0.00	1			
Sal	-0.55	-0.52	-0.47	0.63	-0.64	0.34	0.18	-0.70	-0.39	0.12	0.16	-0.20	-0.38	1		
Org.C %	0.15	0.17	0.19	0.01	-0.08	0.18	0.24	0.23	0.09	0.67	0.60	-0.86	0.09	-0.05	1	
CaCO$_3$ %	-0.46	-0.45	-0.46	-0.47	0.04	-0.76	-0.35	-0.32	-0.41	-0.60	-0.11	0.38	0.64	-0.07	-0.54	1

Monsoon

	Be	Ga	Rb	Sr	Cs	Ba	Pb	Al (%)	Fe (%)	Silt %	Clay %	Sand %	D.O (ml/l)	Sal	Org.C %	CaCO$_3$ %
Be	1															
Ga	0.98	1														
Rb	0.98	0.98	1													
Sr	0.05	0.03	0.13	1												
Cs	0.83	0.78	0.74	-0.31	1											
Ba	0.26	0.29	0.35	0.91	-0.23	1										
Pb	0.63	0.76	0.62	-0.05	0.43	0.31	1									
Al (%)	0.98	0.96	0.95	0.17	0.81	0.36	0.67	1								
Fe(%)	0.94	0.96	0.94	-0.19	0.80	0.08	0.66	0.87	1							
Silt %	0.39	0.44	0.32	-0.31	0.28	-0.03	0.63	0.35	0.38	1						
Clay %	0.36	0.41	0.31	-0.51	0.56	-0.40	0.37	0.32	0.46	0.61	1					
Sand %	-0.41	-0.47	-0.35	0.48	-0.50	0.29	-0.51	-0.37	-0.47	-0.83	-0.95	1				
D.O(ml/l)	0.17	0.17	0.04	-0.48	0.47	-0.46	0.24	0.19	0.14	0.62	0.81	-0.82	1			
Sal	-0.26	-0.32	-0.24	0.67	-0.43	0.51	-0.23	-0.21	-0.47	-0.26	-0.41	0.40	-0.40	1		
Org.C %	0.69	0.73	0.64	-0.41	0.79	-0.22	0.61	0.66	0.75	0.65	0.91	-0.90	0.68	-0.40	1	
CaCO$_3$ %	-0.26	-0.33	-0.34	-0.56	0.30	-0.81	-0.48	-0.28	-0.18	-0.39	0.26	-0.02	0.33	-0.28	0.09	1

The observed high normalisation, enrichment factor and elemental excess for non-transition elements in the estuary, compared to the shelf sediment, clearly point its anthropogenic nature. Pollution in estuaries occurs by the direct introduction of sewage and industrial wastes and also by the transport of pollutants. Estuarine pollution is particularly relevant because of the fact that estuaries and their hinterlands are often sites of human settlement, commercial enterprise and recreation. Rivers are major sources of particulates and dissolved metals. The northern estuary exhibited high enrichment of all metals during both seasons. This could be expected since an annual loading of approximately 63 Mm^3 of effluents from 247 chemical industries situated on the upstream of the northern estuary could lead to such a gross pollution (Shibu et al., 1995; SCMC, 2004; Balachandran et al., 2005). Although estuaries dominate the transport of natural weathering products to the oceans, they are also involved in the transport of pollutants. This could be the reason for enrichment of non-transition elements along the shelf region. Material released into the sea may be swept out by the prevailing currents (Shankar, 2000) or get diluted with open ocean water and deposited along the shelf.

In Table 4.7, the concentrations of non-transition elements reported from some of the coastal and estuarine region are given. A comparison of these values with the average values for Kerala shelf region revealed that the sediments of shelf do not indicate any sign of pollution. However, the high values along the estuarine sediments hints towards contamination of sediments either by riverine or industrial activities.

Table 4.7. Comparison of non-transition elemental levels in the study region to that of other Indian and globally impacted coastal systems [(all in ppm, except Al (% dry weight)].

Elements	Be	Al	Ga	Rb	Sr	Cs	Ba	Pb	References
Bohai Bay, China	---	6.04	10.2	98	217	6.42	497	24.9	Zhang et al., 2002
Pearl estuary, China	---	8.5	13.1	151	68.4	12.4	444	97.1	Zhang and Wang, 2001
Sea bed sediment, U. K.	0.75	4.51	3	33	573	---	336	15	Stevenson, 2001
Central Indian Basin	---	5.2	---	---	248	---	1697	---	Banakar et al., 1998
Namibia, Atlantic coast	---	2.9	---	49	523	---	198	12	Calvert, 1976
Peru margin	---	8.9	---	59	311	---	314	18	Boning et al., 2004
Gulf of California	---	8.91	---	71	167	---	566	17	Brumsack, 2006
Mediterranean sapropels	---	7.7	---	48	693	---	228	11.3	Warning and Brumsack, 2002
Black Sea	---	6.7	---	55	870	---	604	18	Luschen, 2004
Medway Estuary U.K.	---	11.4	---	---	---	---	52	43	Spencer et al., 2006
Furlo, Italy	---	4.2	---	38	1600	4.7	1964	14	Turgeon and Brumsack, 2006
King George Island, Antarctica	---	3.2	---	---	63	---	41	10.5	Santos et al., 2005
Shelf of Kerala	0.80	4.2	4.8	15.4	797.5	0.74	146.8	10.8	Present study
Cochin Estuary	1.47	12.2	14.1	48.5	244.2	1.35	747.9	63	Present study

4.3.1 Statistical approach

To study the metal dependence on each variable and their relative importance in the prediction, multiple regression analysis was employed. Goodness of the best fit regression was tested using ANOVA and the percentage of variability explained was measured using r^2. Similar analysis was done separately for both seasons along the continental shelf and the estuarine system. The results of the multiple regression analysis are presented (Table 4.8a & Table 4.8b).

The study has considered only the significant values with $p<0.05$ to explain the geochemical variability. Along the continental shelf, the regression equation is significant for Sr, Rb, Ga, Cs and Be ($p < 0.0001$) during both seasons, whereas Pb and Ba are significant at $p < 0.05$ during premonsoon, and at $p < 0.05$ and $p < 0.01$ during monsoon, explaining almost all the variability. Al is a positive predictor for almost all elements, since it acts as scavenger of other elements enriched in clay minerals, oxy-hydroxides and particulate organic matter. This is confirmed by the high Al enrichment factor for non-transition elements compared to Fe enrichment factor. This revealed that Al controls the distribution of elements along the shelf of Kerala. In estuarine zone, the regression equation is significant $p < 0.05$ for Rb and Ga for both seasons and Be for premonsoon. The lack of correlation in estuary shows that metal accumulation is controlled by point sources rather than biogeochemical interaction as in shelf region. It may be noted that the processes resulting in the enrichment of elements are not by organic interaction, but through Al/Fe precipitation.

Table 4.8a. Multiple regression model for non-transition elements along the shelf sediments

Premonsoon					
Metal	**Fitted regression equation**	**Anova**	**% variability**	**Significant positive variable**	**Significant negative variable**
Sr	Sr=-206.37+38.910Al-33.204Fe-7.573Silt-0.538 Clay-229.342D.O +38.002Temp+144.956Org.C+93.024 CaCO$_3$	P<0.001	83.4	Org.C, CaCO$_3$	Silt, Clay
Rb	Rb=1.349+3.195Al-0.897Fe-0.01608 Silt-0.139Clay-2.730 D.O +0.363Temp-0.515Org.C-0.158 CaCO$_3$	P<0.001	93.7	Al	Fe, Clay
Pb	Pb=7.983+0.868Al-0.404 Fe - 0.0455 Silt - 0.172 Clay - 2.068 DO +0.278 Temp+1.663 Org. C - 0.324 CaCO3	P<0.05	2.2	---	---
Ga	Ga=0.536+0.946Al+0.122 Fe-0.001399 Silt-0.0001624Clay-0.401 D.O +0.04621Temp -0.1489Org.C -0.09985 CaCO$_3$	P<0.001	98.5	Al, Fe	CaCO$_3$
Cs	Cs= - 0.631+0.155 Al+0.03555Fe +0.04307 Silt -0.001041Clay +0.041276 D.O +0.0126Temp +0.113Org.C-0.00299 CaCO$_3$	P<0.001	92.7	Al, Org.C	---
Be	Be=-0.06834+0.06357 Al +0.109Fe-0.001145 Silt-0.004408Clay-0.003211 D.O +5.321Temp+0.03165Org.C-0.005945 CaCO$_3$	P<0.001	88.1	Al, Fe	---
Ba	Ba=258.041+42.404 Al -33.758Fe -1.466 Silt-3.765Clay-77.807 D.O +5.221 Temp - 20.82Org.C -3.584 CaCO$_3$	P<0.05	44.9	Al, Fe	---
Monsoon					
Metal	**Fitted regression equation**	**Anova**	**% variability**	**Significant positive variable**	**Significant negative variable**
Ga	Ga=0.109+0.139Fe+0.913Al +0.004185Silt +0.00314Clay +0.05130 DO +0.01184 Temp -0.008367Org.C-0.04144 CaCO$_3$	P<0.001	99.4	Fe & Al	
Sr	Sr=-575.048 -36.608 Fe+26.861Al +-2.290 Silt -4.633Clay -10.659 DO +269.673 Temp +27.9340 Org.C+163.062 CaCO$_3$	P<0.001	90.5	CaCO$_3$	
Rb	Rb=9.018-0.939Fe+3.412Al +0.0.09489Silt-0.125Clay +1.437 DO -0.299 Temp +0.380Org.C - 0.277 CaCO$_3$	P<0.001	7.6	Al, Silt	Fe, Clay
Pb	Pb=12.823-0.722Fe+1.071Al -0.125Silt -0.003369 Clay -2.521 DO +0.109 Temp +4.196 Org.C - 1.408 CaCO$_3$	P<0.05	43.9	Org.C	CaCO$_3$
Ba	Ba=250.47-24.981Fe+38.07Al -1.482 Silt-4. 264Clay -28.226 DO -3.8 Temp - 1.605Org.C- 1.533 CaCO$_3$	P<0.01	54.7	Al	Fe, Clay
Be	Be=0.02929 +0.142Fe+0.0558Al -0.001963 Silt-0.008173Clay -0.03987 DO +0.006752 Temp +0.03315Org.C- 0.009829 CaCO$_3$	P<0.001	88.2	Fe & Al	
Cs	Cs=-0.006615+0.0153Fe+0.113Al +0.01091 Silt +0.01070 Clay +0.008088 DO -0.006359 Temp +0.01024Org.C- 0.009054 CaCO$_3$	P<0.001	96.5	Al, Silt, Clay	

Table 4.8b. Multiple regression model for non-transition elements along the estuarine sediments.

Metal	Fitted regression equation	Anova	% variability	Significant positive variable	Significant negative variable
Monsoon					
Rb	Rb= -30.65+2.62 Al+6.5 Fe+0.19 Silt+0.92Clay+4.17Sal-16.58 Org.C+0.19 $CaCO_3$	$P<0.05$	100	Al, Fe	
Ga	Ga= -8.61+0.54 Al+0.46 Fe-0.09 Silt-0.96Clay-0.54Sal+2.46Org.C-36.9 $CaCO_3$	$P<0.05$	100		
Premonsoon					
Rb	Rb= 10.007+2.065 Al+2.923 Fe+0.338 Silt+ 0.0558Clay +0.0403 Sal-4.191 Org.C-0.391 $CaCO_3$	$p<0.05$	100		
Ga	Ga= -8.61+0.54 Al+0.46 Fe-0.09 Silt-0.96Clay-0.54Sal+2.46Org.C-36.9 $CaCO_3$	$p<0.05$	100	Al	
Be	Ga= -8.61+0.54 Al+0.46 Fe-0.09 Silt-0.96Clay-0.54Sal+2.46Org.C-36.9 $CaCO_3$	$p<0.05$	100		

4.4 Summary

1. Aluminium is the most abundant of all non-transition elements, which was distributed in high concentration in the nearshore sediments compared to the deeper ones. In the shelf sediments, high values were generally observed along the northern zone and also in the Kollam transects, indicating their terrigenous source.
2. Sr showed high enrichment in the deeper region, especially along the southern zone during both seasons, which is attributed to the high carbonate content in sediments.

3. Pb showed high enrichment along the shelf and estuarine sediments, indicating its anthropogenic inputs. Pb also showed redox character in oxygen deficient waters along the shelf region.
4. The enrichment factor based on Al was higher than the enrichment factor based on iron in the shelf sediments, whereas it was in the reverse order for the estuarine sediments. This may be due to the different geochemical affinity of Al and Fe in the two regions.
5. In the shelf sediments, the metal accumulation was high during premonsoon, whereas in Cochin estuary, it was during monsoon; indicating the response of environmental parameters on metal distributions in these regions.
6. The low barium content and high organic carbon may be due to the high sedimentation in the shelf region.
7. The high normalisation, enrichment and elemental excess for non-transition elements in the estuary compared to the shelf sediment, clearly points to their lateral inputs in the estuary.
8. Multiple regression studies revealed that Al controls the distribution of elements along the shelf sediments whereas the lack of correlation in estuary shows that metal accumulation is controlled by point sources rather than biogeochemical interaction as in shelf region.
9. The results of premonsoon and monsoon metal data revealed that tsunami has no effect on the distribution of non-transition metals along the shelf and estuary.

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Chapter 5

Geochemical index of transition elements along the shelf of Kerala and Cochin estuarine system

Contents

5.1 Introduction

The transition elements (TEs) are elements having a partially filled '*d*' sub-shell. The TEs have great importance in our lives; they are building blocks for life and are placed in the center of the periodic table. They are found everywhere on earth in various amounts. Most are not found in a pure substance, but rather in compounds buried in the earth's crust. This means that we must extract the metal from the compound in many ways. The interesting thing about transition metals is that their valence electrons. This is the reason why they often exhibit several common oxidation states. The TEs includes 30 elements in groups 3 through 12 of the periodic table. TEs have hundreds of responsibilities; they are key elements in life and evolution. For example, without iron, oxygen would n't make it to the brain and life would not exist. Iron and titanium are the most abundant transition elements. The TEs are ductile, malleable and conduct electricity and heat. They are used as catalysts for many industrial reactions. The bronze, iron, and steel ages would never have happened leaving us in the Stone Age. They have become of utmost importance due to our growing population and economy. Their demand will continue as long as life as we know it continues.

TEs have bio-importance but the toxic effects of many of them are of great concern. They are persistent environmental contaminants since they cannot be degraded or destroyed. In rocks, they exist as their ores in different chemical forms, from which they are recovered as minerals. TEs ores include sulphides, such as iron, zinc, cobalt and nickel sulphides; oxides such as manganese. Some exist and can be recovered as both sulphide and oxide ores such as iron, copper and cobalt. TEs are introduced into the environment by natural and anthropogenic causes. Anthropogenic sources are industries including mining sites, foundries and smelters, combustion by-products and traffics. Some TEs are important to man in medicinal and dietary allowances. The dietary intakes have to be maintained at regulatory limits, as excess will result in poisoning or toxicity (Duruibe, 2007). The harmful effects of heavy metals to the body are when consumed above limits. But the toxic effects, when unduly exposed to them could be potentially life threatening hence, cannot be neglected. While these TEs are in many ways indispensable, good precaution and adequate occupational hygiene should be taken in handling them. Although TEs poisoning could be clinically diagnosed and medically treated, the best option is to prevent heavy metal pollution and the subsequent poisoning. For the present study, 15 TEs were selected on the basis of abundance in nature, toxic effects and environmental interactions, are presented in annexure II.

The estimation of TEs in sediments is useful to assess the status of environmental characteristics, as sediments are potential indicators of the quality of overlying waters (Berrow, 1991; Rand et al., 2003; Singh et al., 2005). Once metals are discharged into the coastal environment, they get rapidly adsorbed onto particulates and are eventually incorporated to sediments (Forstner and Wittmann 1983; Hansen et al. 1993; Jain et al., 2004; Saeedi et al., 2004). The TEs associated with sediments are not essentially sheltered, and under changing environmental conditions, they are remobilized into the water column through various processes. Thus, in aquatic system, sediments may be both a carrier and a source. Although continental shelves cover only 7-9 % of the global oceans, the sediments on the margin are organic-rich and suboxic in nature, which influence the redox-sensitive elements (Legeleux et al., 1994; Anbar and Knoll, 2002). These conditions also create an oxygen minimum zone at intermediate waters in locations such as off Peru (Gulf of California), northwestern Africa, and India. Of these, the Arabian Sea encloses the major oxygen-deficient zones (<0.1 mL/L) from depths of 100 m to more than 1000 m (Qasim, 1982; Lothar et al., 2008). Under these conditions, trace elements change their oxidation states, mostly accompanied by a drastic change in solubility (Saager, 1994; Laluraj and Nair, 2006). These variations have been attributed to (i) the dissolution of Fe-Mn associated particulate matter (Saager et al., 1989), (ii) horizontal transport of particles from the shelf and slope sediments (Saager et al., 1989; Dickens and Owen, 1994), or (iii) mobilization of elements within the reducing sites provided by particle aggregates (Naqvi, 1994).

The west coast of India is under the influence of changing monsoons associated with wind patterns. The coastal currents are southerly from April to September and northerly from November to February. The coastal zone of western India experiences upwelling during summer monsoon (Banse 1959; Naqvi et al. 2000; Jayakumar et al., 2001). The increased productivity in the overlying waters during northeast monsoon (December-February) lead to higher consumption of oxygen intensifying the mid-depth oxygen deficiency and denitrification in the Arabian Sea (De'Souza et al., 1996; Mathupratap et al., 1996; Prasanna kumar et al., 2001; Satya and Ramesh, 2007). These oceanographic conditions are found to influence the biogeochemical cycling of transition metals in the surface sediments of west coast of India.

The present study focuses on the seasonal distribution of the selected TEs in the surficial sediments along the southwestern continental shelf of India as well as in the Cochin estuarine system. These elements share a common trait of being enriched in sediments under reducing conditions. The mechanism of authigic enrichment of TEs in sediments, along with their behavior has a vital role on the distribution of TEs in the region.

5.2 Results

5.2.1 Elemental distribution

Scandium

Scandium is rare in nature and is usually found only in two different kinds of ores. Thortveitite is the primary source of scandium with industrial by-products being an important source. Scandium showed nearshore enrichment followed by a decrease towards the seaward, a slight increase and again decrease towards deeper stations, except the northern most transects (Figure 5.1 a & b).

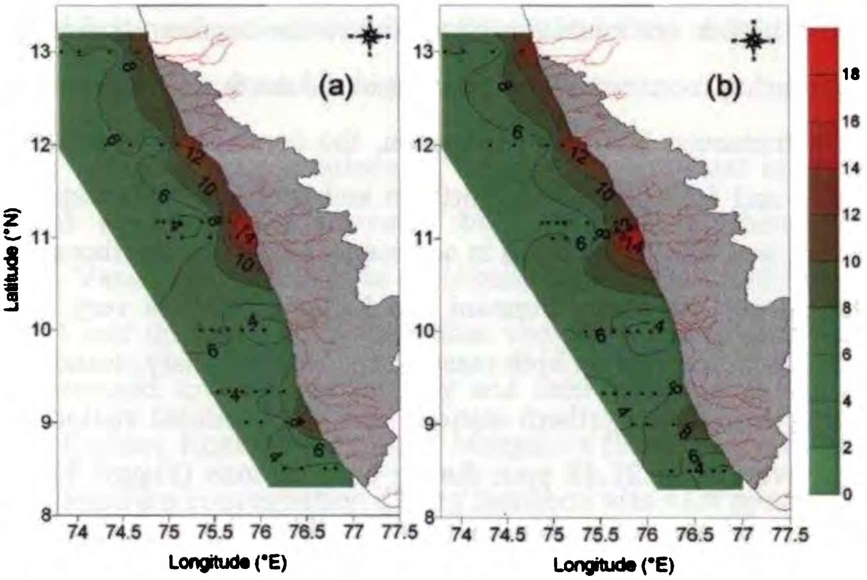

Figure 5.1 a&b. Distribution of scandium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

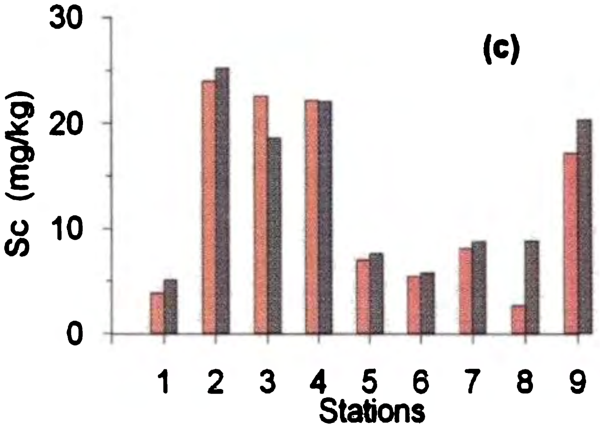

Figure 5.1 c. Distribution of scandium in the Cochin estuary during premonsoon (red) and monsoon (black).

The average Sc concentration along the nearshore sediments (20m) during monsoon was 9.61 ppm and 9.32 ppm during premonsoon. Scandium showed slight enrichment during premonsoon (average 6.1 ppm) compared to monsoon (average 5.6 ppm). The northern transect showed a higher accumulation compared to the southern transects. The average during monsoon was 6.56 ppm in the north and 4.74 ppm in the southern transects. During premonsoon, the corresponding values were 6.91 ppm and 5.32 ppm along northern and southern sides respectively. Scandium was rich (> 10 ppm) in sediments along the nearshore stations of Mangalore, Kannoore, Ponnani and Kollam, but was very low (2.4 ppm) at Kochi transect on both seasons. In Cochin estuary, scandium was very high along the northern stations and southernmost station (no. 9) with an average of 21.48 ppm during both seasons (Figure 5.1c). The remaining stations were poor in concentration with an average of 6.6 ppm. The stations closer to the industrial area (station 2) recorded high Sc levels, while it was very low at the barmouth (station 1) on both seasons. The average concentrations of scandium during monsoon and premonsoon were 13.5 and 12.5 ppm respectively. The average concentrations were 21, 6.1 and 12.6 ppm along the northern, central and southern zones of the estuary during monsoon, whereas they were 22.8, 5.4 and 9.3 ppm during premonsoon. The scandium concentration in the estuary indicates some point sources as industrial at the northern zone, whereas the southern most station has riverine inputs.

Vanadium

Vanadium is a ubiquitous element in the earth's crust, ranking 22nd in abundance with a mean concentration of 150 ppm. The main source of vanadium to the environment is the atmospheric fallout, sewage sludge, domestic wastewater and the industrial effluents specially fertilizers containing materials with high vanadium content. Most of the vanadium entering into the seawater is in suspension or adsorbed on colloids. It does not react chemically with seawater and passes mechanically through it. This is reflected in its association with silt on the sea bed. Only about 10% of the vanadium is present in a soluble form.

The very low concentrations of vanadium in seawater indicate its continuous removal from seawater, but the actual mechanisms are unknown. Vanadium contained in ascidians, holothurians, and in marine algae will end up in the silt. Vanadium showed a coastal enrichment, which decreased towards sea initially and then increased to the deep, except at Kollam, Kochi, Ponnani and Mangalore (Figure 5.2 a & b). The average vanadium concentration during monsoon was 41.4 ppm and 43.0 ppm during premonsoon. The northern region showed enrichment than the southern side. The average concentration of vanadium along the northern region during monsoon was 46.5 ppm, whereas it was 36.8 ppm along the southern side and during premonsoon it was 47.8 ppm and 38.6 ppm along the northern and southern regions respectively. During monsoon, the distribution of vanadium was almost uniform except some variations in the nearshore region, whereas it varied during premonsoon. The nearshore (20m) averages of vanadium during premonsoon and monsoon were 54.8 and 59.1 ppm respectively. The coastal enrichment probably indicates its origin from land. In Cochin estuary, vanadium and scandium behaved identically with high concentrations at the northern and southernmost station (9) and an average of 141.5 and 139.5 ppm during monsoon and premonsoon respectively (Figure 5.2c). The remaining stations showed concentrations < 59 ppm with an average of 44 ppm. The stations near the industrial zone (station 2) registered high values, while it was low at barmouth (station 1) during both seasons. Monsoon showed slightly higher concentrations (average 88.4 ppm) than premonsoon (average 84.4 ppm). The distribution of vanadium at the northern and southern most station indicates point sources either by industrial or riverine inputs.

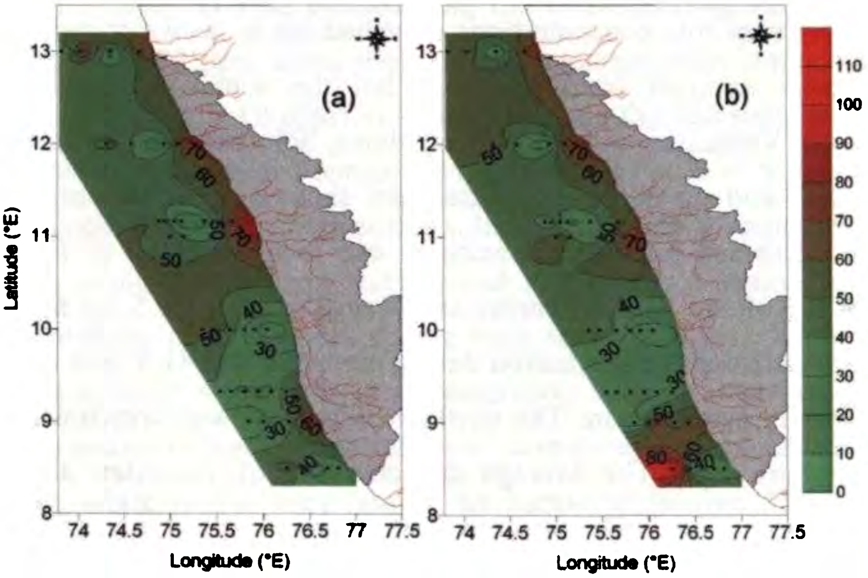

Figure 5.2 a&b. Distribution of vanadium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

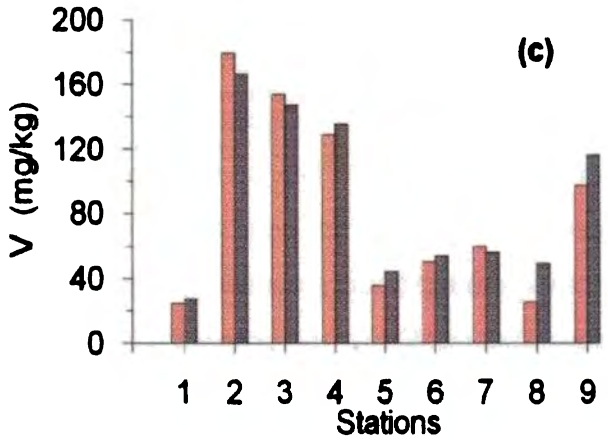

Figure 5.2 c. Distribution of vanadium in the Cochin estuary premonsoon (red) and monsoon (black).

Chromium

Chromium is a white, hard and lustrous metal existing in many oxidation states (I-VI). The principal source of chromium is metal processing, leather tanning, textile dyeing and laundry chemical industries. The biological role of Cr is interesting; it is toxic as well as essential to many mammals. Chromate ion has recently been suggested as a reference toxicant for aquatic phyto-toxicity tests (Wang, 1987). Cr has contributed to environmental contamination because of its wide industrial use.

Cr showed a nearshore enrichment, which decreased towards sea and showed a small enrichment in deeper stations. Chromium varied from 29.2 ppm to 182.2 ppm during monsoon and from 28.7 to 231.2 ppm during premonsoon (Figure 5.3 a & b). It showed slight accumulation during premonsoon compared to monsoon, but a coastal enrichment along the northern transects during monsoon was noticed. In Cochin estuary, it was high along the northern and southern most station (Station 9) with an average of 223.8 ppm during monsoon and 217.4 ppm during premonsoon (Figure 5.3 c). Other stations recorded the value of less than 81 ppm during both seasons (47-76 ppm during monsoon and 31-81 ppm during premonsoon). Very low chromium was observed at barmouth (station 1), which increased rapidly towards the industrial area (250 ppm) during monsoon. The average concentration during monsoon was 135.7 ppm and 126.1 ppm during premonsoon. This high concentrations in the northern and southern most stations clearly indicates its point sources either from industries or rivers.

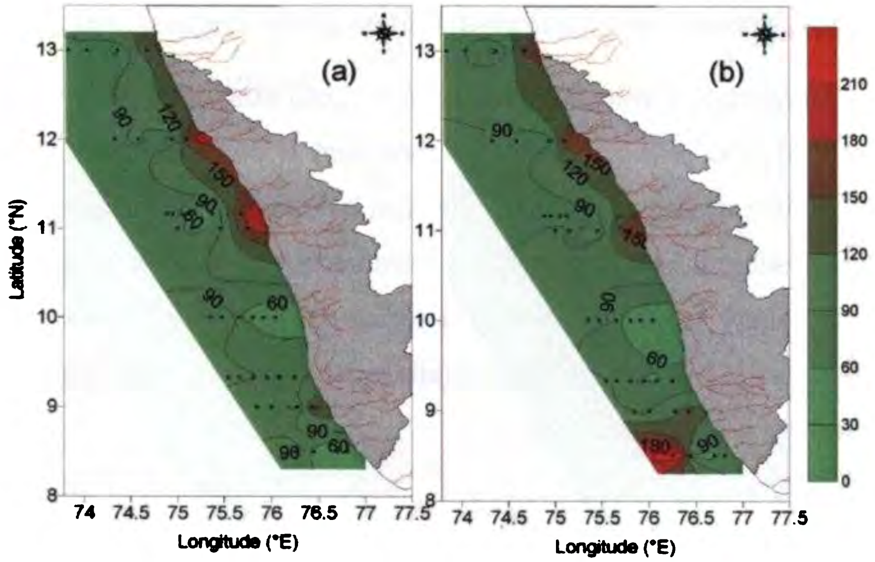

Figure 5.3 a&b. Distribution of chromium [mg/kg dry weight (ppm)] long the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

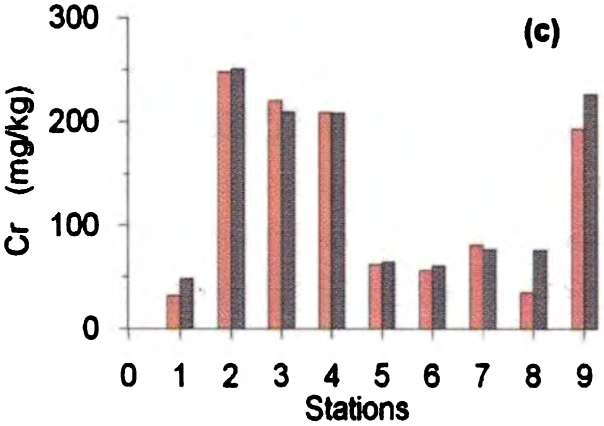

Figure 5.3 c. Distribution of chromium in the Cochin estuary premonsoon (red) and monsoon (black).

Manganese

Manganese is one of the most abundant metals in marine sediments, where it occurs as oxides and hydroxides with various oxidation states. It occurs principally as pyrolusite (MnO_2), and to a lesser extent as rhodochrosite ($MnCO_3$). Mn is an essential element for all species. Some organisms such as diatoms, molluscs and sponges, accumulate manganese. Manganese compounds exist naturally in the sediments and water. Manganese showed an identical distribution pattern during both seasons, generally a nearshore enrichment followed by a gradual decrease towards seaward stations and very low values were estimated at deeper stations (Figure 5.4 a & b).

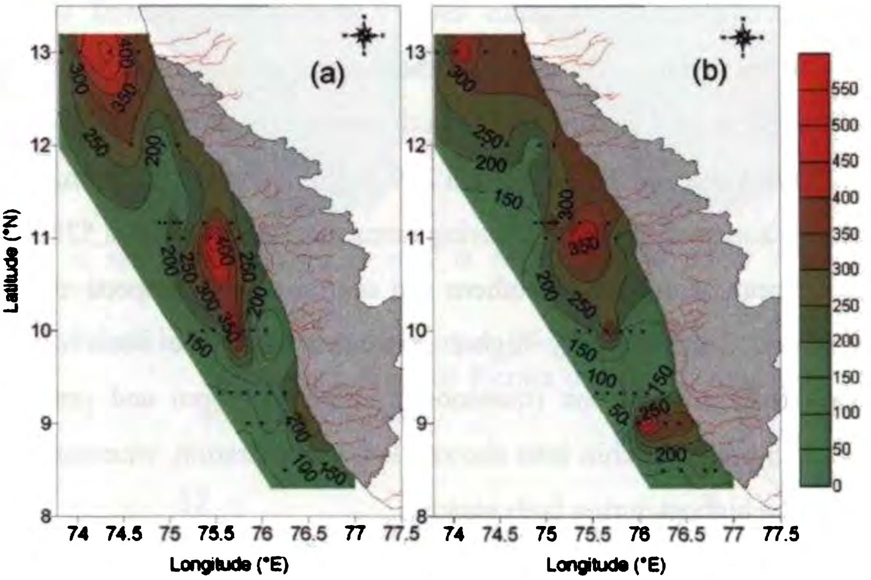

Figure 5.4 a&b. Distribution of manganese [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

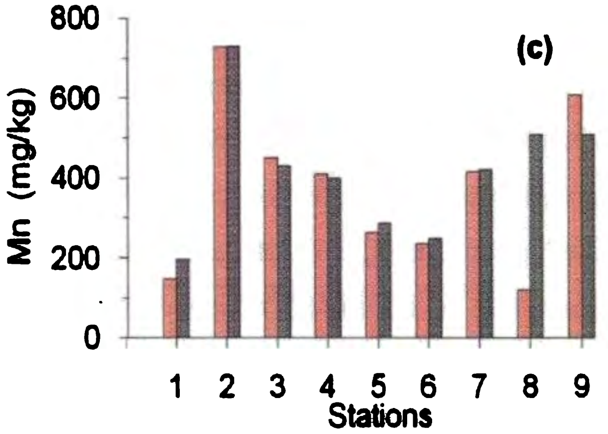

Figure 5.4 c. Distribution of manganese in the Cochin estuary premonsoon (red) and monsoon (black).

There was no enrichment during premonsoon compared to monsoon and the average concentrations were 247.5 ppm during premonsoon and 226.1 ppm during monsoon. It showed a northern enrichment (average 282.9 ppm), but was low towards the southern region (average 174.9 ppm) during monsoon. During premonsoon, it was 304.9 and 195.9 ppm respectively in the northern and southern zones. In Cochin estuary, manganese showed very high concentrations at the northern and southern zones and very low concentration was observed at central zone during both seasons (Figure 5.4c). The average concentrations were 519.1, 479.3 and 244.3 ppm along the northern, southern and central zones of the estuary during monsoon, whereas it was 528.7, 381.1 and 216.2 ppm at northern, southern and central estuary respectively during premonsoon. Comparatively higher concentrations were observed during monsoon than premonsoon (monsoon average 414 ppm and premonsoon average 375 ppm). Cochin inlet showed low concentration, whereas station 2 observed the highest during both seasons.

Iron

Iron is the fourth most abundant element in the earth's crust. While it is naturally released into the environment from weathering, it may also be released into the aquatic environment through human activities, such as burning of coke and coal, acid mine drainage, mineral processing, sewage, iron related industries and the corrosion of iron and steel. On reaching saltwater, suspended iron oxy-hydroxides are rapidly precipitated such that at salinities of 10 PSU or greater, the vast majority of the iron present occurs in particulate form and is effectively removed from solution. In anoxic marine waters, ferrous iron is mobilised from sediments and diffuses into the water column. Iron was the most abundant TEs observed along the study region during both seasons (Figure 5.5 a & b).

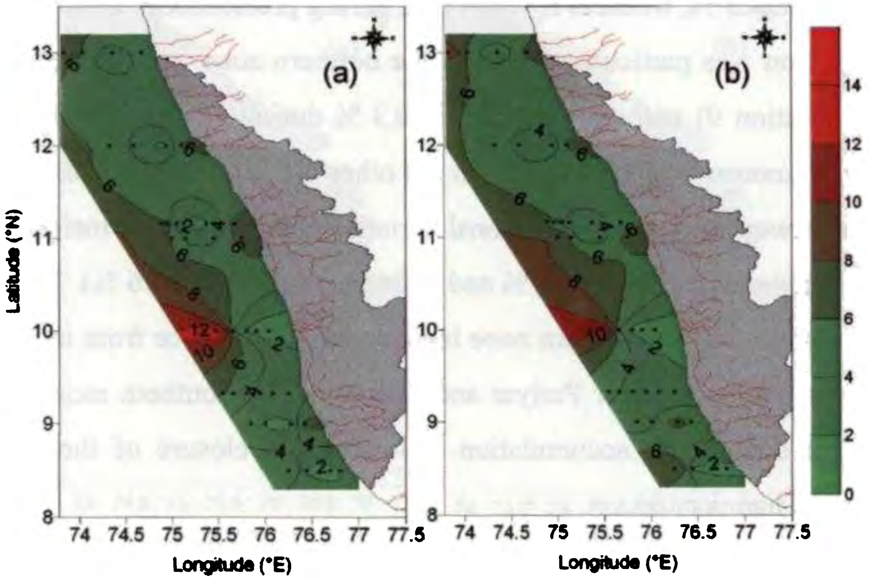

Figure 5.5 a&b. Distribution of iron (% dry weight) long the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

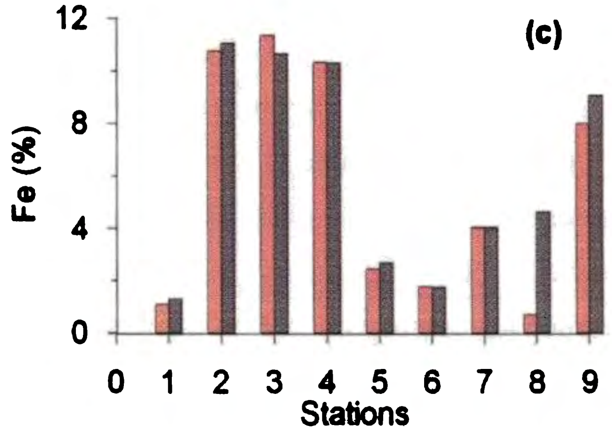

Figure 5.5 c. Distribution of iron in the Cochin estuary during premonsoon (red) and monsoon (black).

The average concentration of iron during monsoon was 4 %, and 4.4 % during premonsoon. Iron was uniformly high in the deeper stations (200 m) and along the shelf at Cochin (11%). The nearshore average of iron during monsoon was 5 %, whereas it was 4.6 % during premonsoon. In the Cochin estuary, iron was particularly high at the northern zone and southern most station (station 9) with an average of 10.3 % during monsoon and 10.1 % during premonsoon (Figure 5.5c). In the other estuarine stations, the values ranged between 4.6-0.70 %. Seasonal variation was found to be insignificant for iron (monsoon average 6.2 % and premonsoon average 5.6 %). The high concentrations in the northern zone indicate its point source from industries along the banks of River Periyar and that along the southern most station might be due to the accumulation following the closure of the salinity barrier at Thannirmukkam.

Cobalt

Cobalt is of relatively low abundance in the earth's crust and in natural waters, which gets precipitated as the highly insoluble cobalt sulfide CoS. Once entered in to the environment, Co reacts with other particles or adsorb on soil particles. Cobalt will mobilize only under acidic conditions, but ultimately most cobalt will end up in soils and sediments. In the marine environment, cobalt is needed by blue-green algae (cyanobacteria) and other nitrogen fixing organisms. However, in seawater, the metal is present primarily as the Co^{2+} ion and its chloro, sulfate, and carbonate complexes and is rapidly removed from the seawater, probably in association with MnO_2 (Knauer et al. 1982). In shallow waters, up to 98% of the metal can be found in the sediments and in suspended particulate matter (Robertson et al., 1973). Cobalt was enriched in the nearshore environment, which decreased towards seaward and a slight increase at deeper stations (Figure 5.6 a & b).

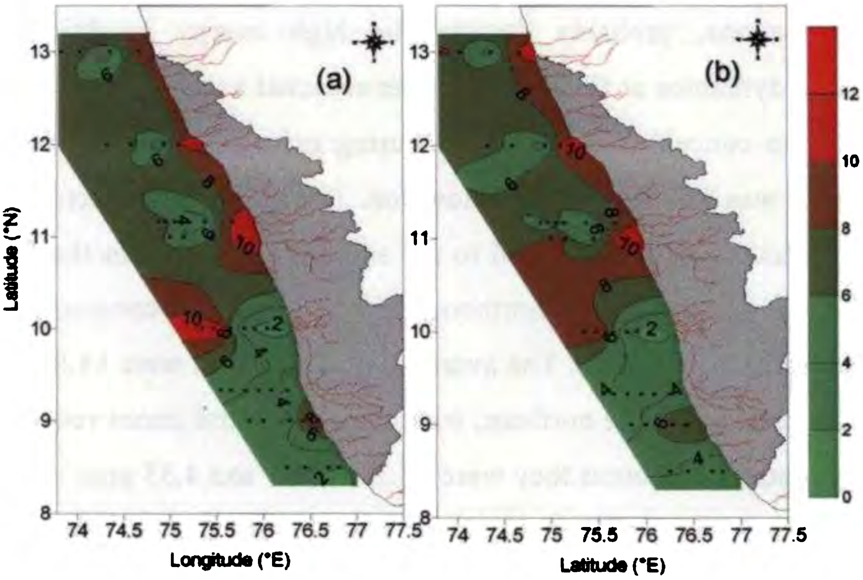

Figure 5.6 a&b. Distribution of cobalt [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

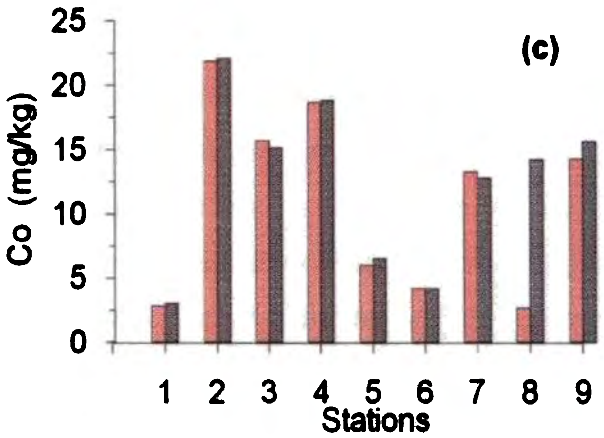

Figure 5.6 c. Distribution of cobalt in the Cochin estuary during premonsoon (red) and monsoon (black).

During seasons, a nearshore (20m) enrichment was evident, the nearshore average concentration during monsoon being 7.49 ppm and during premonsoon being 7.15 ppm. Along the Cochin transect, the coastal region was impoverished in Co concentration compared to the other coastal stations, probably due to the high energy conditions and nearshore dynamics at Cochin inlet. The seasonal variation is negligible; the average concentration of cobalt during premonsoon was 5.56 ppm, whereas it was 5.07 ppm during monsoon. The northern transects showed a slight accumulation compared to the southern transects. In the Cochin estuary, Co was high in the northern and southern zones compared to the central zone (Figure 5.6c). The average concentrations were 18.67, 14.21 and 4.57 ppm along the northern, southern and central zones respectivily during monsoon, whereas they were 18.74, 10.07 and 4.33 ppm along the northern, southern and central zones respectively during premonsoon. Comparatively, higher concentrations were observed during monsoon than premonsoon (monsoon average 12.49 ppm and premonsoon average 11.05 ppm).

Nickel

Nickel is a ubiquitous trace metal that occurs in soil, water, air, and biosphere. The average content in the earth's crust is about 0.008%. The primary sources are the combustion of coal and oil, incineration of waste and sewage sludge, nickel mining, steel manufacture, electroplating and cement manufacturing. Entry into the aquatic environment is from the atmosphere, by surface run-off, by discharge of industrial and municipal wastes and erosion. In rivers, nickel is mainly transported in the form of coating on particles and organic matter. Nickel also gets adsorbed on clay particles or organic matter (detritus, algae, bacteria) such as humic and fulvic acids and proteins. In seawater, it is found as Ni^{2+} (47%) and as chloro complexes. Nickel concentrations showed a nearshore enrichment followed by a decrease towards seaward and then a gentle increase to the deeper stations in both seasons (Figure 5.7 a & b).

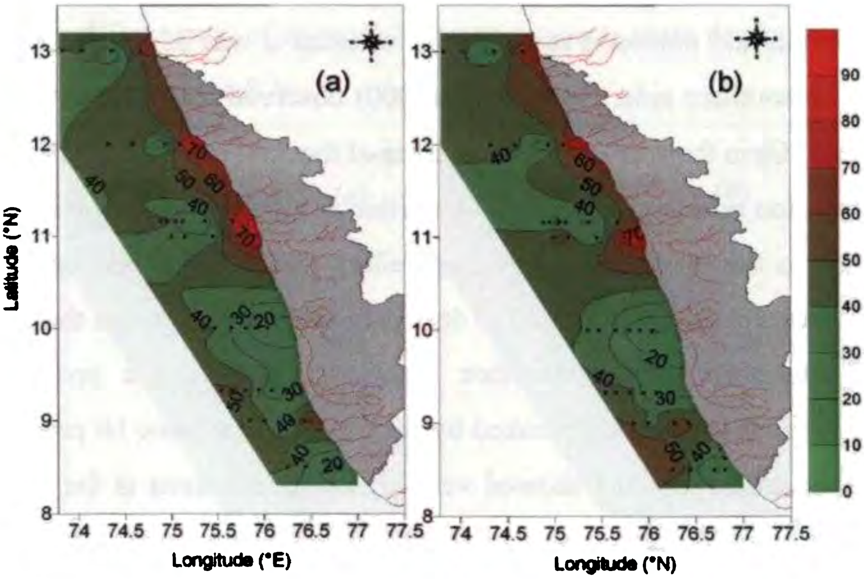

Figure 5.7 a&b. Distribution of nickel [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

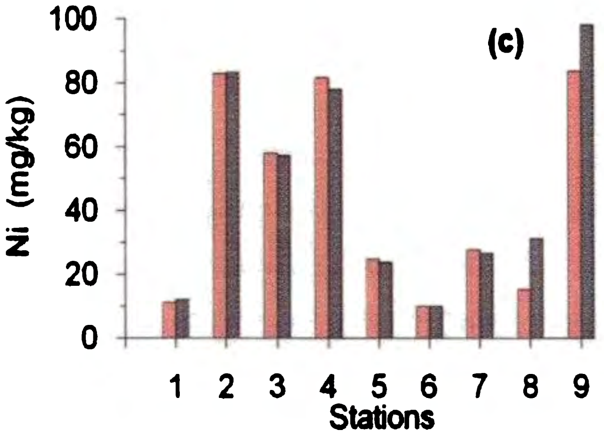

Figure 5.7 c. Distribution of nickel in the Cochin estuary during premonsoon (red) and monsoon (black).

The average concentration of nickel in nearshore sediments during monsoon was 51 ppm, whereas it was 47 ppm during premonsoon. It generally showed a northern enrichment compared to the southern side. The average concentrations along the northern region were 44.4 and 41.5 ppm during premonsoon and monsoon respectively, whereas it was 32.9 and 31.7 ppm along the southern side. Frank et al. (2000) observed that Ni was enriched relative to Cr in the western offshore areas of the Arabian Sea, where marine accumulation rates begin to exceed the lithic accumulation rates. Ni was not enriched in the immediate coastal upwelling areas of Somalia or Arabia, where accumulation rates of lithic dust particles largely exceed the marine contributions. Ni could therefore potentially serve as a productivity indicator, even though it is masked by variations of the lithic Ni proportion. In Cochin estuary, nickel showed very high concentrations at the northern zone compared to central and southern zones (Figure 5.7c). The average concentrations were 72.89, 15.24 and 52.04 ppm along northern, central and southern zones respectively during monsoon, whereas it was 74.11, 15.28 and 42.19 respectively during premonsoon. The high enrichment along the northern zone indicates the influence of industrial zone.

Copper

Copper is a very common element that occurs naturally in the environment. Major industrial sources include mining, smelting, refining and coal-burning industries. Some of these anthropogenic sources enter the aquatic environment either directly via sewage or industrial discharges or through natural sources. Copper exists in aquatic system as Cu^{2+}or complexed with ligands or as suspended particles (Kristian et al., 2008). It gets adsorbed onto sediments or settle as precipitates. The concentration depends on complex interactions including the hardness, alkalinity, salinity, pH, bicarbonate, carbonate, sulphide, phosphate, organic ligands and other metal ion. Copper showed nearshore enrichment followed by a sudden decrease towards seaward and a slight increase in the deeper stations during premonsoon in all transects, whereas the intensity of enrichment in deeper stations and frequency of increase between transects were decreased during monsoon (Figure 5.8 a & b).

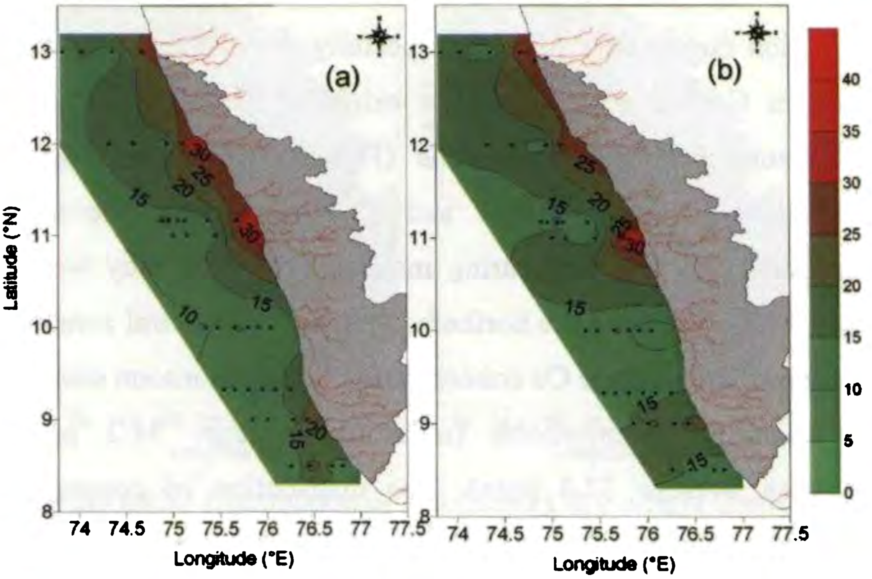

Figure 5.8 a&b. Distribution of copper [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

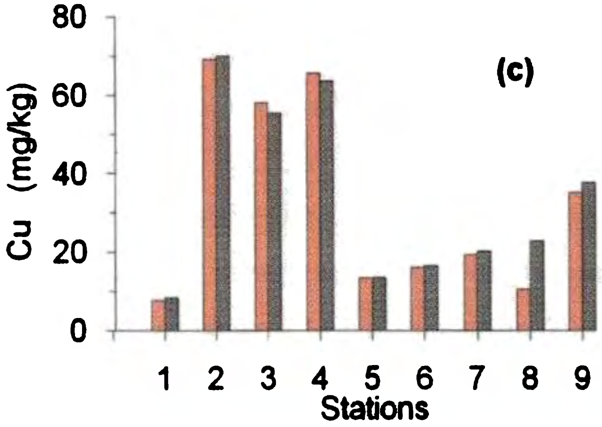

Figure 5.8 c. Distribution of copper in the Cochin estuary during premonsoon (red) and monsoon (black).

It showed a nearshore average concentration of 23.2 ppm during monsoon and 21.3 ppm during premonsoon. However, the overall average concentrations were 15.9 and 15.5 ppm during premonsoon and monsoon respectively. The northern transect showed greater accumulation during both seasons, especially along the nearshore (20m) stations. In Cochin estuary, copper exhibited high concentrations at northern zone during both seasons (Figure 5.8c). The average Cu concentrations were 62.9, 26.9 and 12.7 ppm along the northern, southern and central zones during monsoon, whereas they were 64.3, 21.7 and 12.3 ppm along the northern, southern and central zones during premonsoon. The average Cu concentration during monsoon was slightly higher than the premonsoon (monsoon average. 34.2 ppm and premonsoon average 32.8 ppm). The distribution of copper clearly indicates its point sources at the northern side from industrial zone.

Zinc

Zinc is one of the most ubiquitous and mobile element transported in natural waters as dissolved and suspended forms. It may enter the aquatic environment through natural or anthropogenic sources, including sewage and industrial discharges. In fresh water, zinc is predominantly present in the dissolved form. In estuaries, where concentrations of suspended particles are greater, a greater proportion of the zinc is adsorbed to suspended particles. In low salinity areas of estuaries, zinc can be mobilised from particles by microbial degradation of organic matter and displacement by calcium and magnesium. In the turbidity maximum, zinc will be deposited with flocculated particles. In seawater, much of the zinc is found is dissolved form as inorganic and organic complexes. Zinc showed nearshore enrichment followed by an initial decrease towards sea and a gentle increase further deep along the southern transects (Figure 5.9 a & b).

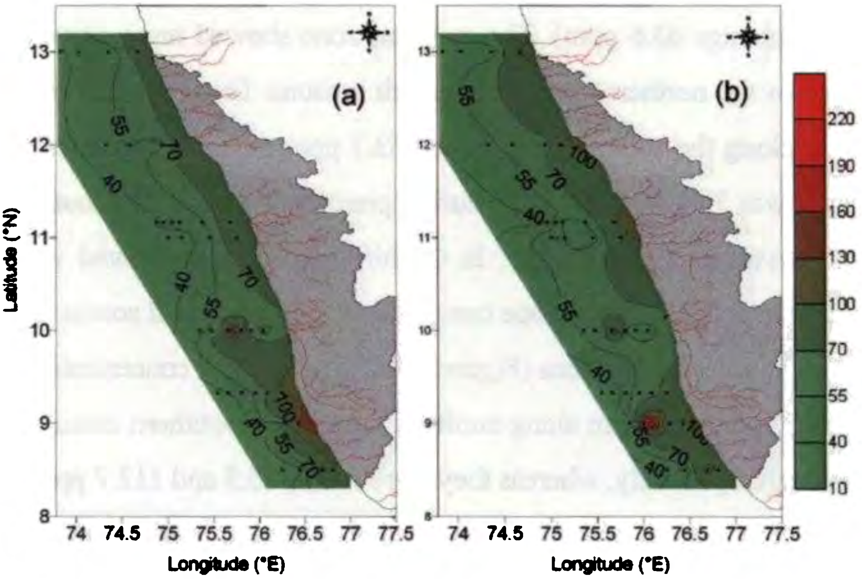

Figure 5.9 a&b. Distribution of zinc [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

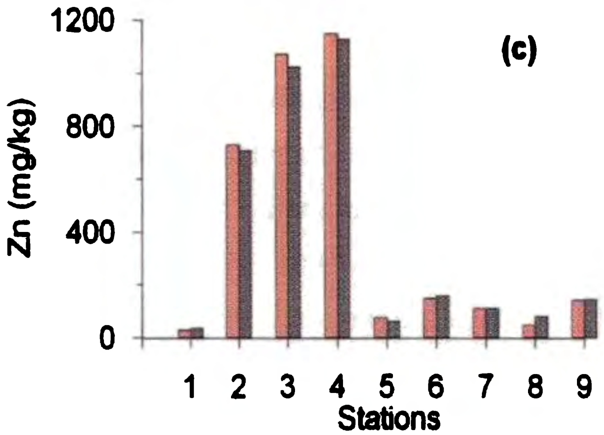

Figure 5.9 c. Distribution of zinc in the Cochin estuary during premonsoon (red) and monsoon (black).

However, the northern transects showed nearshore enrichment and decreased towards deep. The average concentration along the nearshore stations was 93.7 ppm during monsoon, whereas it was 91.4 ppm during premonsoon. It showed not much variation during premonsoon (averages 70 ppm) and monsoon (average 63.6 ppm). The southern zone showed more accumulation compared to the northern zone during both seasons. During monsoon, it was 72.4 ppm along the southern region and 53.7 ppm along the northern region; whereas it was 75.3 and 64.2 ppm during premonsoon along the southern and the northern regions respectively. In Cochin estuary, zinc showed very high accumulation at the northern zone compared to the central and southern part of the estuary during both seasons (Figure 5.9c). The average concentrations were 983.8, 84.7 and 100.6 ppm along northern, central and southern estuary during premonsoon respectively, whereas they were 953.7, 85.9 and 112.7 ppm during monsoon. The overall distribution was almost similar during both seasons (premonsoon average 389.7 ppm and monsoon average 384.1 ppm). The very high zinc concentrations at the northern zone during both seasons might be due to the influence of industrial effluents.

Yttrium

Yttrium is rarely found in nature and hence, it is also incorporated into rare earth elements. Yttrium is found along with all rare earth minerals and in uranium ores. The monazite contains 2.5 % of yttrium and minerals such as barnasite, fergusonite and smarskite contains even small percentage. Yttrium is dumped in the environment in many different places, mainly by petrol-producing industries. Yttrium accumulates in water and soils and eventually leads to bioaccumulation. Yttrium is toxic if inhailed and cause lung embolisms. Yttrium can also cause cancer. It can be a threat to liver when it accumulates in the human body. With aquatic animals, yttrium causes damage to cell membranes, which has several negative influences on reproduction and on the functions of the nervous system.

Yttrium showed a nearshore enrichment followed by a decrease towards the seaward stations (Figure 5.10 a & b).

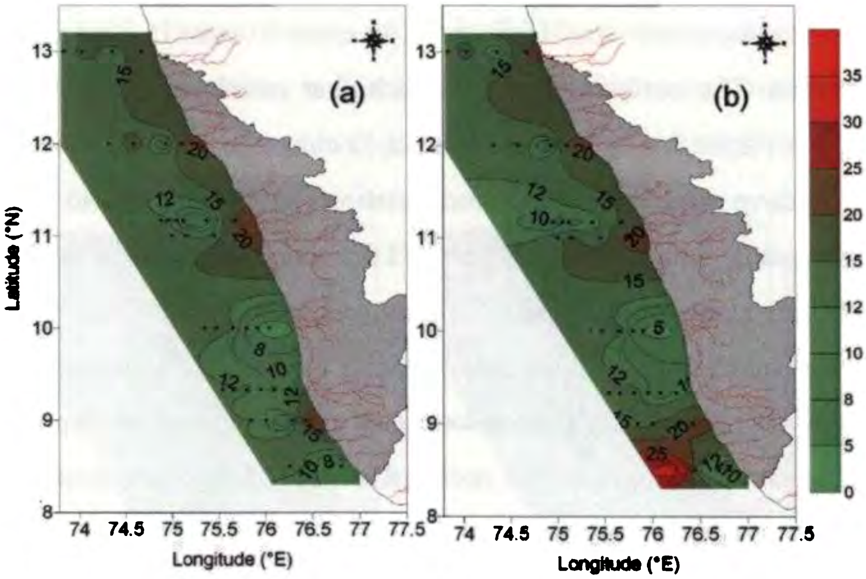

Figure 5.10 a&b. Distribution of yttrium [mg/kg dry weight (ppm)]along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

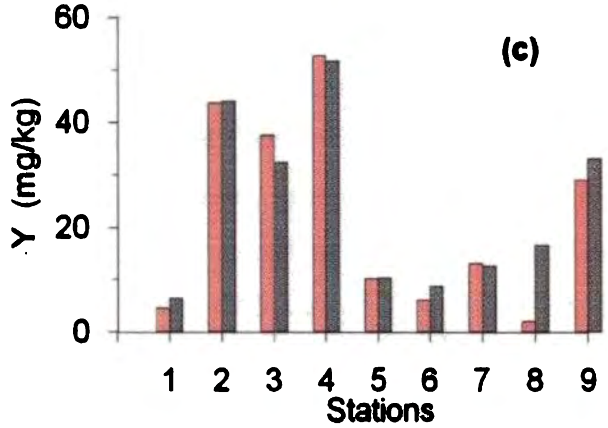

Figure 5.10 c. Distribution of yttrium in the Cochin estuary during premonsoon (red) and monsoon (black).

It showed similar distribution patterns during both seasons, except a high concentration in the deeper station at Trivandrum during premonsoon. The average concentration of yttrium during premonsoon was 13.6 ppm, whereas it was 12.2 ppm during monsoon. The average value for the coastal area during monsoon was 16.6 ppm, whereas it was 15.1 ppm during premonsoon. The northern zone showed higher enrichment of metals than the southern zone during both seasons. In Cochin estuary, yttrium was high in the northern zone and southernmost station (no.9) compared to all other stations during both seasons (Figure 5.10c; monsoon average 44.6 ppm; premonsoon average 40.3 ppm). The concentration was < 16 ppm in the remaining stations during both seasons with the average concentrations of 7.1 and 10.9 ppm during premonsoon and monsoon seasons respectively. The high concentrations at the northern zone and southern most station indicate its point sources.

Zirconium

Zirconium is not a rare element but because it's most common mineral, zircon, is highly resistant to weathering and is only slightly mobile in the environment. Zirconium and its salts generally have low systemic toxicity and are unlikely to present a hazard to the environment. Zirconium showed nearshore enrichment followed by a decrease towards the sea, except at Cochin transect (Figure 5.11 a & b). The average concentration was 46.1 ppm during premonsoon and 35.9 ppm during monsoon. Along the coast, the average concentration during premonsoon was 68.5 ppm and 57.9 ppm during monsoon. It showed almost similar distribution pattern along the northern and southern regions during monsoon, whereas enrichment was found at the southern zone (average 52.3 ppm) compared to the north (average 39.1 ppm) during premonsoon. In Cochin estuary, accumulation of zirconium was observed at northern zone compared to the central and southern zones of estuary (Figure 5.11c). The average concentrations were 84.3, 51.1 and 45.7 ppm along the northern, central and southern zones during premonsoon, whereas they were 70.8, 40.4 and 64.3 ppm during monsoon. The station 6 contained high concentrations, while barmouth (staion1) contained low concentrations of zinc during both seasons. The very high accumulation of zinc along the northern estuary indicates its point source from industries.

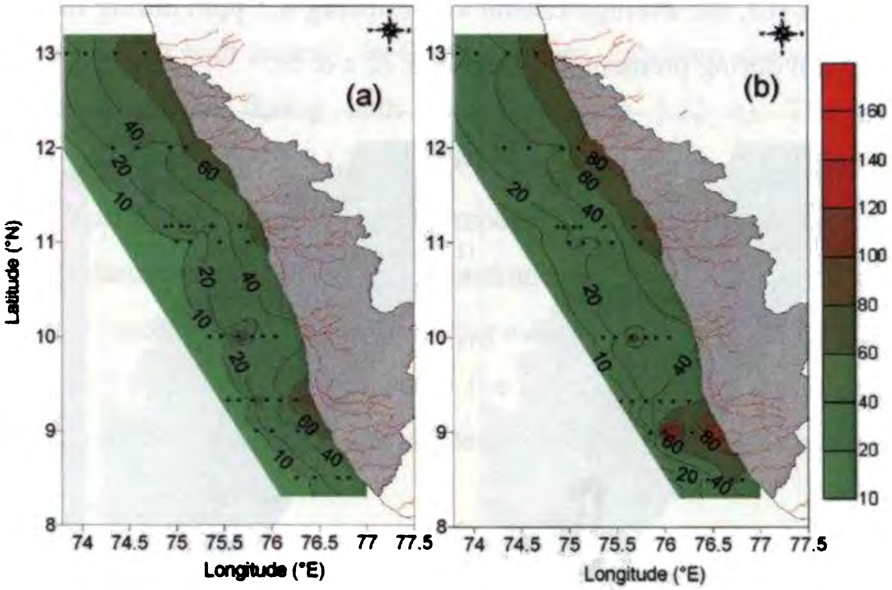

Figure 5.11 a&b. Distribution of zirconium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

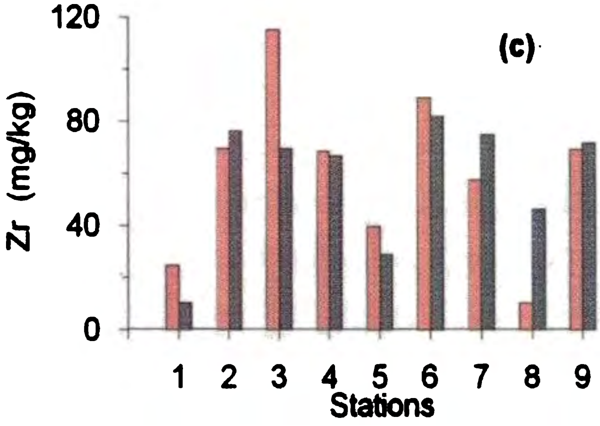

Figure 5.11 c. Distribution of zirconium in the Cochin estuary during premonsoon (red) and monsoon (black).

Nobelium

Nobelium is very unstable in nature and they are quite hard to make and detect Nobelium showed a nearshore enrichment followed by a decrease towards the sea, the average coastal values being 8.1 ppm during monsoon and 8.9 ppm during premonsoon (Figure 5.12 a & b).

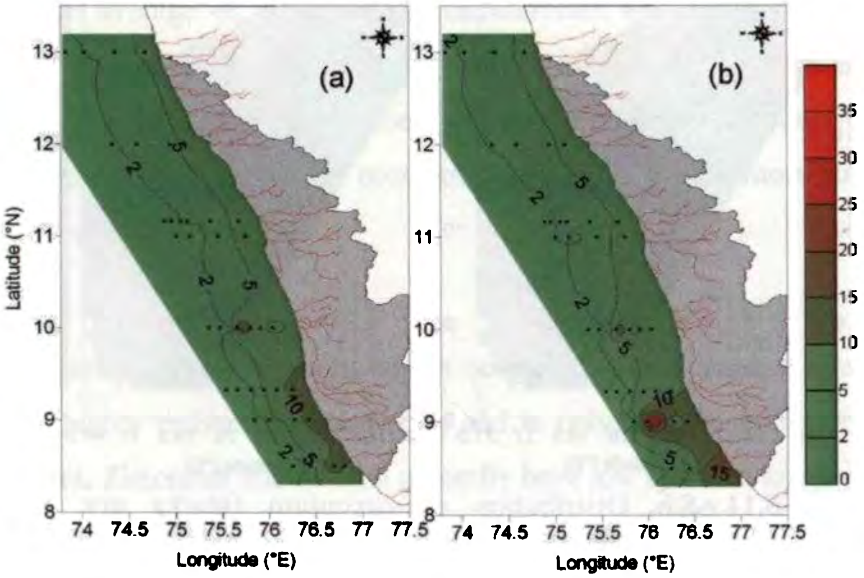

Figure 5.12 a&b. Distribution of nobelium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

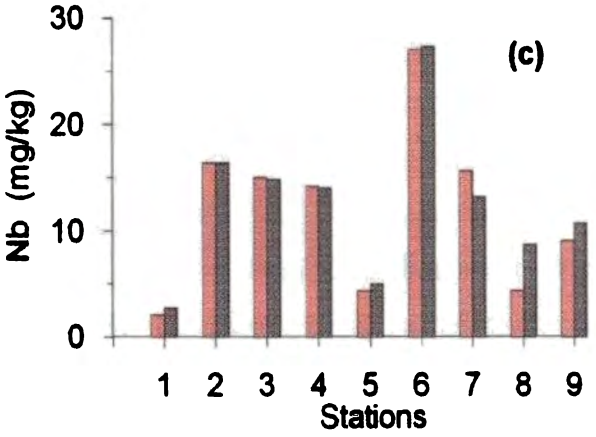

Figure 5.12 c. Distribution of nobelium in the Cochin estuary during premonsoon (red) and monsoon (black).

There was an accumulation of nobelium along the southern transect (6.4 ppm) compared to the northern transects (3.1 ppm) during monsoon, whereas it was 8.9 ppm at the southern side and 3.3 ppm at the northern transect during premonsoon. It showed very high accumulation at Kollam and Trivandrum transects during both seasons. In Cochin estuary, nobelium showed a similar distribution pattern during both seasons (Figure 5.12 c). The average concentrations were 15.2, 11.7 and 10.9 ppm along the northern, central and southern parts of the estuary during monsoon, whereas they were 15.2, 11.2 and 9.7 ppm during premonsoon. The concentrations of nobelium ranged between 2.7 - 27.3 ppm (average 12.5 ppm) during monsoon and between 2.1 - 27 ppm (average 12 ppm) during premonsoon. The low concentration was observed at barmouth (station 1) and high was at Thevara (station 6) during both seasons.

Molybdenum

Molybdenum is a silvery white, very hard transition metal, but is softer and more ductile than tungsten. It has one of the highest melting points of all pure elements and is attacked slowly by acids. Molybdenum showed a nearshore enrichment followed by a sudden decrease towards the seaward stations and then a gentle increase at the deeper stations (Figure 5.13 a & b). It showed very marginal enrichment during monsoon (average 1.1 ppm) as compared to premonsoon (average 0.9 ppm). It also showed a coastal enrichment, the average concentration during premonsoon was 1.2 ppm, whereas it was 1.3 ppm during monsoon. Noteworthy, Mo showed an unusual enrichment along the deeper stations of Kollam transect during both seasons. In Cochin estuary, molybdenum was present uniformly at the northern and southern parts of the estuary with slight high values at the northern zone, whereas the central estuary was impoverished in molybdenum during both seasons (Figure 5.13 c).

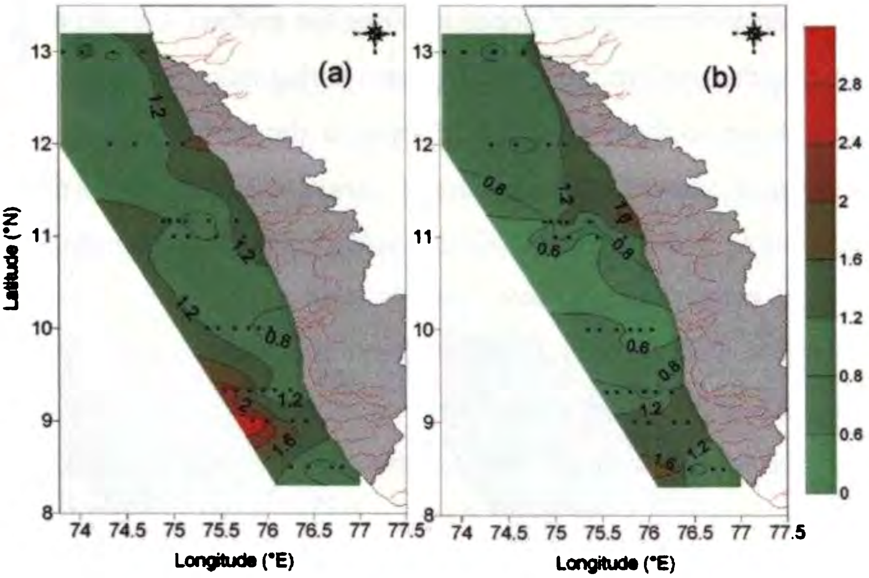

Figure 5.13 a&b. Distribution of molybdenum [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

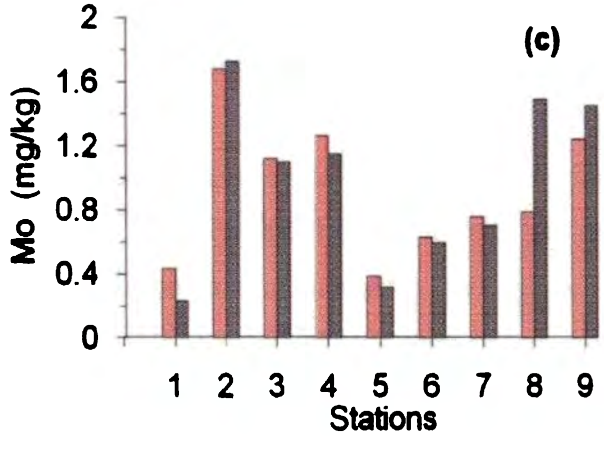

Figure 5.13 c. Distribution of molybdenum in the Cochin estuary during premonsoon (red) and monsoon (black).

The average concentrations were 1.3, 1.2 and 0.4 ppm along the northern, southern and central parts of the estuary during monsoon, whereas they were 1.3, 0.9 and 0.5 ppm in the same regions during premonsoon.

Hafnium

Hafnium is the 45th most abundant element in the earth's crust. In general, igneous and metamorphic rocks contain very small amounts of Hf. The geochemical properties of Hf and Zr are very similar because of their similarity in atomic radius. Hf complexes with sulphates, fluorides and chlorides. They are poorly soluble in aqueous solution, but complexation with natural organic materials may increase the concentrations of Hf in natural freshwater. Sewage is the main anthropogenic source of Hf. There is no biological use or benefit for hafnium when present in seawater in trace amounts. Hafnium showed a similar pattern of distribution during both seasons (Figure 5.14 a & b). It showed a nearshore enrichment followed by a gradual decrease in concentration towards the deeper stations. The average concentration of hafnium during monsoon was 1.1 ppm, whereas it was 1.4 ppm during premonsoon. The nearshore average was 1.8 ppm during monsoon and 2 ppm during premonsoon. The Hf concentration was high along the southern part (monsoon average 1.5 ppm; premonsoon average 1.2 ppm) compared to the northern part (monsoon average 1; premonsoon average 1.2 ppm). In Cochin estuary, hafnium behaved almost uniformly except at barmouth (station 1) during monsoon (Figure 5.14 c). It varied between 0.8 to 2.2 ppm during monsoon, whereas it was between 0.3 - 3.4 ppm during premonsoon, with an average concentration of 1.6 ppm during both seasons. The average concentrations of hafnium were 2.1, 1.1 and 1.8 ppm along the northern, central and southern zones of estuary during monsoon, whereas they were 2.5, 1.3 and 1.3 ppm along the northern, central and southern regions of the estuary respectively during premonsoon.

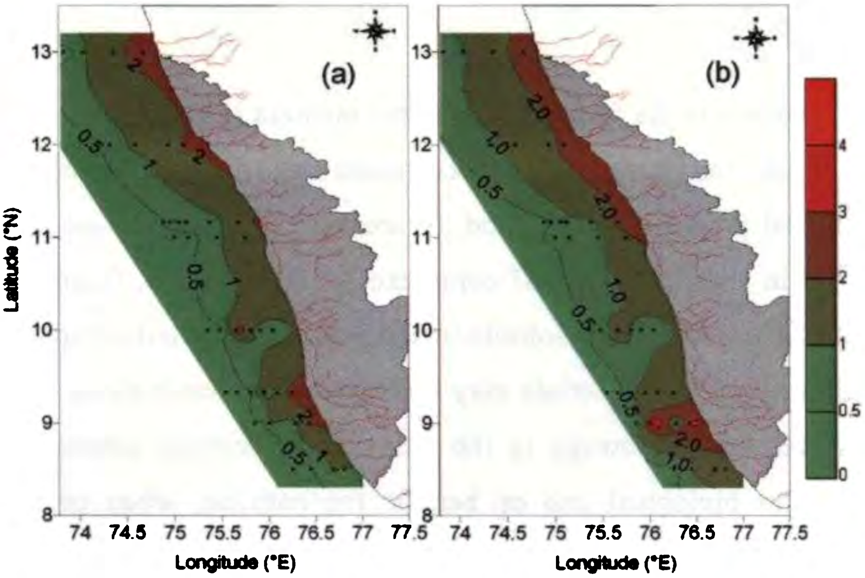

Figure 5.14 a&b. Distribution of hafnium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

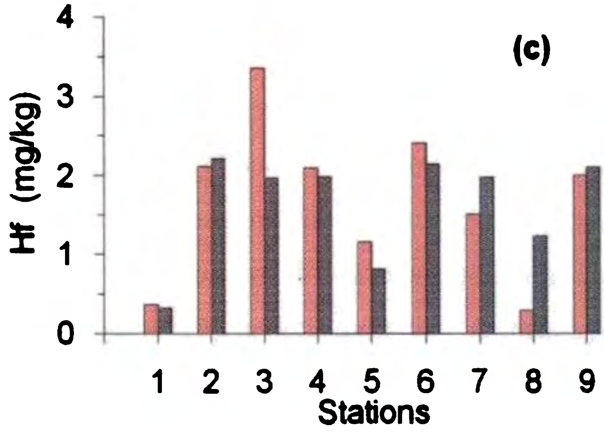

Figure 5.14 c. Distribution of hafnium in the Cochin estuary during premonsoon (red) and monsoon (black).

Tantalum

Tantalum is a shiny, silvery metal which is soft in pure form. It commonly occurring as insoluble tantalum oxides; hence is not found in natural waters. It is inert to chemical changes at temperatures below 150°C. Ta is virtually resistant to corrosion due to an oxide film on its surface. Ta is mostly found with the element niobium and these two elements are so similar that they are very difficult to isolate from one another. It is recovered from ore minerals such as columbite and tantalite. The electronics industry uses most of the tantalum to make components such as capacitors.

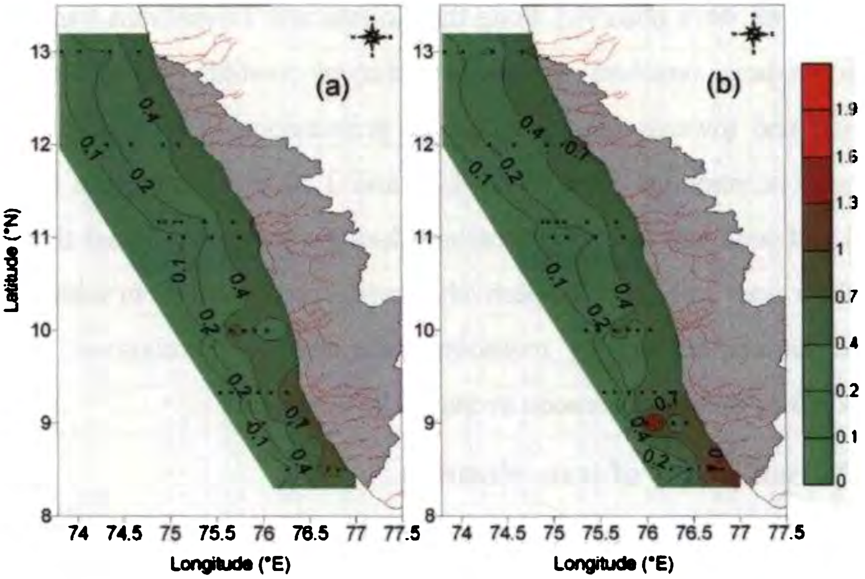

Figure 5.15 a&b. Distribution of tantalum (mg/kg dry weight) along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

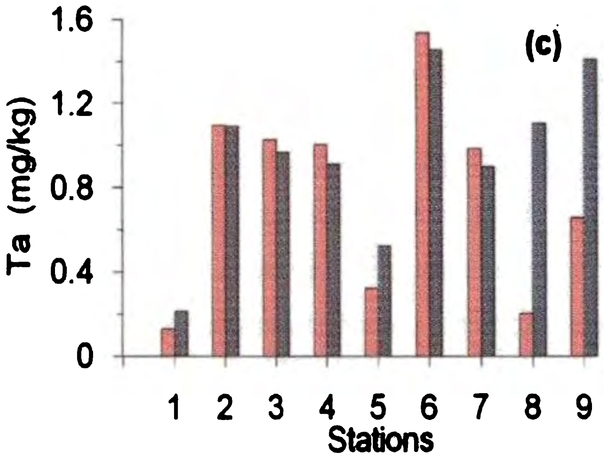

Figure 5.15 c. Distribution of tantalum in the Cochin estuary during premonsoon (red) and monsoon (black).

Tantalum showed similar distribution pattern during both seasons along the shelf (Figure 5.15 a & b). The concentrations ranged from 0.07 to 1.35 ppm with an average of 0.37 ppm during monsoon. The concentrations varied from 0.12 to 2.3 ppm with an average of 0.45 ppm during premonsoon. High concentrations were observed along the Kollam and Trivandrum transects. In Cochin estuary, tantalum showed enrichment towards the south during monsoon and towards the north during premonsoon (Figure 5.15 c). The average concentrations were 0.99, 0.73 and 1.14 ppm along the northern, central and southern parts of the estuary during monsoon, whereas they were 1.04, 0.66 and 0.61 ppm respectively during premonsoon. In addition, Ta showed enrichment during monsoon compared to premonsoon (average monsoon 0.77 ppm; premonsoon average 0.95 ppm).

5.2.2 Normalization of trace elements

Normalization means the concentration of each element in the sample is divided by the concentration of the same element in the global shale. The shale normalised values of transition elements during both seasons are given in tables (Table 5.1a & Table 5.1b). The normalisation factor (NF) < 1 refers to low contamination, 1 > NF < 3 means moderate contamination, 3 > NF< 6 indicates severe contamination, and NF > 6 indicates extreme contamination.

In shelf region, the seasonal contamination is negligible. The TEs such as Cr, Ni, Fe, Zn and Mo showed moderate contamination along the coastal stations of northern zone during both seasons. In addition, the coastal region of Kollam showed moderate contamination for TEs such as Cr, Fe, Zn and Mo. Iron showed moderate contamination along the outer shelves of Cochin and Trivandrum. In Cochin estuary, the northern zone showed moderate contamination for TEs such as Sc, V, Cr, Fe, Co, Ni, Cu and Mo during both seasons.

Table 5.1a. Shale normalised values (transition elements) along the study region during premonsoon.

Shelf														
Transects	**Depth (m)**	**Sc**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Zr**	**Nb**	**Mo**	**Hf**
Manglore	20	0.8	0.5	1.5	0.4	1.5	0.5	1.3	0.6	1.3	0.4	0.4	1.3	0.5
	50	0.2	0.2	0.5	0.4	0.4	0.1	0.5	0.2	0.5	0.2	0.1	0.5	0.3
	100	0.4	0.4	0.8	0.6	1.2	0.3	0.8	0.3	0.7	0.2	0.1	1.3	0.2
	200	0.4	0.4	1.1	0.3	1.9	0.4	0.9	0.3	0.6	0.1	0.1	1.0	0.1
Kannoore	20	0.8	0.5	1.6	0.4	1.5	0.5	1.3	0.6	1.2	0.4	0.4	1.4	0.5
	50	0.2	0.2	0.6	0.2	0.4	0.1	0.4	0.2	0.6	0.2	0.2	0.9	0.2
	100	0.3	0.2	0.8	0.3	0.7	0.2	0.8	0.4	0.7	0.2	0.1	0.7	0.2
	200	0.4	0.4	0.8	0.3	1.1	0.3	0.8	0.4	0.6	0.2	0.1	1.0	0.2
Baypore	20	0.6	0.4	1.2	0.4	1.2	0.4	0.9	0.4	1.2	0.4	0.3	1.8	0.5
	50	0.3	0.2	0.6	0.5	0.7	0.2	0.5	0.3	0.6	0.1	0.2	0.6	0.2
	75	0.2	0.2	0.7	0.3	0.5	0.2	0.6	0.3	0.6	0.1	0.1	1.5	0.2
	100	0.3	0.3	0.8	0.6	0.9	0.3	0.8	0.3	0.9	0.2	0.2	1.5	0.2
	150	0.4	0.4	0.8	0.3	1.8	0.4	0.9	0.3	0.6	0.1	0.1	0.9	0.1
	200	0.3	0.2	0.6	0.1	1.1	0.2	0.5	0.2	0.4	0.1	0.1	0.5	0.1
Ponnani	20	1.0	0.5	1.6	0.3	1.5	0.5	1.4	0.7	1.1	0.3	0.4	1.0	0.4
	50	0.3	0.2	0.6	0.6	0.6	0.2	0.5	0.2	0.5	0.1	0.1	0.5	0.1
	100	0.3	0.3	0.5	0.4	0.9	0.3	0.8	0.3	0.5	0.1	0.1	0.7	0.1
	200	0.5	0.4	1.0	0.3	1.8	0.4	1.0	0.4	0.9	0.1	0.1	0.9	0.2
Cochin	20	0.2	0.1	0.3	0.2	0.2	0.1	0.2	0.1	0.6	0.1	0.4	0.4	0.1
	50	0.2	0.1	0.4	0.2	0.3	0.1	0.3	0.2	0.5	0.1	0.1	0.4	0.1
	75	0.4	0.3	0.6	0.5	0.7	0.2	0.4	0.4	1.7	0.4	1.0	0.8	0.5
	100	0.4	0.2	0.6	0.3	0.7	0.2	0.5	0.2	0.9	0.5	0.3	0.5	0.6
	150	0.4	0.3	0.7	0.3	2.2	0.4	0.6	0.2	0.6	0.1	0.1	0.7	0.1
	200	0.4	0.3	0.9	0.2	2.4	0.4	0.7	0.3	0.8	0.1	0.1	0.7	0.1
Alleppy	20	0.4	0.2	0.7	0.2	0.6	0.2	0.5	0.3	1.0	0.3	0.5	1.3	0.3
	50	0.2	0.2	0.5	0.1	0.5	0.1	0.4	0.3	0.7	0.3	0.4	0.6	0.3
	75	0.3	0.2	0.6	0.2	0.5	0.1	0.5	0.3	0.8	0.2	0.4	0.6	0.2
	100	0.3	0.2	0.4	0.2	0.4	0.1	0.4	0.2	0.9	0.4	0.6	0.5	0.4
	150	0.3	0.1	0.8	0.1	0.8	0.2	0.9	0.3	0.5	0.1	0.1	1.3	0.1
	200	0.3	0.1	0.8	0.1	0.8	0.2	0.8	0.3	0.5	0.1	0.1	0.8	0.1
Kollam	20	0.7	0.4	1.2	0.4	1.1	0.4	0.9	0.4	1.3	0.5	0.7	1.4	0.6
	50	0.4	0.3	1.1	0.4	1.5	0.3	1.1	0.4	0.6	0.1	0.1	1.2	0.2
	100	0.5	0.5	0.8	0.6	0.8	0.2	0.5	0.4	2.8	0.9	2.1	1.7	1.0
	200	0.2	0.1	0.7	0.1	0.4	0.1	0.9	0.3	0.3	0.1	0.1	1.4	0.1
Trivandrum	20	0.2	0.3	0.6	0.1	0.4	0.1	0.4	0.2	1.0	0.2	0.8	1.0	0.2
	50	0.2	0.2	0.5	0.2	0.3	0.1	0.3	0.3	1.4	0.4	1.1	0.9	0.5
	100	0.2	0.1	0.4	0.1	0.3	0.1	0.6	0.2	0.4	0.1	0.1	0.5	0.2
	200	0.4	0.7	2.1	0.1	1.7	0.2	1.0	0.3	0.5	0.1	0.1	1.7	0.1
Estuary														
St.No.	**Depth (m)**	**Sc**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Zr**	**Nb**	**Mo**	**Hf**
1	3	0.2	0.2	0.3	0.2	0.2	0.1	0.2	0.2	0.3	0.1	0.1	0.4	0.1
2	5	1.5	1.2	2.3	0.9	2.4	1.0	1.5	1.4	8.6	0.3	0.9	1.7	0.4
3	3	1.4	1.0	2.0	0.5	2.5	0.7	1.1	1.2	12.6	0.5	0.8	1.1	0.7
4	ND	1.4	0.9	1.9	0.5	2.3	0.8	1.5	1.3	13.5	0.3	0.7	1.3	0.4
5	2	0.4	0.2	0.6	0.3	0.5	0.3	0.4	0.3	0.9	0.2	0.2	0.4	0.2
6	ND	0.3	0.3	0.5	0.3	0.4	0.2	0.2	0.3	1.8	0.4	1.4	0.6	0.5
7	6	0.5	0.4	0.7	0.5	0.9	0.6	0.5	0.4	1.3	0.3	0.8	0.8	0.3
8	4	0.2	0.2	0.3	0.1	0.2	0.1	0.3	0.2	0.6	0.0	0.2	0.8	0.1
9	9	1.1	0.6	1.8	0.7	1.8	0.6	1.5	0.7	1.7	0.3	0.5	1.2	0.4

Table 5.1b. Shale normalised values (transition elements) along the study region during monsoon.

Shelf														
Transects	Depth (m)	Sc	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	Nb	Mo	Hf
Manglore	20	0.7	0.4	1.3	0.4	1.3	0.4	1.1	0.5	1.0	0.4	0.3	1.4	0.5
	50	0.2	0.2	0.5	0.6	0.4	0.2	0.4	0.2	0.5	0.3	0.1	0.6	0.4
	100	0.4	0.5	0.8	0.5	1.3	0.3	0.8	0.3	0.6	0.1	0.1	1.5	0.2
	200	0.3	0.3	0.8	0.3	1.6	0.3	0.7	0.3	0.5	0.1	0.1	0.9	0.1
Kannoore	20	0.8	0.5	1.7	0.3	1.4	0.5	1.3	0.6	1.0	0.3	0.4	1.7	0.4
	50	0.2	0.1	0.4	0.2	0.3	0.1	0.3	0.2	0.6	0.2	0.2	1.0	0.2
	100	0.5	0.3	0.9	0.4	0.8	0.3	1.0	0.4	0.7	0.2	0.2	0.9	0.3
	200	0.4	0.3	0.8	0.3	1.2	0.3	0.8	0.3	0.6	0.1	0.1	1.1	0.1
Baypore	20	0.8	0.5	1.6	0.3	1.5	0.5	1.4	0.6	1.0	0.3	0.3	1.4	0.4
	50	0.2	0.2	0.5	0.3	0.4	0.1	0.4	0.3	0.6	0.1	0.1	0.6	0.1
	75	0.2	0.1	0.5	0.2	0.4	0.1	0.4	0.2	0.5	0.2	0.1	0.8	0.2
	100	0.2	0.2	0.5	0.3	0.5	0.2	0.5	0.2	0.6	0.1	0.1	0.6	0.2
	150	0.2	0.3	0.4	0.2	0.7	0.1	0.6	0.2	0.3	0.0	0.0	1.0	0.0
	200	0.4	0.3	0.8	0.2	1.5	0.3	0.8	0.3	0.6	0.1	0.1	1.3	0.1
Ponnani	20	0.9	0.5	1.6	0.3	1.6	0.5	1.4	0.6	1.1	0.3	0.4	1.6	0.4
	50	0.3	0.2	0.7	0.7	0.8	0.3	0.6	0.3	0.6	0.1	0.2	0.7	0.2
	100	0.2	0.3	0.5	0.3	0.6	0.2	0.6	0.2	0.4	0.0	0.1	0.9	0.1
	200	0.3	0.3	0.5	0.3	1.1	0.2	0.6	0.2	0.3	0.0	0.0	1.0	0.1
Cochin	20	0.1	0.1	0.3	0.1	0.2	0.0	0.2	0.2	0.6	0.1	0.2	0.6	0.1
	50	0.2	0.2	0.5	0.3	0.4	0.1	0.4	0.2	0.8	0.1	0.4	0.8	0.2
	75	0.3	0.3	0.5	0.7	0.7	0.2	0.4	0.4	2.1	0.5	1.1	1.2	0.6
	100	0.3	0.2	0.6	0.3	0.6	0.2	0.5	0.3	0.8	0.4	0.3	0.8	0.5
	150	0.5	0.4	0.9	0.3	2.4	0.5	0.7	0.2	0.7	0.1	0.1	1.1	0.1
	200	0.5	0.3	1.0	0.2	2.6	0.5	0.7	0.2	0.9	0.1	0.1	1.0	0.1
Alleppy	20	0.4	0.3	0.8	0.3	0.8	0.2	0.5	0.4	1.4	0.4	0.7	1.2	0.5
	50	0.2	0.2	0.5	0.2	0.5	0.1	0.3	0.2	0.7	0.1	0.4	0.7	0.2
	75	0.3	0.2	0.7	0.1	0.5	0.1	0.7	0.3	0.7	0.1	0.3	1.5	0.1
	100	0.2	0.2	0.4	0.2	0.4	0.1	0.6	0.2	0.7	0.4	0.3	0.8	0.5
	150	0.2	0.2	0.7	0.1	1.1	0.2	0.7	0.2	0.5	0.1	0.1	0.9	0.1
	200	0.3	0.3	0.9	0.1	1.1	0.2	0.9	0.3	0.6	0.1	0.1	1.9	0.1
Kollam	20	0.8	0.5	1.4	0.4	1.6	0.4	1.2	0.5	1.7	0.3	0.7	1.5	0.4
	50	0.2	0.2	0.5	0.1	0.2	0.1	0.4	0.2	0.6	0.1	0.3	1.5	0.1
	100	0.2	0.2	0.6	0.2	0.4	0.1	0.7	0.3	0.7	0.2	0.2	1.7	0.2
	200	0.2	0.1	0.8	0.1	0.5	0.1	0.9	0.3	0.4	0.1	0.1	2.8	0.1
Trivandrum	20	0.2	0.2	0.5	0.2	0.5	0.1	0.3	0.3	1.0	0.1	0.5	0.9	0.2
	50	0.2	0.2	0.4	0.2	0.3	0.1	0.2	0.2	1.3	0.2	0.8	0.7	0.2
	100	0.2	0.1	0.4	0.1	0.3	0.1	0.5	0.5	0.4	0.1	0.1	0.6	0.1
	200	0.3	0.4	0.9	0.1	1.2	0.2	0.7	0.2	0.4	0.0	0.1	1.0	0.1

Estuary														
St.No.	Depth (m)	Sc	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	Nb	Mo	Hf
1	3	0.3	0.2	0.4	0.2	0.3	0.1	0.2	0.2	0.4	0.0	0.1	0.2	0.1
2	5	1.6	1.1	2.3	0.9	2.4	1.0	1.5	1.4	8.3	0.4	0.9	1.7	0.4
3	3	1.2	1.0	1.9	0.5	2.3	0.7	1.0	1.1	12.1	0.3	0.8	1.1	0.4
4	ND	1.4	0.9	1.9	0.5	2.3	0.8	1.4	1.3	13.3	0.3	0.7	1.1	0.4
5	2	0.5	0.3	0.6	0.3	0.6	0.3	0.4	0.3	0.8	0.1	0.3	0.3	0.2
6	ND	0.4	0.4	0.6	0.3	0.4	0.2	0.2	0.3	1.9	0.4	1.4	0.6	0.4
7	6	0.5	0.4	0.7	0.5	0.9	0.6	0.5	0.4	1.3	0.4	0.7	0.7	0.4
8	4	0.6	0.3	0.7	0.6	1.0	0.6	0.6	0.5	0.9	0.2	0.5	1.5	0.2
9	9	1.3	0.8	2.1	0.6	2.0	0.7	1.8	0.8	1.7	0.3	0.6	1.4	0.4

The extreme contamination for Zn was observed along the northern zone, indicating high metal deposition, might be from the effluents of industrials situated on the banks of Periyar River. The TEs such as Sc, Cr, Fe, Ni, Zn and Mo showed moderate contamination at the station 6 during both seasons. The remaining stations showed low contamination for the entire TEs during both seasons. Enriched Cr contents indicate the intense chemical weathering (Wronkiewitcz and Condie, 1989). Most of the coastal areas in India have lateritic formations. Narayanaswami and Ghosh (1987) have documented four to six fold Cr enrichment in modern lateritic profiles of India.

5.2.3 Enrichment factor

Enrichment factor is also used for determining the contamination levels in sediments. The enrichment factors calculated with respect to Al and Fe are given in the tables (Table 5.2a & Table 5.2b and Table 5.3a & Table 5.3b). Southern zone (south of 10°N) showed higher values for enrichment factor for all non transition elements during both seasons. Similar to the normalisation factor, the enrichment factor (EF) < 1 refers to low enrichment, 1 > EF < 3 means moderate enrichment, 3 > EF< 6 indicates severe enrichment, and EF > 6 indicates extreme enrichment.

5.2.3.1 Enrichment with respect to aluminium

The southern zone showed more TEs enrichment compared to the northern zone during both seasons. Scandium and vanadium showed a moderate enrichment at the deeper stations (100 m onwards) along all transects during both seasons. Chromium and nickel showed moderate enrichment along the coastal stations with more enrichment towards deeper stations. Copper showed moderate enrichment (>1) along the mid depths (100 m) of all transects, expect Kannore. Zinc showed moderate to severe enrichment along the mid-depth stations (50 m and 100m) of all transects.

Table 5.2a. Enrichment factors (transition elements) with respect aluminium along the study region during premonsoon.

Shelf

Transects	Depth (m)	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Zr	Nb	Mo	Hf
Manglore	20	0.6	0.4	1.2	0.3	0.4	1.0	0.5	1.0	0.3	0.3	1.0	0.4
	50	1.1	0.9	2.3	1.8	0.7	2.2	1.1	2.5	0.8	0.5	2.5	1.3
	100	1.2	1.3	2.5	1.8	0.9	2.4	1.0	2.1	0.5	0.4	4.0	0.7
	200	1.0	0.9	2.7	0.7	0.9	2.3	0.9	1.6	0.2	0.2	2.6	0.3
Kannoore	20	0.6	0.4	1.2	0.3	0.3	1.0	0.4	0.9	0.3	0.3	1.0	0.4
	50	0.8	0.6	2.3	0.8	0.5	1.4	0.9	2.6	0.7	0.7	3.5	0.9
	100	0.8	0.6	1.8	0.7	0.6	1.9	0.9	1.8	0.4	0.3	1.7	0.6
	200	0.9	1.0	2.1	0.7	0.7	2.0	0.9	1.7	0.4	0.3	2.6	0.5
Baypore	20	0.6	0.3	1.1	0.4	0.3	0.8	0.4	1.1	0.3	0.3	1.7	0.4
	50	0.7	0.5	1.5	1.1	0.5	1.2	0.6	1.5	0.3	0.3	1.5	0.4
	75	0.9	0.7	2.7	1.0	0.6	2.3	1.1	2.4	0.6	0.5	6.0	0.8
	100	1.0	0.9	2.6	1.7	1.0	2.4	1.0	2.7	0.5	0.6	4.7	0.7
	150	1.3	1.1	2.6	1.0	1.3	2.8	1.0	1.8	0.3	0.3	3.0	0.3
	200	1.2	1.0	2.6	0.6	0.9	2.5	0.9	1.8	0.3	0.3	2.4	0.4
Ponnani	20	0.7	0.4	1.2	0.2	0.4	1.1	0.5	0.8	0.2	0.3	0.8	0.3
	50	0.9	0.6	1.7	1.7	0.6	1.5	0.7	1.6	0.4	0.4	1.4	0.4
	100	1.6	1.2	2.5	2.0	1.3	3.6	1.2	2.3	0.3	0.3	3.2	0.4
	200	1.0	0.8	2.1	0.6	0.9	2.2	0.9	2.0	0.3	0.3	2.0	0.3
Cochin	20	1.0	0.6	1.5	0.8	0.4	0.9	0.8	3.3	0.7	2.1	2.3	0.8
	50	0.6	0.4	1.2	0.5	0.3	1.0	0.6	1.6	0.3	0.4	1.3	0.4
	75	1.0	0.8	1.5	1.3	0.5	1.1	0.9	4.2	0.9	2.5	2.0	1.1
	100	0.7	0.3	1.1	0.6	0.4	1.0	0.5	1.7	0.9	0.6	0.9	1.1
	150	1.1	0.8	2.0	0.7	1.0	1.7	0.6	1.7	0.2	0.2	1.9	0.3
	200	1.0	0.8	2.1	0.6	1.1	1.6	0.7	1.9	0.2	0.2	1.6	0.3
Alleppy	20	0.7	0.5	1.2	0.4	0.3	0.9	0.6	1.8	0.4	0.9	2.5	0.5
	50	0.9	0.7	2.0	0.5	0.4	1.4	1.0	2.6	0.9	1.6	2.1	1.2
	75	1.1	0.6	2.0	0.6	0.5	2.0	1.0	2.9	0.8	1.5	2.2	0.9
	100	1.7	1.2	2.3	1.2	0.7	2.5	1.3	5.2	2.1	3.7	2.9	2.6
	150	1.1	0.5	2.8	0.4	0.6	3.2	0.9	1.7	0.3	0.4	4.8	0.4
	200	1.0	0.5	2.8	0.4	0.6	2.8	1.0	1.9	0.3	0.4	3.0	0.5
Kollam	20	0.6	0.4	1.2	0.4	0.4	0.9	0.4	1.3	0.5	0.7	1.4	0.6
	50	1.1	0.9	2.8	0.9	0.9	2.8	0.9	1.6	0.3	0.3	3.1	0.4
	100	2.0	2.0	2.9	2.4	0.9	2.0	1.6	10.4	3.0	7.7	6.2	3.7
	200	1.2	0.7	3.5	0.3	0.6	4.3	1.5	1.6	0.3	0.4	6.9	0.4
Trivandrum	20	1.7	2.2	5.3	1.1	0.8	3.4	2.1	8.8	1.6	6.9	8.4	1.9
	50	1.4	1.3	3.0	1.3	0.6	1.9	1.6	8.3	2.2	6.4	5.5	2.7
	100	1.3	0.8	2.6	0.6	0.6	3.7	1.3	2.4	0.8	0.8	2.7	1.1
	200	1.9	3.1	9.4	0.5	0.8	4.6	1.5	2.2	0.3	0.6	7.7	0.4

Estuary

St.No.	Depth (m)	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Zr	Nb	Mo	Hf
1	3.0	0.3	0.2	0.3	0.2	0.1	0.2	0.2	0.4	0.1	0.1	0.5	0.1
2	4.5	0.7	0.6	1.1	0.4	0.5	0.7	0.7	4.2	0.2	0.4	0.8	0.2
3	2.5	0.8	0.6	1.2	0.3	0.4	0.6	0.7	7.4	0.3	0.5	0.7	0.4
4	ND	0.7	0.4	0.9	0.2	0.4	0.7	0.7	6.7	0.2	0.4	0.6	0.2
5	1.5	0.4	0.2	0.5	0.3	0.2	0.4	0.2	0.8	0.2	0.2	0.3	0.2
6	ND	1.6	1.6	2.3	1.3	0.8	0.8	1.5	8.1	1.8	6.5	2.9	2.2
7	5.5	0.7	0.5	1.0	0.7	0.8	0.7	0.5	1.8	0.4	1.1	1.0	0.4
8	4.0	1.1	1.2	2.2	1.0	0.8	1.9	1.4	3.8	0.3	1.6	5.4	0.4
9	8.5	0.7	0.4	1.1	0.4	0.4	1.0	0.4	1.1	0.2	0.3	0.8	0.3

Table 5.2b. Enrichment factors (transition elements) with respect aluminium along the study region during monsoon.

Shelf													
Transects	**Depth (m)**	**Sc**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**Zr**	**Nb**	**Mo**	**Hf**
Manglore	20	0.7	0.4	1.2	0.4	0.4	1.1	0.5	0.9	0.3	0.3	1.3	0.4
	50	1.1	0.7	2.3	2.9	0.7	1.7	1.0	2.1	1.3	0.5	2.9	1 7
	100	1.4	1.7	2.6	1.7	0.9	2.4	1.1	1.9	0.5	0.4	4.9	0.6
	200	1.2	1.1	2.8	0.9	1.1	2.6	0.9	1.7	0.2	0.2	3.1	0.3
Kannoore	20	0.6	0.4	1.3	0.3	0.4	1.1	0.5	0.8	0.3	0.3	1.3	0.3
	50	1.0	0.6	2.2	0.8	0.5	1.6	1.1	2.9	0.7	0.8	4.9	1.0
	100	1.0	0.6	1.9	0.7	0.6	2.0	0.9	1.4	0.4	0.4	2.0	0.5
	200	1.0	1.0	2.2	0.9	0.8	2.3	1.0	1.7	0.3	0.3	3.0	0.4
Baypore	20	0.6	0.4	1.2	0.2	0.3	1.0	0.4	0.7	0.2	0.3	1.1	0.3
	50	0.7	0.6	1.6	1.1	0.5	1.3	0.9	2.1	0.2	0.4	2.1	0.3
	75	1.1	0.7	2.6	0.9	0.6	1.9	1.2	2.6	0.7	0.6	3.7	1.0
	100	1.1	0.9	2.3	1.4	0.8	2.1	1.2	3.0	0.6	0.7	3.1	0.8
	150	1.8	2.0	3.5	1.7	1.0	4.4	1.7	2.2	0.2	0.3	7.4	0.4
	200	1.0	0.9	2.2	0.6	0.8	2.1	0.9	1.5	0.2	0.3	3.4	0.3
Ponnani	20	0.6	0.4	1.1	0.2	0.4	1.0	0.4	0.7	0.2	0.2	1.1	0.2
	50	0.7	0.6	1.7	1.6	0.6	1.3	0.6	1.4	0.3	0.4	1.7	0.4
	100	1.4	1.5	2.6	1.5	0.9	3.6	1.3	2.2	0.3	0.3	4.8	0.4
	200	1.9	2.0	3.5	1.7	1.4	3.8	1.4	2.0	0.2	0.3	6.6	0.4
Cochin	20	0.8	0.5	1.4	0.6	0.2	0.9	1.1	3.1	0.5	1.1	3.4	0.7
	50	0.6	0.5	1.2	0.7	0.3	1.0	0.6	2.1	0.3	1.0	2.1	0.5
	75	1.1	1.1	1.8	2.4	0.6	1.4	1.2	7.2	1.5	3.7	3.9	2.0
	100	0.6	0.3	1.1	0.5	0.4	1.0	0.5	1.6	0.8	0.6	1.6	1.0
	150	1.0	0.9	2.0	0.6	1.0	1.5	0.5	1.5	0.2	0.2	2.3	0.3
	200	1.1	0.7	2.0	0.5	1.0	1.4	0.5	1.9	0.2	0.2	2.2	0.3
Alleppy	20	0.7	0.5	1.3	0.4	0.3	0.9	0.6	2.3	0.6	1.1	2.0	0.8
	50	0.8	0.6	1.8	0.6	0.4	1.3	0.8	2.7	0.5	1.4	2.6	0.6
	75	0.9	0.7	2.3	0.5	0.5	2.4	0.9	2.6	0.3	0.9	5.4	0.5
	100	1.8	1.7	3.5	1.4	0.8	4.6	1.7	5.2	3.1	2.5	6.0	4.0
	150	1.0	0.9	2.6	0.4	0.6	2.6	0.8	1.9	0.3	0.3	3.5	0.4
	200	0.9	0.9	2.8	0.4	0.6	3.0	0.9	2.0	0.2	0.3	6.4	0.3
Kollam	20	0.6	0.4	1.1	0.3	0.3	0.9	0.4	1.3	0.2	0.5	1.2	0.3
	50	0.9	0.9	3.0	0.6	0.4	2.2	1.2	3.6	0.6	1.8	9.2	0.8
	100	0.9	0.8	2.4	0.6	0.5	2.7	1.1	2.5	0.6	0.9	6.4	0.8
	200	1.0	0.6	3.6	0.3	0.6	4.3	1.3	1.8	0.3	0.3	13.3	0.4
Trivandrum	20	1.8	2.3	4.4	1.7	0.7	2.8	2.5	9.6	1.2	4.3	8.1	1.6
	50	1.2	1.2	2.3	1.0	0.6	1.3	1.4	7.1	0.9	4.5	4.0	1.2
	100	2.3	1.2	3.4	0.8	0.8	4.9	5.1	3.6	0.5	1.0	5.5	0.8
	200	1.2	1.8	4.2	0.5	0.7	3.6	1.1	1.9	0.2	0.3	4.9	0.3

Estuary													
St.No.	**Depth (m)**	**Sc**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**Zr**	**Nb**	**Mo**	**Hf**
1	3.0	0.3	0.2	0.5	0.2	0.1	0.2	0.2	0.4	0.1	0.2	0.2	0.1
2	4.5	0.7	0.5	1.1	0.4	0.4	0.7	0.6	3.8	0.2	0.4	0.8	0.2
3	2.5	0.8	0.7	1.3	0.3	0.5	0.7	0.8	8.2	0.2	0.5	0.8	0.3
4	ND	0.7	0.4	0.9	0.2	0.4	0.7	0.6	6.6	0.1	0.4	0.6	0.2
5	1.5	0.4	0.3	0.5	0.3	0.2	0.4	0.2	0.7	0.1	0.2	0.3	0.1
6	ND	1.7	1.7	2.6	1.4	0.8	0.8	1.5	8.7	1.7	6.7	2.8	2.0
7	5.5	0.7	0.5	0.9	0.6	0.7	0.6	0.5	1.6	0.4	0.9	0.9	0.5
8	4.0	0.7	0.4	0.8	0.7	0.7	0.7	0.6	1.1	0.3	0.6	1.8	0.3
9	8.5	0.7	0.4	1.1	0.3	0.4	1.0	0.4	0.9	0.2	0.3	0.8	0.2

Table 5.3a. Enrichment factors (transition elements) with respect iron along the study region during premonsoon.

Shelf													
Transects	**Depth (m)**	**Sc**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**Zr**	**Nb**	**Mo**	**Hf**
Manglore	20	0.6	0.3	1.0	0.3	0.3	0.8	0.4	0.9	0.3	0.2	0.9	0.4
	50	0.5	0.4	1.1	0.9	0.3	1.1	0.5	1.2	0.4	0.2	1.2	0.6
	100	0.3	0.3	0.7	0.5	0.2	0.6	0.3	0.5	0.1	0.1	1.0	0.2
	200	0.2	0.2	0.6	0.1	0.2	0.5	0.2	0.3	0.0	0.0	0.5	0.1
Kannoore	20	0.5	0.3	1.1	0.3	0.3	0.9	0.4	0.8	0.3	0.2	0.9	0.4
	50	0.5	0.4	1.4	0.5	0.3	0.9	0.6	1.6	0.4	0.4	2.1	0.6
	100	0.5	0.3	1.1	0.4	0.4	1.1	0.5	1.0	0.3	0.2	1.0	0.4
	200	0.3	0.3	0.7	0.3	0.2	0.7	0.3	0.6	0.1	0.1	0.9	0.2
Baypore	20	0.5	0.3	1.0	0.3	0.3	0.8	0.4	1.0	0.3	0.3	1.6	0.4
	50	0.4	0.3	0.9	0.7	0.3	0.8	0.4	0.9	0.2	0.2	0.9	0.2
	75	0.5	0.4	1.5	0.6	0.3	1.3	0.6	1.3	0.3	0.3	3.3	0.4
	100	0.4	0.3	0.9	0.6	0.4	0.9	0.4	1.0	0.2	0.2	1.7	0.3
	150	0.2	0.2	0.4	0.2	0.2	0.5	0.2	0.3	0.0	0.0	0.5	0.1
	200	0.2	0.2	0.5	0.1	0.2	0.5	0.2	0.3	0.1	0.1	0.5	0.1
Ponnani	20	0.6	0.3	1.1	0.2	0.3	0.9	0.4	0.7	0.2	0.3	0.7	0.2
	50	0.5	0.3	0.9	0.9	0.3	0.8	0.4	0.9	0.2	0.2	0.8	0.2
	100	0.4	0.3	0.6	0.5	0.3	0.9	0.3	0.6	0.1	0.1	0.8	0.1
	200	0.3	0.2	0.6	0.2	0.2	0.6	0.2	0.5	0.1	0.1	0.5	0.1
Cochin	20	0.7	0.4	1.1	0.7	0.3	0.7	0.6	2.6	0.5	1.6	1.8	0.6
	50	0.7	0.4	1.3	0.6	0.3	1.1	0.7	1.8	0.4	0.5	1.5	0.4
	75	0.5	0.4	0.8	0.7	0.3	0.6	0.5	2.3	0.5	1.4	1.1	0.6
	100	0.5	0.2	0.8	0.5	0.3	0.7	0.4	1.2	0.7	0.5	0.7	0.8
	150	0.2	0.1	0.3	0.1	0.2	0.3	0.1	0.3	0.0	0.0	0.3	0.0
	200	0.2	0.1	0.4	0.1	0.2	0.3	0.1	0.3	0.0	0.0	0.3	0.1
Alleppy	20	0.6	0.4	1.0	0.3	0.3	0.7	0.5	1.5	0.4	0.7	2.1	0.4
	50	0.5	0.4	1.1	0.3	0.2	0.8	0.6	1.5	0.5	0.9	1.2	0.6
	75	0.6	0.4	1.2	0.3	0.3	1.1	0.6	1.7	0.5	0.9	1.3	0.5
	100	0.7	0.5	1.0	0.5	0.3	1.1	0.6	2.2	0.9	1.6	1.2	1.1
	150	0.4	0.2	1.0	0.1	0.2	1.1	0.3	0.6	0.1	0.1	1.7	0.1
	200	0.4	0.2	1.0	0.1	0.2	1.0	0.4	0.7	0.1	0.2	1.1	0.2
Kollam	20	0.6	0.4	1.1	0.4	0.3	0.8	0.4	1.1	0.5	0.6	1.2	0.6
	50	0.3	0.2	0.7	0.2	0.2	0.7	0.2	0.4	0.1	0.1	0.8	0.1
	100	0.7	0.7	1.0	0.8	0.3	0.7	0.6	3.5	1.1	2.6	2.1	1.2
	200	0.6	0.3	1.7	0.2	0.3	2.1	0.7	0.8	0.2	0.2	3.3	0.2
Trivandrum	20	0.5	0.6	1.5	0.3	0.2	0.9	0.6	2.4	0.4	1.9	2.3	0.5
	50	0.7	0.6	1.5	0.6	0.3	1.0	0.8	4.1	1.1	3.1	2.7	1.3
	100	0.6	0.4	1.3	0.3	0.3	1.8	0.6	1.2	0.4	0.4	1.3	0.5
	200	0.3	0.4	1.2	0.1	0.1	0.6	0.2	0.3	0.0	0.1	1.0	0.1

Estuary													
St.No.	**Depth (m)**	**Sc**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**Zn**	**Zr**	**Nb**	**Mo**	**Hf**
1	3.0	1.0	0.7	1.2	0.7	0.5	0.8	0.6	1.4	0.5	0.5	1.8	0.3
2	4.5	0.6	0.5	1.0	0.4	0.4	0.6	0.6	3.6	0.1	0.4	0.7	0.2
3	2.5	0.6	0.4	0.8	0.2	0.3	0.4	0.5	5.1	0.2	0.3	0.4	0.3
4	ND	0.6	0.4	0.8	0.2	0.4	0.7	0.6	6.0	0.1	0.3	0.6	0.2
5	1.5	0.8	0.4	1.0	0.6	0.5	0.8	0.5	1.7	0.4	0.4	0.7	0.4
6	ND	0.9	0.9	1.3	0.7	0.5	0.5	0.8	4.5	1.1	3.7	1.6	1.2
7	5.5	0.6	0.5	0.8	0.6	0.7	0.6	0.4	1.5	0.3	0.9	0.9	0.3
8	4.0	1.1	1.1	2.0	0.9	0.8	1.8	1.4	3.6	0.3	1.5	5.1	0.4
9	8.5	0.6	0.4	1.0	0.4	0.4	0.9	0.4	1.0	0.2	0.3	0.7	0.2

Table 5.3b. Enrichment factors (transition elements) with respect iron along the study region during monsoon.

Shelf

Transects	Depth (m)	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Zr	Nb	Mo	Hf
Manglore	20	0.6	0.4	1.1	0.3	0.3	0.9	0.4	0.8	0.3	0.3	1.1	0.4
	50	0.6	0.4	1.2	1.5	0.4	0.9	0.5	1.1	0.7	0.3	1.5	0.9
	100	0.3	0.4	0.6	0.4	0.2	0.6	0.3	0.5	0.1	0.1	1.2	0.1
	200	0.2	0.2	0.5	0.2	0.2	0.4	0.2	0.3	0.0	0.0	0.5	0.1
Kannoore	20	0.6	0.3	1.2	0.2	0.3	0.9	0.4	0.7	0.2	0.2	1.2	0.3
	50	0.7	0.4	1.6	0.6	0.4	1.1	0.8	2.1	0.6	0.6	3.5	0.7
	100	0.6	0.3	1.2	0.5	0.4	1.3	0.5	0.9	0.3	0.2	1.2	0.3
	200	0.3	0.3	0.6	0.3	0.2	0.7	0.3	0.5	0.1	0.1	0.9	0.1
Baypore	20	0.5	0.3	1.1	0.2	0.3	0.9	0.4	0.7	0.2	0.2	0.9	0.2
	50	0.5	0.5	1.3	0.8	0.4	1.0	0.7	1.6	0.2	0.3	1.6	0.2
	75	0.6	0.4	1.5	0.5	0.4	1.1	0.7	1.5	0.4	0.3	2.1	0.5
	100	0.5	0.4	1.0	0.6	0.3	0.9	0.5	1.3	0.3	0.3	1.4	0.3
	150	0.3	0.4	0.7	0.3	0.2	0.9	0.3	0.4	0.0	0.1	1.5	0.1
	200	0.2	0.2	0.6	0.1	0.2	0.5	0.2	0.4	0.1	0.1	0.9	0.1
Ponnani	20	0.6	0.3	1.0	0.2	0.3	0.9	0.4	0.7	0.2	0.2	1.0	0.2
	50	0.4	0.3	0.9	0.9	0.4	0.7	0.3	0.8	0.2	0.2	0.9	0.2
	100	0.4	0.4	0.7	0.4	0.3	1.0	0.4	0.6	0.1	0.1	1.3	0.1
	200	0.3	0.3	0.5	0.2	0.2	0.5	0.2	0.3	0.0	0.0	0.9	0.1
Cochin	20	0.8	0.5	1.6	0.6	0.3	1.0	1.2	3.4	0.6	1.2	3.7	0.7
	50	0.5	0.4	1.1	0.6	0.3	0.9	0.5	1.9	0.3	0.9	1.9	0.4
	75	0.4	0.4	0.7	0.9	0.3	0.6	0.5	2.9	0.6	1.5	1.6	0.8
	100	0.5	0.3	0.9	0.4	0.3	0.8	0.4	1.3	0.7	0.5	1.3	0.8
	150	0.2	0.2	0.4	0.1	0.2	0.3	0.1	0.3	0.0	0.0	0.4	0.1
	200	0.2	0.1	0.4	0.1	0.2	0.3	0.1	0.3	0.0	0.0	0.4	0.1
Alleppy	20	0.6	0.4	1.0	0.3	0.3	0.7	0.5	1.8	0.5	0.9	1.5	0.7
	50	0.5	0.4	1.0	0.4	0.2	0.7	0.5	1.5	0.3	0.8	1.5	0.4
	75	0.5	0.4	1.3	0.3	0.3	1.4	0.5	1.5	0.2	0.5	3.1	0.3
	100	0.6	0.5	1.1	0.4	0.3	1.4	0.5	1.6	1.0	0.8	1.8	1.2
	150	0.2	0.2	0.6	0.1	0.1	0.6	0.2	0.5	0.1	0.1	0.8	0.1
	200	0.3	0.3	0.8	0.1	0.2	0.9	0.3	0.6	0.1	0.1	1.8	0.1
Kollam	20	0.5	0.3	0.9	0.2	0.3	0.7	0.3	1.1	0.2	0.4	1.0	0.3
	50	0.7	0.7	2.1	0.5	0.3	1.6	0.9	2.6	0.4	1.3	6.7	0.5
	100	0.5	0.5	1.5	0.4	0.3	1.7	0.7	1.6	0.4	0.6	4.0	0.5
	200	0.5	0.3	1.6	0.1	0.3	1.9	0.6	0.8	0.1	0.1	6.0	0.2
Trivandrum	20	0.4	0.5	1.0	0.4	0.2	0.6	0.6	2.2	0.3	1.0	1.8	0.4
	50	0.6	0.6	1.2	0.6	0.3	0.7	0.7	3.8	0.5	2.4	2.1	0.7
	100	0.8	0.4	1.2	0.3	0.3	1.7	1.8	1.3	0.2	0.3	2.0	0.3
	200	0.2	0.3	0.7	0.1	0.1	0.6	0.2	0.3	0.0	0.0	0.8	0.1

Estuary

St.No.	Depth (m)	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Zr	Nb	Mo	Hf
1	3.0	5.1	2.9	6.9	3.7	2.1	3.5	2.6	6.5	0.8	2.3	3.7	1.0
2	4.5	2.9	2.1	4.3	1.6	1.8	2.8	2.6	15.6	0.7	1.6	3.2	0.8
3	2.5	2.3	1.9	3.7	1.0	1.3	2.0	2.1	23.4	0.6	1.5	2.1	0.8
4	ND	2.8	1.8	3.8	0.9	1.6	2.9	2.6	26.7	0.6	1.5	2.3	0.8
5	1.5	3.6	2.3	4.5	2.6	2.2	3.3	2.1	5.8	1.1	2.0	2.4	1.3
6	ND	4.2	4.2	6.5	3.4	2.1	2.1	3.9	22.0	4.6	16.9	7.0	5.0
7	5.5	2.8	1.9	3.6	2.6	2.9	2.5	2.1	6.8	1.8	3.6	3.6	2.0
8	4.0	2.5	1.5	3.1	2.7	2.8	2.5	2.0	4.2	1.0	2.0	6.7	1.1
9	8.5	2.9	1.8	4.7	1.4	1.5	4.1	1.7	3.9	0.8	1.3	3.3	1.0

Nobelium showed moderate enrichment along the southern zone. Molybdenum showed severe and extreme enrichment along almost all transects from coastal to seaward stations and the intensity of enrichment increased from north to south. However, Co, Zr and Hf showed low enrichment along all the stations during both seasons. In Cochin estuary, the northern zone showed moderate enrichment for TEs such as Sc, V, Cr, Fe, Ni, Cu, Mo and extreme enrichment for Zn. In addition, the southern most station also showed moderate enrichment for metals such as Sc, Cr, Fe, Ni, Zn and Mo. However, the TEs such as Mn, Co, Zr, Nb and Hf showed low enrichment along almost all the stations during both seasons. The remaining stations of the central and southern zones showed low enrichment for all TEs during both seasons.

5.2.3.2 Enrichment with respect to Iron

In shelf region, iron enrichment was low compared to the aluminum enrichment during both seasons. However, the pattern of enrichment with respect to iron was similar to that of aluminium. Southern zone showed high enrichment compared to the northern zone during both seasons. Cr showed moderate enrichment along the coastal and mid-depth stations during both seasons. Ni also exhibited moderate enrichment along the coastal and mid depth stations along the study region; however, the extent was less than that of Cr. Zn showed moderate enrichment along the coastal and mid-depth stations along the southern zone. Mo observed moderate enrichment along almost all the stations and severe enrichment along Kollam transects during both seasons. The TEs showed low enrichment along the remaining shelf region during both seasons. In Cochin estuary, the TEs generally showed drastic enrichment during monsoon compared to premonsoon where iron enrichment was higher than aluminum enrichment. The zinc enrichment was particularly high (15-20 times) because of the industrial establishments along the northern zone.

The distribution of Co and Sc in the sediments suggests a non-linearity during weathering, erosion, or sedimentation (Wronkiewicz and Condie, 1989). Co has been widely used in determining the provenance, source and characteristics of sedimentary rocks, because it is immobile along with Ta, La, Yb and Sc. Enrichment of Co and Sc in sedimentary rocks are assumed to be derived from mafic sources (Nath et al, 2000). The enrichment of TMs like Cr and Mo relative to their crustal abundances indicates that the host sediments accumulated under anoxic conditions, although not necessarily under anoxic bottom waters.

5.2.4 Elemental excess

The concentration of an element, in excess of its content in the global shale, is called the elemental excess (El_{ex}). This represents the fraction of element that is structurally bound to detrital component to the total concentration of that element in the sediment. Elemental excess was high, indicating sources of elements other than PAAS (Table 5.4a & Table 5.4b). Monsoon recorded slightly higher El_{ex} compared to premonsoon and the southern zone observed high El_{ex} compared to the northern zone. Cr and Mo showed positive El_{ex} along the study region during both seasons. In addition, Ni and Cr showed high El_{ex} during both seasons. Fe observed high El_{ex} along the shelf except Cochin; however, high and low El_{ex} was observed along the outer and coastal stations respectively. Zn showed positive El_{ex} along the shelf region (except coastal stations along the northern zone) which increased from north to south. The remaining TEs showed insignificant El_{ex} values along the shelf during both seasons, indicating absence of any external source of the element.

Table 5.4a. Elemental excess (transition elements) along the study region during premonsoon.

Shelf														
Transects	**Depth (m)**	**Sc**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Zr**	**Nb**	**Mo**	**Hf**
Manglore	20	-7.4	-119.7	21.6	-745.4	8768.4	-18.7	-1.7	-34.1	-2.2	-182.9	-17.5	0.0	-3.8
	50	0.4	-2.9	28.2	136.6	9740.8	-1.5	13.7	0.9	24.9	-6.1	-2.0	0.3	0.3
	100	1.0	14.2	53.8	205.0	41434.0	-0.9	24.7	0.5	28.9	-32.0	-3.5	0.9	-0.5
	200	-0.2	-4.3	74.5	-111.8	68590.8	-0.9	28.3	-2.6	19.5	-64.8	-5.9	0.6	-1.4
Kannoore	20	-8.5	-123.5	30.7	-820.2	6562.3	-20.3	-1.5	-38.1	-12.9	-195.8	-18.5	0.0	-4.0
	50	-0.6	-14.2	35.2	-50.5	7280.2	-2.7	5.9	-1.0	33.7	-15.4	-1.4	0.6	-0.1
	100	-1.3	-26.1	38.0	-90.4	13169.4	-3.7	21.2	-2.6	26.5	-46.2	-5.2	0.3	-0.8
	200	-0.6	-0.4	46.6	-84.2	32913.5	-2.6	22.0	-1.4	21.7	-48.4	-4.8	0.6	-0.9
Baypore	20	-7.5	-107.6	11.2	-593.7	2769.9	-16.8	-10.6	-33.1	6.5	-153.1	-15.2	0.7	-3.1
	50	-2.1	-32.8	22.1	21.8	11417.2	-5.1	4.8	-9.5	17.4	-67.9	-5.5	0.2	-1.4
	75	-0.5	-10.7	45.7	3.9	9406.8	-2.2	17.7	1.1	29.8	-21.9	-2.2	1.2	-0.3
	100	0.0	-5.3	56.8	194.3	26896.1	-0.1	25.6	0.7	47.9	-29.8	-2.4	1.2	-0.5
	150	1.7	6.1	54.3	12.7	68732.4	2.1	30.3	0.7	22.2	-47.4	-4.3	0.6	-1.0
	200	0.8	0.0	37.0	-74.0	41961.4	-0.5	17.6	-0.7	14.2	-30.9	-3.0	0.3	-0.6
Ponnani	20	-6.0	-125.7	29.5	-912.3	7839.9	-19.7	3.8	-33.4	-19.5	-219.1	-18.4	-0.3	-4.9
	50	-0.6	-19.2	27.0	203.8	13339.9	-3.2	9.8	-4.7	17.7	-44.8	-3.7	0.2	-1.0
	100	2.0	7.3	36.4	184.0	31345.2	1.6	31.3	2.6	24.0	-31.4	-2.7	0.5	-0.6
	200	0.3	-11.7	58.4	-138.6	58767.8	-1.2	29.7	-2.6	40.0	-71.7	-6.1	0.4	-1.5
Cochin	20	-0.1	-12.0	9.1	-22.7	2395.7	-2.6	-1.2	-2.1	35.3	-11.4	3.8	0.2	-0.2
	50	-1.9	-30.2	7.7	-125.5	-1240.6	-5.2	0.2	-5.7	15.9	-44.0	-3.5	0.1	-1.0
	75	-0.3	-12.2	22.4	113.8	15372.3	-4.7	2.3	-1.6	109.0	-5.6	11.6	0.4	0.3
	100	-2.6	-52.9	5.7	-176.5	7923.2	-6.8	-1.0	-13.8	29.4	-4.9	-3.5	0.0	0.3
	150	0.8	-11.7	39.4	-86.2	84605.6	0.3	13.2	-7.3	21.4	-60.2	-5.1	0.3	-1.3
	200	0.1	-14.4	51.5	-138.4	92015.4	0.6	13.5	-6.7	30.6	-63.7	-6.0	0.3	-1.3
Alleppy	20	-2.3	-43.9	14.4	-286.5	4984.0	-8.1	-3.0	-11.9	36.9	-59.6	-1.4	0.8	-1.2
	50	-0.3	-13.6	28.5	-104.8	9322.6	-3.5	6.0	0.1	36.9	-1.7	3.2	0.3	0.2
	75	0.3	-15.3	31.0	-104.5	8885.3	-3.3	14.5	-0.2	44.0	-11.3	2.7	0.3	-0.1
	100	1.9	5.3	25.1	32.7	10341.4	-1.2	14.5	3.0	60.9	42.9	8.7	0.3	1.4
	150	0.3	-20.1	56.5	-150.5	23414.7	-2.6	33.9	-1.0	16.4	-38.2	-3.3	1.1	-0.8
	200	-0.1	-19.2	55.3	-146.4	22119.4	-2.7	27.8	-0.3	20.3	-36.6	-3.0	0.6	-0.7
Kollam	20	-5.8	-86.7	21.2	-507.8	5542.5	-15.2	-5.2	-29.2	21.7	-98.5	-5.4	0.4	-1.9
	50	0.5	-6.3	74.3	-22.1	53167.9	-0.9	37.7	-1.2	18.8	-52.6	-5.0	0.8	-1.1
	100	4.2	40.9	57.9	312.5	23876.5	-0.8	14.8	8.4	216.8	124.7	34.3	1.4	3.6
	200	0.6	-9.6	57.0	-113.8	10232.4	-1.8	37.5	5.1	10.4	-28.9	-2.2	1.2	-0.6
Trivandrum	20	1.4	20.1	55.3	9.5	14111.8	-0.6	15.1	6.2	77.7	15.8	13.1	0.9	0.5
	50	1.0	7.8	36.8	42.7	7907.3	-1.4	8.7	4.8	104.5	47.0	17.3	0.8	1.5
	100	0.8	-5.2	30.2	-55.2	7928.0	-1.5	25.4	2.4	20.7	-6.4	-0.6	0.3	0.1
	200	3.2	72.3	206.5	-103.2	67510.0	-0.8	43.8	5.6	23.6	-31.5	-1.8	1.5	-0.6
Estuary														
St. No.	**Depth (m)**	**Sc**	**V**	**Cr**	**MN**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Zr**	**Nb**	**Mo**	**Hf**
1	3.0	-10.1	-106.1	-63.9	-592.6	-28580.3	-17.2	-36.8	-36.0	-44.7	-158.3	-14.5	-0.4	-4.0
2	4.5	-8.8	-127.8	22.4	-1013.6	14444.0	-25.2	-29.7	-33.3	556.6	-360.8	-22.5	-0.4	-8.1
3	2.5	-4.6	-100.3	33.6	-990.1	36376.0	-23.3	-35.3	-26.6	926.7	-240.5	-17.1	-0.6	-5.1
4	ND	-10.0	-172.7	-12.4	-1299.5	11707.0	-27.6	-29.0	-34.9	979.2	-353.7	-24.0	-0.8	-8.0
5	1.5	-11.8	-140.8	-67.5	-734.0	-29063.1	-21.0	-39.9	-45.4	-24.6	-207.2	-18.0	-0.8	-4.7
6	ND	2.0	18.2	32.1	50.3	7678.0	-0.8	-2.0	5.1	130.9	43.2	22.9	0.4	1.3
7	5.5	-3.5	-49.2	0.5	-202.7	7209.1	-3.5	-12.3	-17.1	48.2	-95.6	1.8	0.0	-2.1
8	4.0	0.3	3.8	18.7	-4.1	432.0	-0.7	7.3	3.2	34.8	-20.1	1.6	0.6	-0.4
9	8.5	-8.3	-141.1	18.4	-744.1	7630.9	-22.3	-3.9	-44.3	9.3	-264.7	-21.1	-0.3	-5.9

Table 5.4b. Elemental excess (transition elements) along the study region during monsoon.

Shelf

Transects	Depth (m)	Sc	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	Nb	Mo	Hf
Manglore	20	-5.5	-93.9	29.0	-589.7	9060.7	-15.0	3.8	-26.6	-4.8	-148.0	-14.2	0.4	-3.0
	50	0.4	-8.1	30.7	342.4	9327.4	-1.3	7.9	-0.4	20.2	18.3	-2.0	0.4	0.7
	100	1.9	32.0	53.1	183.1	43620.7	-0.5	24.3	1.6	24.6	-34.0	-3.5	1.2	-0.7
	200	0.8	2.3	54.2	-24.5	60540.0	0.7	24.3	-1.0	16.5	-46.2	-4.2	0.6	-1.0
Kannoore	20	-7.6	-118.0	42.5	-804.2	7647.0	-18.9	3.8	-32.7	-21.8	-195.0	-17.4	0.4	-4.2
	50	0.1	-11.7	26.5	-37.6	3547.7	-2.3	6.2	1.4	31.5	-9.1	-0.8	0.8	0.0
	100	-0.2	-32.2	46.4	-108.6	13133.9	-4.3	27.4	-3.1	15.8	-59.1	-5.8	0.5	-1.1
	200	0.1	-1.0	46.6	-24.7	39171.2	-1.2	25.6	-0.7	22.3	-51.8	-4.7	0.7	-1.1
Baypore	20	-8.3	-125.1	31.0	-884.7	7652.4	-20.4	0.2	-38.3	-29.0	-227.4	-19.2	0.1	-5.0
	50	-1.5	-17.1	19.3	15.0	3535.1	-3.6	4.9	-1.1	26.7	-45.1	-3.2	0.3	-1.0
	75	0.2	-9.0	36.2	-12.6	7004.2	-1.6	10.1	1.6	27.4	-10.3	-1.6	0.6	0.0
	100	0.5	-3.3	29.8	77.8	12027.5	-1.2	13.2	1.6	35.7	-17.6	-1.2	0.4	-0.3
	150	1.6	18.9	35.2	80.9	24174.6	0.1	24.3	4.9	13.2	-20.4	-1.6	0.8	-0.4
	200	-0.3	-7.8	51.5	-135.2	51456.8	-1.3	23.1	-2.3	15.1	-60.7	-5.4	0.9	-1.2
Ponnani	20	-8.5	-137.2	23.5	-962.2	6430.7	-21.4	-0.8	-39.8	-31.7	-243.5	-20.5	0.1	-5.4
	50	-1.8	-28.1	31.2	209.0	15661.0	-3.5	8.0	-8.7	13.6	-62.6	-5.3	0.3	-1.3
	100	1.1	12.6	32.2	71.5	21060.0	-0.3	25.5	2.8	18.1	-27.8	-2.3	0.7	-0.6
	200	2.2	22.1	40.9	96.1	42863.0	1.3	23.7	3.2	12.7	-23.7	-2.1	0.9	-0.5
Cochin	20	-0.7	-14.9	8.9	-67.0	-722.2	-3.2	-0.7	0.7	33.3	-17.2	0.3	0.4	-0.3
	50	-2.8	-31.7	7.6	-101.5	1921.4	-6.4	0.0	-8.4	38.2	-54.1	-0.1	0.4	-1.1
	75	0.5	2.8	25.2	344.1	20515.5	-2.4	6.7	3.6	156.0	36.0	15.2	0.9	1.5
	100	-3.4	-51.3	7.8	-202.5	5440.5	-7.4	0.1	-13.4	25.0	-18.1	-4.2	0.3	0.0
	150	0.0	-6.0	50.8	-158.3	89717.9	0.0	12.0	-12.6	19.6	-78.7	-7.0	0.6	-1.7
	200	0.4	-24.2	53.6	-199.4	94385.2	-0.4	10.3	-12.8	35.0	-81.6	-7.2	0.6	-1.7
Alleppy	20	-2.9	-42.1	17.4	-307.3	7548.4	-9.3	-5.0	-13.1	65.5	-46.7	1.4	0.6	-0.5
	50	-0.8	-15.2	23.8	-87.4	9588.3	-3.8	4.0	-2.3	39.3	-28.9	1.9	0.4	-0.5
	75	-0.4	-14.4	40.9	-121.5	9723.4	-3.5	21.5	-1.3	39.2	-39.7	-0.3	1.2	-0.7
	100	1.7	13.6	34.8	48.4	13034.7	-0.5	25.4	4.6	45.6	61.0	3.7	0.6	1.9
	150	-0.2	-5.0	44.0	-129.7	37393.3	-2.2	22.8	-2.1	19.9	-39.0	-3.6	0.7	-0.8
	200	-0.4	-3.7	61.9	-159.8	35383.2	-2.8	34.2	-1.5	24.9	-49.7	-4.1	1.6	-1.0
Kollam	20	-8.3	-116.8	15.2	-782.4	12476.0	-20.0	-7.0	-39.4	36.3	-203.4	-12.0	0.2	-4.4
	50	-0.2	-1.7	35.9	-52.2	2950.6	-2.3	11.0	1.9	37.1	-13.7	2.7	1.4	-0.2
	100	-0.6	-8.6	39.4	-95.7	7232.8	-3.1	25.4	0.7	33.6	-18.9	-0.3	1.4	-0.2
	200	0.1	-11.4	59.7	-118.9	11615.0	-2.0	37.8	3.5	14.1	-30.9	-2.7	2.6	-0.6
Trivandrum	20	1.4	20.8	39.7	67.1	16645.5	-0.6	10.7	7.9	78.3	5.5	6.7	0.8	0.3
	50	0.5	4.9	26.3	5.0	7090.9	-1.8	2.7	3.2	94.4	-2.1	12.0	0.5	0.2
	100	2.2	3.7	28.3	-21.3	8779.2	-0.6	22.6	21.6	23.7	-10.2	-0.1	0.5	-0.1
	200	0.8	25.7	72.8	-95.8	45487.6	-1.2	28.9	1.1	16.2	-33.7	-2.8	0.8	-0.7

Estuary

St. No	Depth (m)	Sc	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr	Nb	Mo	Hf
1	3.0	-9.8	-112.0	-54.5	-593.4	-29297.1	-18.4	-39.1	-38.3	-44.6	-185.0	-14.9	-0.7	-4.3
2	4.5	-9.5	-159.1	12.0	-1117.0	11802.9	-27.9	-36.2	-38.7	523.0	-379.9	-24.9	-0.4	-8.7
3	2.5	-4.9	-72.2	48.3	-815.0	39862.7	-18.5	-23.3	-17.9	899.8	-238.1	-13.0	-0.4	-5.3
4	ND	-10.4	-168.0	-14.4	-1320.5	10990.5	-27.7	-33.1	-37.5	957.3	-358.1	-24.4	-0.9	-8.1
5	1.5	-10.6	-126.2	-60.4	-680.0	-24872.6	-19.7	-38.8	-43.5	-32.8	-210.1	-16.6	-0.8	-4.9
6	ND	2.3	21.8	37.2	65.5	7788.5	-0.8	-1.9	5.8	140.9	36.7	23.2	0.4	1.1
7	5.5	-4.3	-65.8	-13.0	-270.7	3140.0	-5.9	-18.0	-20.5	42.3	-96.0	-2.2	-0.1	-2.1
8	4.0	-4.4	-74.3	-14.8	-192.9	8701.5	-4.8	-14.1	-18.4	10.3	-127.0	-7.0	0.7	-2.9
9	8.5	-9.0	-158.9	24.7	-1051.4	7353.6	-26.6	-2.9	-54.1	-9.8	-313.7	-24.2	-0.4	-7.1

Cochin estuary showed negative/very low El_{ex} for almost all TEs during both seasons. However, Zn showed very high El_{ex} (90% of the total elemental concentration) during both seasons along the northern zone and positive values for remaining stations (except 1 & 5), which is due to high zinc concentration in the estuary. Fe showed positive El_{ex} along the northern and southern regions of the estuary during both seasons, indicating its external sources.

5.3 Discussion

The study on the geochemistry of sediments distinguishes the various TEs bearing components, and delineates the processes leading to their enrichment/depletions in the sediments. Aquatic sediments which are organic-rich and suboxic exert a strong influence on oceanic chemical budgets as well as biogeochemical cycling of redox-sensitive elements (Legeleux et al., 1994). Redox-sensitive transition element concentrations or ratios are among the most widely used indicators of redox conditions in modern and ancient sedimentary systems (Calvert and Pedersen, 1993; Pailler et al., 2002; Algeo and Maynard, 2004). An enrichment of these redox sensitive elements suggests that reducing condition does prevail in this environment, which is impinged by low oxygen waters and high organic carbon. This pattern exists because (1) many redox sensitive transition metals have multiple valences, and the reduced forms are more readily complexed with organic acids and authigenic sulfides, or precipitated as insoluble oxy-hydroxides, and (2) TEs are affected by processes such as Mn/Fe redox cycling, increased availability of organic substrates, and presence of H_2S at sediment redox boundaries (Calvert and Pedersen, 1993; Morse and Luther, 1999). Because all of these processes are operative primarily or exclusively at dissolved oxygen levels low enough to exclude benthic organisms (~< 0.2 ml l^{-1}); elements such as V, Cr, Co, Ni, Cu, Zn and Mo showed little enrichment and depletion for Mn at deeper sediments owing to very low oxygen and high organic content. The following section evidences that the redox sensitive elements are accumulating in deep shelf stations due to the presence of a more pronounced suboxic/anoxic interface. In order to explain this, a brief review of what is known about the behavior of redox sensitive metals under suboxic/anoxic conditions are presented.

In oxic environments, V exists as (+5) in vanadate ion such as HVO_4^{2-} and $H_2VO_4^-$ (Sadiq, 1988; Wehrli and Stumm, 1989). Under mildly reducing conditions, V(+5) converts to V(+4) and forms the vanadyl ion (VO^{2+}) related hydroxyl species (e.g., $VO(OH)_3^-$), or an insoluble hydroxide ($VO(OH)_2$; Van der Sloot et al., 1985). In oxic environments, Zn may exist as Zn^{2+} or $ZnCl^+$ (Calvert and Pedersen, 1993), although most Zn probably complexes with humic and fulvic acids (Achterberg et al., 1997). In oxic environments, Cr is present mainly as Cr (+6) in the chromate anion (CrO_4^{2-}) and to a lesser extent (~5%) as Cr (+3) in aqua hydroxyl cations, Cr $(H_2O)_4(OH)_2^+$ (Cranston and Murray, 1978; Calvert and Pedersen, 1993). In modern marine environments, Cr is commonly associated with organic matter, although most Cr uptake occurs in the sediment rather than in the water column (Francois, 1988). Cr (+3) uptake by authigenic Fe-sulfides is very limited owing to structural and electronic incompatibilities with pyrite crystals (Huerta-Diaz and Morse, 1992; Morse and Luther, 1999). In oxic environments, Mn forms highly insoluble Mn (+3) or Mn (+4) hydroxides or oxides (MnO_2) that are rapidly deposited in particulate form (Sholkovitz et al., 1992; Calvert and Pedersen, 1993). Under anoxic conditions, Mn is reduced to Mn (+2) and forms soluble Mn^{2+} or $MnCl^+$ cations. Because dissolved Mn is not readily taken up by any organic or mineral phase (although present in trace in pyrite; Huerta-Diaz and Morse, 1992), it diffuses upward out of the sediment or from the sediment-water interface into the water column in anoxic systems. Mn-Fe redox cycling is important for metal enrichment in anoxic systems because it can accelerate export of metals from seawater to the sediment-water interface. Redox sensitive transition elements subjected to uptake by particulate Mn- Fe-oxyhydroxides include cations of chalcophilic elements (Ni_2^+, Cu_2^+, Zn_2^+ and Co_2^+) and ionic species of certain oxides and hydroxides. In oxic environments, Co is present as a cation (Co_2^+) complexed with humic and fulvic acids (Achterberg et al., 1997). In anoxic waters, Co forms an insoluble sulfide (CoS) that can be taken up in solid solution by authigenic Fe-sulfides (Huerta- Diaz and Morse, 1992). However, Co uptake is kinetically slow, tending to limit its concentration in authigenic sulfides (Morse and Luther, 1999). The degree to which Co is influenced by Fe-Mn redox cycling is uncertain. In oxic environments, Ni may exist as Ni^{2+} or $NiCl^+$ ions (Calvert and Pedersen, 1993), although most Ni is present in solution as a Ni-carbonate complex ($NiCO_3$) or adsorbed on humic and fulvic acids (Achterberg et al., 1997). Removal of Ni to the sediment may be accelerated by sedimentation with organic matter but, remineralization of the latter below the sediment-water interface can liberate Ni to pore waters. Under anoxic conditions, Ni forms an insoluble sulfide (NiS) that can be taken up in solid solution by authigenic pyrite (Huerta-Diaz and Morse, 1992). However, Ni uptake is kinetically slow, tending to limit its concentration in authigenic sulfides (Morse and Luther, 1999). The strong association of Ni with organic carbon may support the hypothesis of Lewan and Maynard (1982) that Ni is taken up mainly as tetrapyrrole complexes, preservation of which occurs only in anoxic/euxinic facies. In oxic environments, Cu is present mainly in organo-metal ligands and, to a lesser extent, as $CuCl^+$ (Calvert and Pedersen, 1993; Achterberg et al., 1997). Removal of Cu to the sediment may be accelerated by: (1) formation of organo-metal compounds with humic acids, and (2) adsorption onto particulate Fe-Mn-oxyhydroxides and settling to the sediment. Release of Cu through remineralization of organic matter by sulfate-reducing bacteria or reductive dissolution of Fe-Mn-oxyhydroxides may liberate Cu within the sediment or at the sediment-water interface. Under anoxic conditions, it may be reduced from Cu (+2) to Cu (+1) with subsequent precipitation as an independent sulfide (CuS or Cu_2S) or Fe-sulfide (Huerta-Diaz and Morse, 1992; Achterberg et al., 1997; Morse and Luther, 1999). In anoxic waters, dissolved Zn is rapidly precipitated as ZnS or as an independent authigenic sphalerite (Brumsack, 1980; Morse and Luther, 1999). Decay of organic matter by sulfate-reducing bacteria may liberate Zn facilitating the uptake of Zn by authigenic Fe-sulfides . Mo is present in seawater as molybdate (MoO_4^{2-}) in relatively high concentration (~10 ppb). Mo is enriched in organic-rich sediments through a series of reactions. Transfer of MoO_4^{2-} to the sediment-water interface is promoted through adsorption onto humic substances (Brumsack, 1989; Helz et al., 1996) or particulate Mn-Fe-oxyhydroxides. In the latter case, it is associated with redox cycling of Mn and Fe (Magyar et al., 1993; Adelson et al., 2001). In anoxic waters, MoO_4^{2-} released from organic matter decay by sulfate-reducing bacteria is reduced to Mo (V and IV) (Calvert and Pedersen, 1993; Zheng et al., 2000). Mo (IV) is deposited as organic thiomolybdates or after further reduction to MoS_4^{2-} with Fe-sulfides (Huerta-Diaz and Morse, 1992; Helz et al., 1996; Morse and Luther, 1999; Adelson et al., 2001). This could be the possible reaction for the enrichment of redox sensitive transition elements along the deeper stations of continental shelf.

Percentage of clay in the sediment is one of the important factors in regulating the trace metal geochemistry of marine sediments. The samples with high trace metal concentration showed higher clay percentage. In addition, metals like, Cr, Co, Ni, Cu, Zn and Fe, which have affinity for biota, and have nutrient-like distribution in the oceans are important. Fe and Mn are enriched in marine sediments due to their direct precipitation from seawater as hydroxides (Landing and Bruland, 1987), whereas elements like Zn, Cu, Ni, and Co are scavenged by their incorporation and/or adsorption to authigenic minerals (Altschuler, 1980). Murthy et al. (1973) reported that the fine-grained sediments in the inner shelf and slope regions contain relatively high Ni in the outer shelf. In the present study, Ni concentration is low for the southern coastal locations (Cape Comorin to Cochin), while other coastal samples (Calicut to Porbandar) showed high Ni concentration compared to deeper ones. Mn, Cu and Ni are present in terrigenous material in small quantities, which is dominant along coastal stations. Except the deep sea region, these elements are associated with authigenic formation of manganese nodules. Cu responds to the redox condition of overlying water and may get precipitated as sulphide in reducing environment.

Removal of dissolved metals to the sediment can be influenced either by biogenic or non-biogenic processes. Biogenic processes involve uptake of metals that serve as minor bio-nutrients. TEs that are consumed during biological uptake in the open ocean such as Zn, Cu, and Ni are depleted in surface waters by a factor of five or more relative to deep waters (Bruland, 1980; Brumsack, 1986; Piper, 1994). The significance of this process is that it may accelerate export of trace elements to deep waters during intense primary production. Many other trace metals including Mo, V, and Cr, are conservative in marine systems (Calvert and Pedersen, 1993; Morford and

Emerson, 1999). A few trace metals including Co and Pb are depleted in deep relative to surface waters owing to high rates of particle scavenging (Brumsack, 1986). The high sedimentation rate, typical of upwelling zones occupying suboxic waters are not generally conducive for elemental enrichment (Brumsack, 1986). Moreover, such enrichments are more favored by a combination of slow sedimentation and intense anoxia (Lewan and Maynard, 1982; Brumsack, 1986).

The high concentration found along the coastal stations could be due to the anthropogenic activities and riverine inputs. It is well known that Fe and Mn are enriched in oxic sediments due to the precipitation as their corresponding oxyhydroxides (Klinkhammer et al., 1982). More than 50 % of Mn in the sediments are non-lithogenous, indicating its high chemical reactivity in marine environment (Balachandran et al, 2003).The low Fe and Mn concentrations in the sediments of deeper stations were mainly due to reducing conditions (Sullivan et al., 1997; Manford et al., 2001; Nameroff et al., 2002). The reducing conditions developed due to the high productivity in the water and high organic matter accumulation are effective in stripping elements from the sediments (Calvert and Perderson, 1993; Sagar, 1994). The geochemistry of Mn and Ce are almost identical, where both elements exhibit oxidative precipitation and reductive dissolution (Moffett, 1990). Dickens and Owen (1994) have suggested that the redox-sensitive Mn oxyhydride dissolves on entering an OMZ (oxygen minimum zone) and gets precipitated in oxygenated environments (Dickens and Owen, 1994; Nath et.al, 1997). Fe was concentrated in the deep. Indus provenance for this sediment may be a reason for this anomalous behavior (Rao and Rao, 1995; Kessarkar et al., 2003). Mn is an important constituent of pelagic sediments controlling other transition metals. Similar trend was exhibited by Fe and Mn indicating their common biogeochemical behavior in the marine environment. The concentrations of Co along the nearshore stations were high, which decreased with depth. The adsorption onto the clay minerals, iron and manganese oxides may be contributing to the distribution of Co. The studies on anoxic water revealed that the reduced species of Mn, Fe and Co are more soluble than the oxidised one. A similar association of Co with Mn has been reported in anoxic waters (Haraldsson and Westerlund, 1988; Dyressen and Kremling, 1990; Lewis and Landing, 1991). The maximum concentrations were observed in the northern transect and minimum were in the western transect. This geochemical variability in their distributional characteristics is mainly attributed to the scavenging or co-precipitation of Fe- and Mn-hydroxides on these metals. The increase in the concentrations of redox sensitive metals such as V, Cr, Co, Ni, Cu, Zn and Mo at the oxygen minimum layers (deeper stations along the shelf) is due to the reducing conditions, under this condition, they forms highly insoluble sulphides. They exist as a network of interconnected sulphur complexes and sulphides and are removed from seawater by diffusion (Calvert and Perderson, 1993; Manford et al., 2001; Marcus et al., 2003). So an enrichment of V, Cr, Co, Ni, Cu, Zn and Mo in the continental slope suggests that a reducing condition does prevails. The enrichment of metals was comparatively high in northern transect. Hence, these elements (V, Cr, Co, Ni, Cu, Zn and Mo) can be used as indicator of redox condition. Among these metals, Cr showed higher values in all stations, possibly due to their high enrichment in earth crust, and especially to their marine origin.

Anthropogenic activity is a significant source for these metals in sediments. The nearshore environment is more oxic due to turbulence, which increases the elemental deposition. The enrichment of these elements is consistent with previous studies in other areas (Sanudo-Wilhelmy and

Flegal, 1996). The elevated coastal concentrations have been attributed to remobilisation including particle resuspension, diffusion, upwelling and weathering (Martin and Gordon, 1988; Westerlund and Ohman, 1991). The reversing surface currents along the west coast of India, and the coastal upwelling are important mechanisms of metal transport into the coastal waters and their subsequent sedimentation on the continental shelf (Naqvi et al., 2000; Shankar, 2000). Several studies have proved that coastal processes can regulate trace metal concentrations in aquatic environments (Bruland, 1980; Jones and Murray, 1984).

Sc is generally considered as in natural origin (crust-derived particles). The high concentrations of Sc in the estuarine and nearshore sediments during both seasons indicate its riverine origin. The carrier phase of these elements is probably titanomagnetite and other mafic minerals derived from the rivers. The extremely high values indicate contamination. The presence of Sc and Fe in sediments is commonly used to identify terrigenous supply. Pattan and Jauhari (2001) studied in the calcareous ooze, siliceous ooze, and red clay from the central Indian Ocean basin and reported 8ppm, 17 ppm, and 36 ppm for Sc and 22 ppm, 70 ppm and 95 ppm respectively for V. But studies on Sc and V in the western continental margin of India are not reported on our notice. Zirconium, hafnium and yttrium are generally resistant to weathering and alteration (Taylor and McLennan 1985, Bhatia and Crook 1986; Nath et al., 1997) and hence, are classified as high energy elements. The reason for depletion of Hf could be size sorting. Hf and Zr are concentrated mostly in sand as zircons (Condie, 1993), which undergo mechanical sorting. Hence, Hf will be in the sand, leading to its depletion from clay. The high values of Ta and Nb along the Kollam and Trivandrum transects indicate its association with black sand minerals of smaller grain size.

Table 5.5. Pearson correlation for transition elements with biogeochemical parameters along the shelf sediments (Metals are in ppm).

Premonsoon																							
	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	Al (%)	Fe (%)	Silt %	Clay %	Sand %	D.O (ml/l)	Sal (PSU)	Org.C (%)	$CaCO_3$ (%)
Sc	1																						
V	0.97	1																					
Cr	0.99	0.97	1																				
Mn	0.84	0.85	0.88	1																			
Co	0.94	0.93	0.94	0.91	1																		
Ni	0.93	0.86	0.95	0.87	0.91	1																	
Cu	0.98	0.97	0.96	0.77	0.92	0.88	1																
Zn	0.87	0.85	0.81	0.48	0.76	0.69	0.92	1															
Y	0.97	0.92	0.95	0.76	0.93	0.93	0.98	0.90	1														
Zr	0.66	0.69	0.65	0.54	0.56	0.46	0.62	0.63	0.57	1													
Nb	0.31	0.41	0.31	0.33	0.35	0.15	0.36	0.34	0.28	0.75	1												
Mo	0.88	0.91	0.92	0.86	0.89	0.90	0.89	0.68	0.85	0.46	0.32	1											
Hf	0.73	0.75	0.72	0.60	0.63	0.55	0.69	0.69	0.65	0.99	0.72	0.54	1										
Ta	0.46	0.54	0.45	0.46	0.49	0.30	0.50	0.46	0.43	0.82	0.98	0.43	0.81	1									
Al (%)	0.92	0.84	0.90	0.78	0.86	0.90	0.87	0.75	0.92	0.45	0.02	0.73	0.52	0.19	1								
Fe(%)	1.00	0.97	0.99	0.83	0.94	0.92	0.97	0.87	0.96	0.69	0.31	0.87	0.75	0.46	0.90	1							
Silt %	0.27	0.20	0.20	-0.19	0.11	0.14	0.31	0.58	0.37	0.14	-0.17	0.03	0.11	-0.11	0.34	0.29	1						
Clay %	-0.06	0.03	-0.07	-0.10	-0.13	-0.16	0.04	0.06	-0.03	0.31	0.69	-0.01	0.27	0.62	-0.19	-0.11	-0.03	1					
Sand %	-0.08	-0.12	-0.03	0.18	0.06	0.08	-0.19	-0.33	-0.15	-0.34	-0.54	0.00	-0.30	-0.50	0.01	-0.04	-0.45	-0.88	1				
D.O(ml/l)	-0.26	-0.19	-0.20	-0.20	-0.30	-0.26	-0.26	-0.22	-0.33	0.22	0.39	-0.05	0.19	0.29	-0.58	-0.21	-0.32	0.18	0.00	1			
Sal (PSU)	-0.67	-0.75	-0.72	-0.68	-0.68	-0.63	-0.67	-0.51	-0.57	-0.50	-0.36	-0.84	-0.56	-0.43	-0.39	-0.70	0.12	0.16	-0.20	-0.38	1		
Org.C (%)	0.24	0.29	0.18	-0.20	0.02	-0.01	0.34	0.58	0.27	0.43	0.40	0.10	0.40	0.39	0.09	0.23	0.67	0.60	-0.86	0.09	-0.05	1	
$CaCO_3$ (%)	-0.34	-0.39	-0.25	-0.03	-0.31	-0.08	-0.44	-0.60	-0.39	-0.13	-0.04	-0.13	-0.13	-0.09	-0.41	-0.32	-0.60	-0.11	0.38	0.64	-0.07	-0.54	1

Monsoon																							
	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	Fe (%)	Al (%)	Silt %	Clay %	Sand %	DO (ml/l)	W.T.B	Org.C (%)	$CaCO_3$ (%)
Sc	1																						
V	0.86	1																					
Cr	0.95	0.84	1																				
Mn	0.32	0.37	0.20	1																			
Co	0.91	0.85	0.88	0.39	1																		
Ni	0.86	0.78	0.93	0.11	0.79	1																	
Cu	0.84	0.65	0.79	0.22	0.63	0.78	1																
Zn	0.46	0.40	0.35	0.40	0.31	0.16	0.43	1															
Y	0.87	0.86	0.86	0.38	0.81	0.89	0.71	0.28	1														
Zr	0.46	0.30	0.34	0.47	0.28	0.23	0.44	0.70	0.37	1													
Nb	0.22	0.18	0.11	0.29	0.02	-0.06	0.28	0.93	0.05	0.67	1												
Mo	0.36	0.35	0.51	-0.14	0.28	0.60	0.34	0.12	0.40	0.05	0.03	1											
Hf	0.49	0.33	0.37	0.46	0.30	0.25	0.46	0.72	0.38	1.00	0.69	0.07	1										
Ta	0.35	0.28	0.24	0.29	0.14	0.06	0.41	0.94	0.14	0.69	0.98	0.07	0.72	1									
Fe(%)	0.67	0.77	0.69	0.19	0.88	0.61	0.32	0.17	0.64	0.01	-0.12	0.24	0.04	-0.03	1								
Al (%)	0.96	0.75	0.93	0.27	0.81	0.81	0.83	0.50	0.79	0.51	0.29	0.35	0.54	0.41	0.53	1							
Silt %	0.75	0.63	0.69	0.42	0.65	0.72	0.76	0.30	0.77	0.40	0.12	0.27	0.41	0.21	0.35	0.70	1						
Clay %	0.71	0.49	0.71	0.08	0.50	0.72	0.79	0.14	0.58	0.29	0.04	0.46	0.30	0.17	0.23	0.72	0.47	1					
Sand %	-0.84	-0.67	-0.81	-0.33	-0.68	-0.83	-0.89	-0.27	-0.80	-0.41	-0.11	-0.39	-0.42	-0.22	-0.35	-0.82	-0.92	-0.78	1				
DO(ml/l)	0.54	0.33	0.49	0.32	0.34	0.35	0.54	0.27	0.37	0.50	0.24	0.06	0.51	0.35	0.07	0.59	0.34	0.63	-0.52	1			
W.T.B	0.33	0.08	0.24	0.15	0.03	0.06	0.47	0.47	0.03	0.50	0.53	-0.03	0.51	0.58	-0.31	0.48	0.28	0.42	-0.39	0.64	1		
Org.C (%)	-0.01	0.14	0.09	-0.21	0.08	0.39	0.04	-0.44	0.32	-0.39	-0.48	0.43	-0.39	-0.48	0.20	-0.13	0.16	0.12	-0.16	-0.33	-0.62	1	
$CaCO_3$(%)	-0.28	-0.06	-0.21	-0.17	-0.11	0.11	-0.28	-0.56	0.09	-0.42	-0.55	0.14	-0.43	-0.58	0.11	-0.43	-0.15	-0.19	0.19	-0.51	-0.79	0.80	1

The high elemental association between Nb and Ta ($r > 0.98$) also (Table 5.5) indicates its similarity in reaction as well as associations. Grousset et al. (1983) found Ta associated with silt, suggesting a relatively high bottom current capable of transporting Ta-bearing particles.

The present study indicates that although the geochemistry of fine grained terrigenous clastic sediments is controlled by source composition, a number of factors such as weathering, hydraulic sorting during transport, elements adsorption in clay particles, tectonic setting, diagenesis and metamorphism play significant roles in regulating their concentrations in sediment (Wronkiewicz and Condie, 1989; McLennan et al., 1990; McLennan et al., 1993). Studies on Sc, V, Zr, Y, Nb, Hf and Ta in the western continental margin/shelf of India are not reported so far. The present study can be used as a baseline for the above TEs such as Ta and Nb from the continental shelf and Cochin estuarine system.

The TEs have shown enrichment in the northern and southern limbs of the estuary. It is evident that metal association in Cochin estuary is not according to textural characteristics. Apart from organic association, precipitation initiated through iron/manganese complexes support metal accumulation in the estuarine sediments. Natural processes have only limited control on the distribution of most metals, as Zn is influenced by anthropogenic input. Cochin harbor region is not enriched in metals but, in the northern part, an enrichment of metals, especially Zn is evident. The poor correlation between organic carbon and the metals in the estuary (Table 5.6), unlike in the case of coastal sediments, indicates that metal enrichment in the estuary may possibly be initiated by inorganic processes, such as precipitation and scavenging by hydroxides of Fe and Mn.

Table 5.6. **Pearson correlation for transition elements with biogeochemical parameters along the estuarine sediments (Metals are in ppm).**

Premonsoon

	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	Fe (%)	Al (%)	Silt %	Clay %	Sand %	DO (ml/l)	Temp (°C)	Org.C (%)	$CaCO_3$ (%)
Sc	1																						
V	0.76	1																					
Cr	0.78	0.86	1																				
Mn	0.37	0.40	0.12	1																			
Co	0.83	0.67	0.66	0.44	1																		
Ni	0.79	0.67	0.84	0.16	0.78	1																	
Cu	0.93	0.76	0.78	0.38	0.75	0.82	1																
Zn	0.46	0.47	0.18	0.52	0.22	0.03	0.51	1															
Y	0.73	0.86	0.90	0.25	0.63	0.81	0.70	0.19	1														
Zr	0.47	0.36	0.15	0.44	0.14	0.02	0.46	0.89	0.19	1													
Nb	0.17	0.25	-0.06	0.32	-0.13	-0.24	0.22	0.91	-0.02	0.84	1												
Mo	0.46	0.62	0.65	0.23	0.34	0.54	0.55	0.38	0.56	0.30	0.23	1											
Hf	0.49	0.38	0.17	0.46	0.17	0.05	0.49	0.89	0.21	1.00	0.81	0.31	1										
Ta	0.25	0.29	0.01	0.31	-0.07	-0.17	0.30	0.92	0.01	0.85	0.98	0.27	0.83	1									
Fe(%)	0.57	0.65	0.63	0.17	0.84	0.63	0.44	0.01	0.60	-0.13	-0.25	0.26	-0.11	-0.22	1								
Al (%)	0.92	0.54	0.67	0.29	0.72	0.69	0.85	0.33	0.55	0.41	0.03	0.37	0.45	0.14	0.39	1							
Silt %	0.53	0.30	0.34	0.32	0.43	0.47	0.55	0.13	0.38	0.26	-0.09	0.13	0.30	-0.02	0.12	0.63	1						
Clay %	0.62	0.27	0.43	0.04	0.36	0.53	0.60	0.09	0.35	0.21	-0.07	0.29	0.25	0.02	0.08	0.71	0.48	1					
Sand %	-0.66	-0.33	-0.44	-0.24	-0.47	-0.57	-0.66	-0.13	-0.43	-0.27	0.09	-0.22	-0.32	0.01	-0.12	-0.77	-0.91	-0.80	1				
DO(ml/l)	0.28	0.00	0.09	0.19	0.01	-0.02	0.24	0.15	-0.09	0.21	0.11	-0.01	0.24	0.19	-0.27	0.49	0.20	0.40	-0.33	1			
Temp(°C)	0.21	-0.07	-0.04	0.26	-0.08	-0.13	0.20	0.24	-0.17	0.33	0.23	-0.03	0.35	0.30	-0.42	0.42	0.21	0.34	-0.30	0.94	1		
Org.C	-0.07	0.03	0.17	-0.25	0.12	0.46	0.03	-0.44	0.29	-0.48	-0.45	0.16	-0.48	-0.47	0.25	-0.18	0.05	0.08	-0.07	-0.56	-0.66	1	
$CaCO_3$ (%)	-0.32	-0.09	-0.07	-0.16	-0.04	0.15	-0.32	-0.57	0.18	-0.57	-0.51	-0.17	-0.57	-0.57	0.19	-0.46	-0.07	-0.25	0.17	-0.65	-0.67	0.70	1

Monsoon

	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	Al (%)	Fe (%)	Silt %	Clay %	Sand %	D.O (ml/l)	Sal	Org.C (%)	$CaCO_3$ (%)
Sc	1																						
V	0.97	1																					
Cr	0.99	0.97	1																				
Mn	0.76	0.71	0.72	1																			
Co	0.90	0.85	0.85	0.90	1																		
Ni	0.95	0.86	0.95	0.72	0.85	1																	
Cu	0.96	0.97	0.93	0.71	0.89	0.83	1																
Zn	0.76	0.84	0.74	0.35	0.65	0.58	0.89	1															
Y	0.96	0.92	0.93	0.66	0.88	0.90	0.96	0.84	1														
Zr	0.52	0.60	0.54	0.51	0.55	0.47	0.55	0.41	0.48	1													
Nb	0.19	0.33	0.21	0.14	0.15	0.07	0.31	0.31	0.20	0.84	1												
Mo	0.77	0.73	0.76	0.92	0.89	0.78	0.74	0.43	0.73	0.55	0.23	1											
Hf	0.62	0.69	0.64	0.56	0.63	0.58	0.64	0.49	0.59	0.99	0.79	0.61	1										
Ta	0.36	0.39	0.40	0.46	0.40	0.41	0.33	0.12	0.31	0.85	0.75	0.62	0.83	1									
Al (%)	0.93	0.84	0.90	0.65	0.80	0.91	0.84	0.65	0.90	0.20	-0.16	0.62	0.32	0.04	1								
Fe(%)	0.97	0.97	0.97	0.74	0.91	0.91	0.96	0.81	0.94	0.53	0.19	0.79	0.63	0.37	0.87	1							
Silt %	0.48	0.50	0.41	0.29	0.41	0.32	0.60	0.56	0.60	0.46	0.60	0.34	0.50	0.32	0.35	0.38	1						
Clay %	0.54	0.56	0.58	0.26	0.30	0.55	0.49	0.35	0.51	0.66	0.70	0.43	0.70	0.75	0.32	0.46	0.61	1					
Sand %	-0.57	-0.60	-0.57	-0.30	-0.37	-0.52	-0.59	-0.47	-0.60	-0.65	-0.73	-0.44	-0.69	-0.66	-0.37	-0.47	-0.83	-0.95	1				
D.O(ml/l)	0.30	0.23	0.28	0.17	0.16	0.37	0.21	0.01	0.31	0.54	0.55	0.22	0.55	0.61	0.19	0.14	0.62	0.81	-0.82	1			
Sal	-0.42	-0.45	-0.40	-0.52	-0.56	-0.41	-0.43	-0.31	-0.41	-0.74	-0.52	-0.54	-0.74	-0.71	-0.21	-0.47	-0.26	-0.41	0.40	-0.40	1		
Org.C (%)	0.83	0.81	0.84	0.56	0.62	0.82	0.76	0.55	0.79	0.66	0.53	0.67	0.74	0.65	0.66	0.75	0.65	0.91	-0.90	0.68	-0.40	1	
$CaCO_3$ (%)	-0.18	-0.25	-0.11	0.06	-0.10	0.08	-0.36	-0.57	-0.26	0.25	0.10	0.20	0.21	0.61	-0.28	-0.18	-0.39	0.26	-0.02	0.33	-0.28	0.09	1

The mechanism appears to be estuarine coagulation/flocculation of elements as colloids in association with hydrous iron oxides under fluctuating salinity (Sholkovitz, 1978; Freely et al., 1981). Hence, the northern estuary favors early flocculation of Fe followed by scavenging other elements, whereas Mn is transported further downstream where salinity is higher. Inadequate flushing of pollutants released to flow restricted water bodies can promote coagulation or co-precipitation of metals under the prevailing ionic (salinity) condition (Cobelo-Garcia and Prego, 2004). These processes could be critical in estuaries such as the Cochin estuary, which is characterized by frequent development of null zones of relatively long residence time. A seasonally-oscillating zone has been noted earlier here as quoted, "*because of the position of these two mouths, which are exposed to the same tidal cycles, the high tides and low tides each producing two opposite flows respectively converge and diverge leaving a null zone, almost free of the tidal effect, around Kadakkara, situated midway between Cochin and Azhikode*" (Ramamirtham and Muthusamy, 1986). The geomorphology (ox-bow shape) of the estuary and meandering flow can induce the formation of perennially-undulating water bodies or null zones. The weak flushing could result in entrapment of fine particles in this region, thereby increasing the metal contamination. Identifying and estimating the carrying capacity of such zones is of great significance in regulating the estuarine pollution. The metal enrichments observed along the northern zone of the estuary were not consistent with the uniformly-high organic content in the estuary. This kind of heavy metal accumulation in Cochin estuarine sediments is reported earlier also (Nair, 1990, Shibu et al., 1995; Shajan, 2001; Balachandran et al., 2005; Balachandran et al., 2006).

The moderate enrichment of chromium along the shelf could be due to the estuarine mixing. An alternate possibility could be the intense weathering of Cr compounds (Wronkiewicz and Condie, 1989). Cr is enriched during tropical weathering (Narayanaswamy and Ghosh, 1987). The highest normalisation and enrichment factors were obtained for sediments in the northern estuary during both seasons. These values declined steadily towards the shelf, indicating a progressive diffusion of metal. The significant correlation among these metals indicates a common source of contamination, typical of any impacted coastal marine areas (Ruiz, 2001). Specific contamination due to harbour activities, a common feature of other estuaries (Rubio et al., 2000), seems to be less in Cochin estuary. Periodic dredging and moderate flushing in the harbour region may be preventing long-term accumulation. Given the enrichment of certain elements in the estuary, it will be worth to assess their potential toxicity towards benthic organisms. This is expected since the annual loading of ~ 80 t of Zn and 63 Mm^3 of effluents from 247 chemical industries situated upstream of the northern estuary could lead to such a gross pollution (Shibu et al., 1995; SCMC, 2004). The persistent stress on the Cochin estuary might have induced a gradual shift in benthic community (Saraladevi and Venugopal, 1989). One of the adverse effects has been the marked decline in the clam fishery (Villorita sp.) of this estuary over the years. Here, pollution tolerant benthic organisms (opportunistic species) like polychaetes are found to take over the vacated niche (Saraladevi et al., 1992). The reduced biodiversity and high biomass of such tolerant species observed in this region are also indicative of pollution stress. The possible impacts from industry and agricultural run off of excessive nutrients have been noted (Balachandran, 2002).

The monsoonal regimes that govern the environment and biological destinies could be an important mitigating factor minimizing the gross pollution.

The pressures are deemed inevitable with growth initiated in the harbour and associated mega city development in the offing. In view of the projected population stress (0.6 Million in 1975 to 3 Million in 2002 and an expected 5 Million population by 2025), adequate conservation plans should be made to minimize the inevitable pollution, consequent to developmental activities. However, the El_{α} has no significance along the shelf as well as estuarine regions (except for zinc along the northern zone of the estuary) during both seasons. The El_{α} for zinc indicates its high anthropogenic inputs from industries.

In Table 5.7, the concentrations of TEs reported from some of the coastal and estuarine regions are given. A comparison of these values with the average values for Kerala shelf region revealed that the sediments of shelf do not indicate any sign of pollution. However, the high values along the estuarine sediments hints towards contamination of sediments either by riverine or industrial activities.

5.3.1 Statistical approach

5.3.1.1 Burial of elements in the shelf and estuarine sediments

The processes by which TEs are preferentially segregated can be represented by a model, sketching the matrix obtained through linear correlation analysis. This linear relationship (Pearson correlation) explains the behavior of TEs during their burial processes in sediments (Table 5.5 and Table 5.6). The TEs alone are considered for this analysis because the comparison would provide the influence of anthropogenic activity in the region. The correlation coefficient for the shelf sediments $r > 0.85$ is considered as significant (±1 level) association and r between 0.65 and 0.85 as moderate association. Similarly, for estuarine sediments ($n = 9$), $r > 0.9$ indicates significant association and r between 0.7 and 0.9 as moderate association.

Table 5.7. Comparison of transition elemental levels in the study region to that of other Indian and globally impacted coastal systems [(all in ppm, except Fe (% dry weight)].

Region	Sc	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	References
Portuguese shelf	--	---	46.5	209.5	1.79		24.5	18	57		664	---	--	---	---	Araujo et al., 2002
Sea bed . U.K	---	25	36	370	1.84	6	12	4	39	11	210	---	---	---	---	Stevenson, 2001
Atlantic Shelf	---	31	55	400	4.24	7	32	15	57	22	201	---	---	---	---	Stevenson, 2001
Turkish coast	---	---	72.1	662.4	5.89	23.4	25.1	54.5	175	---	--	---	---	---	---	Ergul et al.,2008
Andaman Backarc	---	---	103	252	4.58	29.6	156	75.7	78	32.3	---	---	23.6	---	---	Kurian et al., 2008
Irrawaddy shelf	---	---	156	126	6.03	26	140.3	31.3	63.3	34.5	---	---	1.03	---	---	Kurian et al., 2008
Bohai Bay, China	9.0	77.3	58.7	695	2.94	12.9	34.8	27.0	98.2	20.5	230	13.2	1.14	5.1	1.45	Zhang et al., 2002
Pearl River, China	8.98	113	71.4	908	4.42	16.2	37.7	54.5	202	35.0	312	24.6	2.47	8.8	1.83	Zhang and Wang, 2001
Pearl estuary, China	---	---	88.4	659	3.85	14.7	35.5	49.5	142	---	---	---	---	--	---	Carman et al.,2007
Nambia coast	--	---	123	124	1.62	5	123	68	68	23	78	---	53	---	---	Calvert, 1976
Peru margin	---	152	98	260	3.1	6.1	74	49	106	---	100	---	42	---	---	Boning et al., 2004
Gulf of California	---	101	44	193	3.1	6.6	38	27	88	---	---	---	12	---	---	Brumsack, 2006
Black Sea	---	100	43	430	3.2	21	57	59	65	---	62	---	51	---	---	Luschen, 2004
Furlo Italy	6.2	15	19	640	2.3	4.2	6.9	21	22	16	17	3.2	9.2	---	---	Turgeon and Brumsack, 2006
Medway Estuary	---	46	---	523	2.3	8	23	32	106	---	4	---	---	---	---	Spencer et al.,2006
Shelf of Kerala	5.9	42.2	84.9	236.8	4.2	5.4	37.4	15.7	66.9	12.9	41.1	5.6	1.1	1.3	0.44	Present study
Cochin Estuary	13.1	86.3	130.9	394.8	5.9	11.8	45.3	33.5	387	23.1	59.5	12.3	0.95	1.7	0.86	Present study

The correlation demonstrates the different associations, which are in agreement with the texture of sediment and the relative enrichment (such as organic carbon, clay, silt, Al and Fe), suggesting well-defined carriers of the metals to the sediment.

The variation in metals with respect to the carrier phases (clay, silt, Al and Fe) is indicative of a basic shift in the geochemical properties in response to the texture on moving from estuary to the shelf. In the shelf sediments, normalization of TEs among the three carrier phases is probably masking their enrichment (Balachandran et al., 2005). This representation shows that the sedimentological and hydrologic processes chiefly regulate the TEs concentrations in the shelf sediments (Figure 5.16 a & b) and estuarine sediments (Figure 5. 16 c& d).

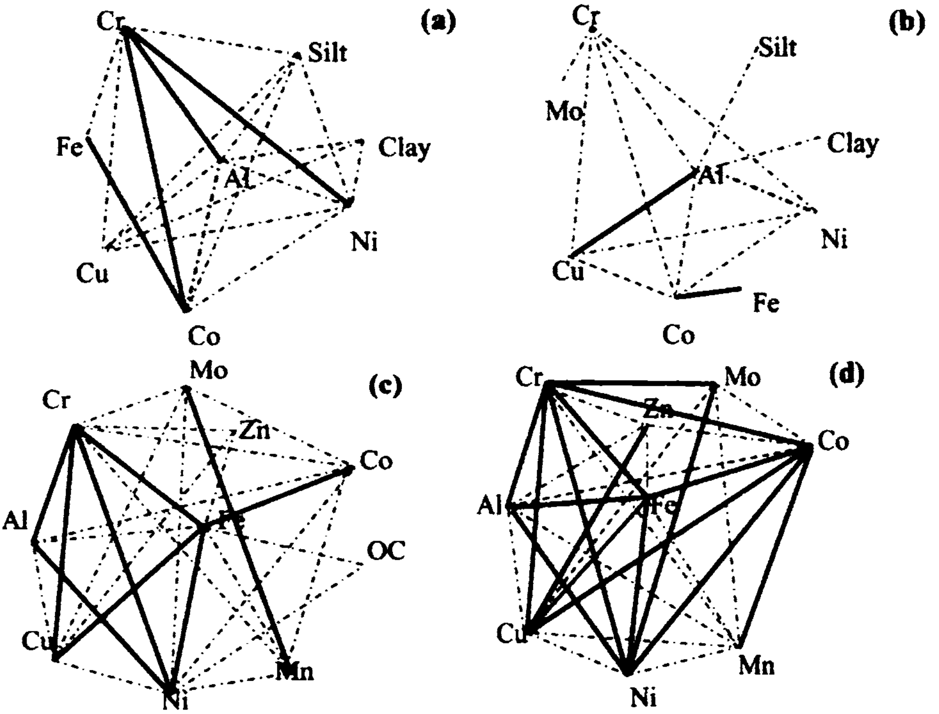

Figure 5.16 a-d. Schematic representation of sediment geochemistry along continental shelf of Kerala based on linear inter-element correlation during monsoon (a) and premonsoon (b) and esturarine sediment during monsoon (c) and premonsoon (d).

In general, the sediment geochemistry along the shelf is quite different from that exists in the Cochin estuary. In the shelf sediments, the influence of clay and silt on the deposition of TEs is very dominant, although there was a seasonal change in this relationship. Another peculiarity of shelf sediments is their lithogenic characteristics, and associations with alluvial silt. Al is considered as a major carrier element in the shelf sediments, which controls deposition of other elements, evinced by its interaction with silt and clay. In the estuarine sediments, the TEs are not influenced by either clay or silt content. Furthermore, whereas Al is the major carrier element in the shelf region, it is by Fe in the estuarine sediments. A more striking difference was the association of more TEs in the estuarine sediments, while in the shelf sediments, the elemental associations are obscured by the interaction with clay and silt. In the outer shelf, heavy metal concentrations are very close to those determined for unpolluted sediment. The accumulation rate of modern contaminated sediment in this area must be insignificant because outer shelf surface deposits are rich in relict sand. These components produce a sharp increase in their carbonate content and also large grain size and hence, TEs are impoverished in these sediments.

5.3.1.2 Multiple regressions

A multiple regression analysis is applied using TEs as the dependent variable and direct and first order interaction effects of the independent variables such as Al, Fe, silt, clay, temperature, dissolved oxygen, organic carbon and $CaCO_3$, to examine the controlling role of any particular parameter or group of parameters on metal distribution. The coefficients are called standard partial regression coefficients indicating relative importance of parameters. The model has been fitted by least square method considering the parameters and also their interaction effects of first order as the independent variables.

Table 5.8a. Multiple regression model for transition elements along the shelf sediments during premonsoon.

Metal	Fitted regression equation	Anova	% variability	Significant positive variable	Significant negative variable
Fe	Fe=10.741+0.89Al-0.0359Silt-0.0607Clay+ 1.063D.O-0.505Temp -0.373Org.C+0.241$CaCO_3$	$P<0.001$	71.4	Al	temp
Hf	Hf=2.07-0.124 Fe+0.188Al+0.002423Silt-0.00166Clay -0.607D.O+0.03298Temp -0.25 Org.C -0.0891$CaCO_3$	$P<0.001$	57.9		
Sc	Sc=-0.0759+0.271Fe+0.794Al-0.0109Silt +0.009549Clay -0.785D.O+0.1317Temp -0.03795Org.C-0.00154$CaCO_3$	$P<0.001$	90.9	Fe, Al	
Ta	Ta=0.812-0.0259Fe+0.01528Al-0.000868Silt-0.000581Clay -0.243 D.O+0.0247Temp -0.0497Org.C-0.0743$CaCO_3$	$P<0.02$	43.7		$CaCO_3$
Zr	Zr=75.745-4.978Fe+7.271Al+0.01828Silt-0.154Clay -23.417D.O+1.268Temp -8.835Org.C -3.329$CaCO_3$	$P<0.001$	57.6		
Zn	Zn=78.451+0.04697Fe+3.533Al+0.03744Silt-0.221 Clay -25.612D.O+2.595Temp -5.056Org.C- 6.188 $CaCO_3$	$P<0.008$	48		$CaCO_3$
Y	Y=-0.423+0.436Fe+1.449Al-0.0288Silt-0.0395 Clay - 1.441D.O+0.244Temp+0.509Org.C + 0.593$CaCO_3$	$P<0.001$	61	Al	
V	V=8.611+4.599Fe+1.589Al+0.07034Silt+0.02781Clay -3.854D.O+ 0.668Temp -0.307Org.C-0.506$CaCO_3$	$P<0.003$	52.7	Fe	
Ni	Ni=-7.824+1.105Fe+4.51Al-0.11 Silt-0.0828Clay -2.537D.O+0.75Temp+5.824Org.C + 1.021$CaCO_3$	$P<0.001$	88	Al, Org.C	
Nb	Nb=13.053-0.459Fe+0.161Al- 0.0225 Silt-0.0131 Clay -4.668D.O+ 0.457Temp -0.928 Org.C – 1.214$CaCO_3$	$P<0.02$	43.6		$CaCO_3$
Co	Co=-4.539+0.794Fe+0.416Al+0.005825 Silt -1.68Clay -1.034 D.O+0.276Temp +269Org.C+ 0.01252$CaCO_3$	$P<0.001$	92.8	Fe, Al, Temp	D.O
Cr	Cr=61.938+4.297Fe+9.346Al-0.263Silt-0.133Clay +8.211 D.O-2.118 Temp +4.496 Org.C0.691$CaCO_3$	$P<0.001$	65	Al	
Cu	Cu=2.634+286Fe+1.467Al-0.00435Silt-0.00752Clay -2.3 D.O+0.431Temp +1.181 Org.C- 0.28$CaCO_3$	$P<0.001$	78.9	Al	

Table 5.8b. Multiple regression model for transition elements along the shelf sediments during monsoon.

Metal	Fitted regression equation	Anova	% variability	Significant positive variable	Significant negative variable
Fe	Fe=15.267+0.778Al-0.0093Silt-0.03532Clay+ 0.387D.O-0.7 Temp -0.2 Org.C -0.05139 $CaCO_3$	$P<0.001$	73.7	Al	temp
Hf	Hf=1.243-0.142 Fe+0.153Al-0.0072 Silt-0.01337Clay +0.351 D.O-0.0288Temp -0.225 Org.C-0.05835$CaCO_3$	$P<0.01$	50		
Sc	Sc=0.323+0.351Fe+0.515Al+0.0266 Silt-0.02597 Clay +0.2 D.O-0.0317Temp -0.117 Org.C-0.05776 $CaCO_3$	$P<0.001$	98	Fe,Al,Silt, Clay	
Ta	Ta=-0.275-0.00308Fe+0.03715Al-0.00104 Silt-0.00585Clay -0.03602 D.O +0.0348Temp-0.00643Org.C-0.009709$CaCO_3$	$P<0.05$	43		
Zr	Zr=49.879-3.877Fe+5.06Al+0.281 Silt-0.4Clay +12.065 D.O-1.367 Temp -8.496 Org.C +2.108$CaCO_3$	$P<0.01$	49		
Zn	Zn=19.572+0.71Fe+5.551Al-0.03981Silt-0.881 Clay -8.621 D.O+2.354Temp -0.792Org.C-1.883$CaCO_3$	$P<0.01$	47.5		
Y	Y=6.8+0.11Fe+1.143Al+0.0737Silt-0.04841Clay +14.805D.O-0.259Temp +0.108 Org.C + 0.506 $CaCO_3$	$P<0.001$	90.8	Al,silt,D.O, $CaCO_3$	
V	V=-23.26+4.57Fe+1.124Al+0.161 Silt-0.03127 Clay +1.246 D.O+ 1.619Temp +0.649 Org.C+ 0.949$CaCO_3$	$P<0.001$	80.4	Fe	
Ni	Ni=11.645+0.38Fe+3.515Al+0.114 Silt+0.194Clay -0.0548 D.O-0.306Temp +1.704 Org.C+ 1.26$CaCO_3$	$P<0.001$	94	Al, Silt, CaCO3	
Nb	Nb=-1.658-0.244Fe+0.648Al- 0.02184 Silt-0.119 Clay -0.849 D.O+ 0.424Temp -0.00743 Org.C – 0.212$CaCO_3$	$P<0.05$	39.2		
Mo	Mo=0.613+0.003849Fe+0.03872 Al-0.00395 Silt+0.00899Clay -0.165D.O +0.01361Temp+0.186 Org.C-0.02884$CaCO_3$	$P<0.05$	41.1	Org.C	
Mn	Mn=319.414+7.129Fe-14.491Al+4.417 Silt-0.374 Clay +21.9 D.O-8.852Temp -49.849 Org.C+ 8.298 $CaCO_3$	$P<0.05$	40.8	Silt	
Co	Co=1.736+0.738Fe-0.21Al+0.03476 Silt+0.0159 Clay +0.257 D.O-0.0706Temp -0.269 Org.C+ 0.038$CaCO_3$	$P<0.001$	96.2	Fe, Al, Silt	
Cr	Cr=37.173+3.852Fe+7.463Al+0.111 Silt+0.322 Clay +2.252 D.O-0.649 Temp +2.599 Org.C-0.326$CaCO_3$	$P<0.001$	94.3	Fe, Al	
Cu	Cu=4.462-0.05643Fe+0.626Al+ 0.0947 Silt+ 0.175Clay -0.816 D.O+0.241Temp -0.03638 Org.C+ 0.11$CaCO_3$	$P<0.001$	85.5	Silt, Clay, Al	

Table 5.8c. Multiple regression model for transition elements along the estuarine sediments.

Monsoon

Metal	Fitted regression equation	Anova	% variability	Significant positive variable	Significant negative variable
V	V= 107.378 – 2.370 Al + 5.218 Fe – 1.389 Silt – 1.202 Clay – 7.696 Sal + 36.189 Org. C – 4.610 $CaCO_3$	$p<0.05$	100		
Sc	Sc= 6.885 + 0.257 Al + 0.594 Fe – 0.03687 Silt – 0.148 Clay – 0.585 Sal + 3.379 Org. C – 0.132 $CaCO_3$	$p<0.05$	100		
Cu	Cu = 21.416 – 0.596 Al + 4.299 Fe – 0.253 Silt – 0.335 Clay – 1.076 Sal + 6.041 Org. C – 0.915 $CaCO_3$	$p<0.05$	100		
Cr	Cr= 67.461 + 0.805 Al + 8.066 Fe – 1.833 Silt – 0.476 Clay – 4.170 Sal + 41.419 Org. C – 2.723 $CaCO_3$	$p<0.05$	99.9		
Co	Co= 17.239 – 0.183 Al + 1.316 Fe + 0.125 Silt – 0.476 Clay – 1.445 Sal + 5.483 Org. C + 0.239 $CaCO_3$	$p<0.05$	100		

Premonsoon

Metal	Fitted regression equation	Anova	% variability	Significant positive variable	Significant negative variable
Sc	Sc= 1.024 + 0.379 Al + 1.316 Fe- 0.03257 Silt + 0.01833Clay - 0.119 Sal + 0.525 Org.C - 0.008023 $CaCO_3$	$p<0.05$	99.9		
Cr	Cr= -27.210 + 6.605 Al + 7.257 Fe- 0.298 Silt + 0.312Clay - 3.782 Sal +5.431 Org.C – 1.406 $CaCO_3$	$p<0.05$	100	Al	Sal

The significance of the regression coefficients is tested using ANOVA and the percentage of variability was measured using r^2. Similar analysis was done separately for both seasons along the continental shelf and estuarine system (Table 5.8a, Table 5.8b & Table 8c). In this study, only the significant correlation ($p<0.05$) explaining the variability of Al, Fe, silt, clay, dissolved oxygen, temperature, organic carbon and $CaCO_3$ are considered.

In general, the number of TEs having significant correlation increased during monsoon (13 metals during premonsoon and 15 elements during monsoon); however, the significance level of fitted regression was high during premonsoon. Along the shelf sediments, the fitted equation is significant for Fe, Sc, Y, Ni, Co, Cr, Cu ($p<0.001$) during both seasons. During premonsoon, the correlation of V changed from significant level <0.001 to <0.003. However, the regression significant level was increased for Hf and Zr from <0.01 to <0.001 during premonsoon. Nb and Ta showed significant level of <0.02 during premonsoon and <0.05 during monsoon. In addition, Mo and Mn showed significant regression level of <0.05 during monsoon. The regression equation explains the variability in the data. Al is the major predictor for transition elements such as Fe, Sc, Y, Ni, Co, Cr and Cu during both seasons. Where as Fe showed positive predictor for Sc, V and Co during both seasons. This pointed out that Al acts as a scavenger for the metals on clay minerals, metal oxy-hydroxides and particulate organic matter. This mechanism was confirmed by the observed metal enrichment with respect to aluminium compared to iron. This revealed that Al is the major element controlling the distribution of elements along the shelf of Kerala. In addition, transition elements such as Sc, Y, Ni, Mn, Co and Cu showed affinity towards silt compared to clay and sand. $CaCO_3$ showed negative predictors for transition elements. In estuarine zone, the fitted regression equation is significant at $p<0.05$ for metals such as Sc, V, Cr, Co and Cu during monsoon and for Sc and Cr during premonsoon. This reveals that the metal accumulation is controlled by some point sources rather than any biogeochemical interaction as in shelf region. It may be noted that the dominant forces resulting in the enrichment of elements are not due to their interaction through Al/Fe precipitation alone, but through their common source and interaction between elements.

5.4 Summary

1. The study showed that the redox sensitive transition elements such as V, Cr, Co, Ni, Cu, Zn and Mo showed higher values in the nearshore sediments, which decreased towards seaward, but again increased slightly in the oxygen minimum zone along all the transects during both seasons, indicating its accumulation under redox conditions.
2. Iron is the most abundant transition element (11%) along the Cochin transect and it might be due to the influence of water exchanged from the Cochin estuary. In the Cochin estuary, the northern zone showed very high values of iron compared to the southern and central zones indicating its point sources from industries.
3. Chromium showed a high enrichment along the western coastal margins, which indicates its marine origin.
4. The enrichment factor calculated with respect to Al showed higher values compared to enrichment factor calculated with respect to iron along the shelf, whereas it was in the reverse order in the Cochin estuary, indicating the different geochemical affinity of Al and Fe in the two environments.
5. In Cochin estuary, the northern zone was observed to be a sink for almost all transition elements, indicating high anthropogenic input from industrial zone. The flow restrictions and weak fleshing in this region probably supported the deposition of elements in the sediments, placing the region among the impacted estuaries in the world.
6. The high normalization and enrichment values for transition elements in the estuary compared to shelf indicate their lateral inputs.

7. The comparatively high elemental excess for transition elements along southern shelf indicates their abundance in rare-earth mineral deposits in the region.
8. The transition elements accumulation along the shelf sediments was high during premonsoon, whereas it was during monsoon in the Cochin estuary, indicating the differences in the seasonal response along the two regions.
9. The estuarine sediments were characterized by the association of more transition elements, whereas the elemental associations in the shelf sediments were obscured by the interaction with clay and silt.
10. Regression studies revealed that Al is the major element controlling the distribution of elements along the shelf sediments whereas in estuary dominant forces resulting in the enrichment of elements are not due to their interaction through Al/Fe precipitation alone, but through their common source and interaction between elements.
11. The results of premonsoon and monsoon metal data revealed that tsunami has no effect on the distribution of transition metals along the shelf and estuary.

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Chapter 6

Distribution of rare-earth elements along the shelf of Kerala and Cochin estuarine system

Contents

6.1 Introduction

The Rare Earth Elements (REEs), lanthanum to lutetium (atomic numbers 57-71) are Group IIIA members in the periodic table possessing identical chemical and physical properties. They form a very coherent group, though Ce and Eu develop anomalies due to their different oxidation states. Lanthanides between Nd and Sm which can be produced by nuclear reactions do not exist significantly in nature. REEs can be grouped into three: those from La to Sm (ie, lower atomic numbers and masses) referred to as Light Rare Earth Elements (LREEs), Middle Rare Earth Elements (MREEs) consisting of elements from Pm to Ho and Heavy Rare Earth Elements (HREEs) consisting of elements from Er to Lu (higher atomic numbers and masses). The interest in the geochemistry of REEs has come about because the REEs indicate its genesis and capability to detect at very low concentration (Henderson, 1984; Trinh et al., 2007).

REEs are difficult to separate because of their similarity with regard to the electronic configuration (Möller, 1968). Lanthanum has an outer electronic configuration of $5d^1$ $6s^2$ but, the next element Ce has one electron in the $4f$ sub-shell. The subsequent electrons enter the 4f sub-shell until it is filled for ytterbium. The $4f$ electrons are shielded by the eight electrons in the $5s^2$ and $5p^6$ sub-shells, so that they remain inert. Hence, addition of electrons in the $4f$ sub-shell does not change their behaviour and occur in nature as a group (Henderson, 1984). The REEs occupy a variety of co-ordination complexes from (6-12 fold). The smaller REEs ions occupy six fold (CN = 6) co-ordination sites but, is rarely seen in heavier minerals. A correlation between co-ordination and ionic radius is observed, ie, the larger ions will tend to occupy larger sites and vice versa. Most of the REEs show a constant valency of three in their chemistry and geochemistry, while Ce and Eu exist in different oxidation states.

The lanthanides were originally called rare-earth elements. The word 'earth' was used for oxides (means earth) and 'rare' means their scarce occurrence. Now many more elements occur even more rarely than lanthanides. The rare-earth elements form about 0.02% of the earth's upper crust by weight. They occur in high concentrations in a considerable number of minerals. Basic (alkaline) rocks generally contain lesser amounts of REEs than do the acidic rocks. Thorium and uranium are the two commonly occurring actinides, which have major roles in aquatic biogeochemical processes. In India, a large amount of thorium ore (monazite) is found in placer deposits of the western and eastern coasts, particularly in the Kerala and Tamil Nadu. Uranium is a radioactive element naturally occurring in aquatic systems and is soluble under oxidising conditions. The occurrence, sources, residence time and toxicity of selected REEs, Th and U are presented in annexure III.

The rare-earth elements occupy hexagonally close packed crystals sharing a common outer electronic configuration of 4*f* orbital. They exhibit a unique property called lanthanide contraction, where the addition of electrons to the poorly shielded 4*f* orbitals increases the effective nuclear charge to decrease the ionic radii. REEs are difficult to separate because of similarity of their atoms and ions (Möller, 1968). They occur in nature as group rather than singly or as a combination (Henderson, 1984). REEs are strongly electropositive and most of their compounds have ionic than covalent bonding. Most of the REEs show a constant valency of +3; but, +2 oxidation state may be shown by Eu and Yb and +4 by Ce and Tb. The multiple oxidation states are due to the stability of half filled (Eu^{2+} & Tb^{4+}) and completely filled (Yb^{2+}) 4*f* sub-shells, while Ce^{4+} has the electronic configuration of the noble gas xenon. In natural systems, Eu^{2+} and Ce^{4+} exists but, Tb^{4+} has not been recorded. Yb^{2+} requires extremely reducing conditions. Geochemically, Ce^{4+} and Eu^{2+} possess other oxidation states. Oxidation of Ce^{3+} into Ce^{4+} in seawater and its incorporation to Mn oxides/hydroxides explains the impoverishment of Ce in sediment. Ce is also affected by its multiple oxidation states like Fe, Mn, U, V and Cr. Seawater is depleted in Ce compared to ferromanganese nodules. Ce and Eu anomaly is used to identify the redox reactions from other processes affecting their oceanic distribution (De Baar et al., 1988; Pattan et al., 2005). Reduction of Eu is noticed in magmatic processes. Changes in europium from +2 to +3 are observed at high temperature and pressure associated with the formation of minerals, rocks and hydrothermal waters (Henderson, 1984; Douville, 2002). The hydrothermal vents are characterized by positive Eu anomalies as a result of water/basalt reactions (German et al., 1990, Klinkhammer et al., 1994; Douville, 2002).

The major sources of REEs to the ocean are rivers (Goldstein and Jacobsen, 1988; Sholkovitz et al., 1999; Tosiani et al., 2004), oceanic crust (Michard and Albarede, 1986; Johnson et al., 1995; Daizhao et al., 2006) and sediment diagenesis. The diagenetic flux is small relative to the other two (Elderfield and Sholkovitz, 1987). Goldberg et al (1963) found that REEs in deep waters were higher than those of the surface waters. There is a strong relationship between REEs patterns and water masses (Høgdahl et al., 1968). Piepgras and Jacobsen (1992) confirmed this by looking at the differences in the isotopic compositions of Nd in different water masses. Various biogeochemical processes can remove the REEs from seawater through inorganic precipitation, incorporation to biogenic material or hydrogenous minerals, halmyrolitic reaction of seawater with lithogenous material, hydrothermal solutions and the igneous oceanic lithosphere at ocean ridges (Fleet, 1984; Bierlein et al., 1999).

The REEs contents of the sedimentary rocks naturally reflect the minerals and their deposits. The chondrite normalized pattern indicates that LREEs are enriched compared to HREEs (Fleet, 1984). REEs contents of most sediments and sedimentary rocks are identical although they differ in absolute concentrations (Balashov et al., 1964). REEs have occupied an important role in marine geochemical research, particularly to describe the pathways of sediment preservation and authigenesis (Piper, 1974; Araújo et al., 2002). REEs in sediments are increasingly used as indicators of geological and oceanographic processes, paleo-redox conditions (Liu et al, 1988; Nath et al, 1992; Pattan et al., 2005), burial grounds and also as crustal sources (Taylor and McLennan, 1985; Tchameni et al., 2001). The different patterns in marine phases have recognized the fractionation of the REEs in the oceans, despite their chemical similarities. It is important to ascertain whether the redox changes observed in the water column are imparted to the underlying sediments. Hence, studies on modem sediments will help in the estimation of the depositional environment of ancient sediments (Macharlane et al., 1994). REEs variations in ancient sediments and oxygen-poor sediments have been used to reconstruct paleo-redox conditions of an environment (Wright et al., 1984; Liu et al., 1988; Brian et al., 2004). Studies have shown that Ce anomalies are insignificant in the deep-sea sediments of the central Indian basin overlain by oxygen rich Antarctic bottom waters and those deposited away from the influence of Antarctic bottom waters (Nath et al., 1992; Pattan et al., 2005). Estuarine reactions play an important role in keeping consistency in geochemical composition and act as a link between the continents and oceans (Shotkovitz, 1993). REEs are severely altered during estuarine mixing. The present data explains the distribution of REEs including uranium and thorium in estuarine and adjoining continental shelf sediments overlain by waters with large differences in oxygen contents as well as other electrolytic state.

6.2 Results

6.2.1 Elemental distribution

Lanthanum

Lanthanum is an abundant rare-earth element. It is chemically active; oxidizes rapidly in air and reacts with water to form the hydroxide. Lanthanum is dangerous in the working environment, because the gasses can be inhaled. Lanthanum is dumped in the environment mainly by petrol-producing industries. It also enters the environment when household equipment is thrown away. Lanthanum accumulates in soils and will eventually lead to bioaccumulation in humans, animals and soil particles. Lanthanum showed nearshore enrichment followed by a decrease towards seaward in all transects during both seasons (Figure 6.1 a & b).

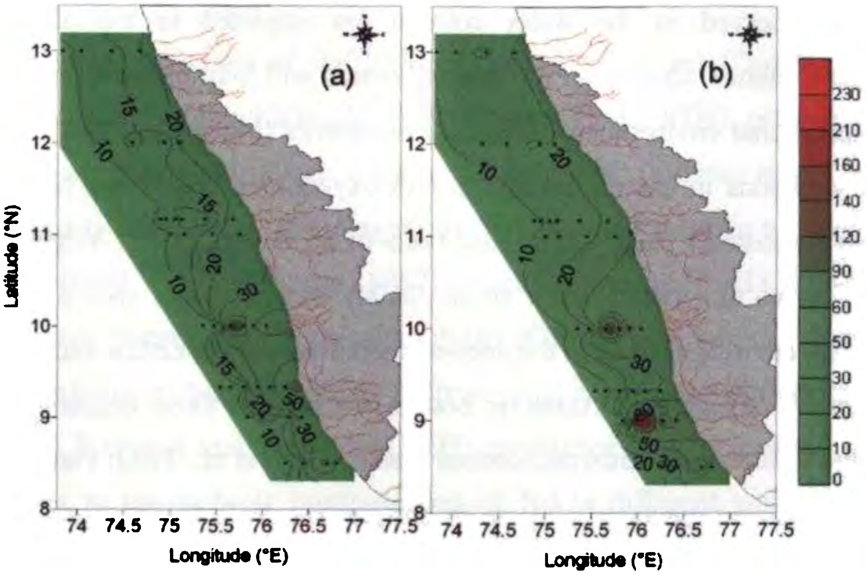

Figure 6.1 a&b. Distribution of lanthanum [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

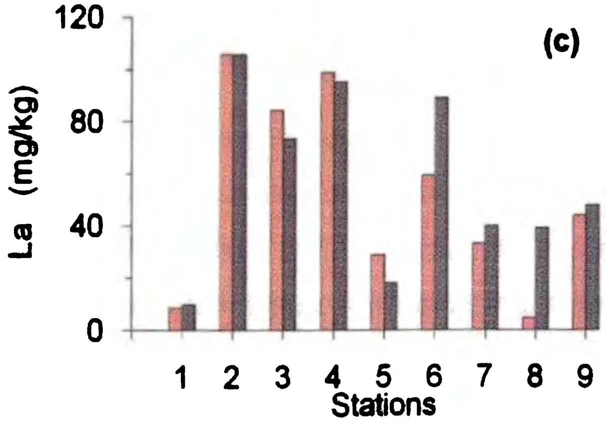

Figure 6.1 c. Distribution of lanthanum in the Cochin estuary during premonsoon (red) and monsoon (black).

It showed a slight enrichment during premonsoon season (average 35.2 ppm) than monsoon (average 25.2 ppm). Comparatively high values were observed along the southern zone (south of 10°N) than the northern zone during both seasons. The average concentrations were 14.3 and 34.9 ppm along the northern and southern zones during monsoon, whereas they were 16.1 and 52.4 ppm respectively during premonsoon. The Kollam and Kochi transects showed maximum accumulation than the other transects. In Cochin estuary, lanthanum showed high concentrations in the northern zone as well as station 6 (entrance of Muvattupuzha River) compared to the remaining stations during both seasons (Figure 6.1c; monsoon average 91 ppm; premonsoon average 87.2 ppm). There was little monsoonal enrichment compared to postmonsoon (average 57.8 ppm) and premonsoon (average 52.1 ppm). The average concentrations along the northern, central and southern zones were 91.6, 39.2 and 42.6 ppm respectively during monsoon, whereas they were 96.3, 32.6 and 27.6 ppm along the northern, central and southern zones respectively during premonsoon. The high concentrations observed along the northern zone could be due to either industrial or riverine sources. The maximum concentration was observed at station 2 (near to the industrial zone) during both seasons.

Cerium

Cerium is the most abundant of the rare-earth elements. It makes up about 0.0046 % of the earth's crust by weight and comes mainly from the major lanthanide ores, perovskite, a titanium mineral and allanite. It is very reactive, as it tarnishes readily in the air; oxidizes slowly in cold water and rapidly in hot water. Cerium can cause lung embolisms, especially during long-term exposure. Cerium can be a threat to the liver when it accumulates in the human body. Cerium has no known biological role, but stimulates metabolism. Cerium showed a nearshore enrichment, a mid-depth increase followed by a decrease towards deep in all transects during both seasons (Figure 6.2 a & b).

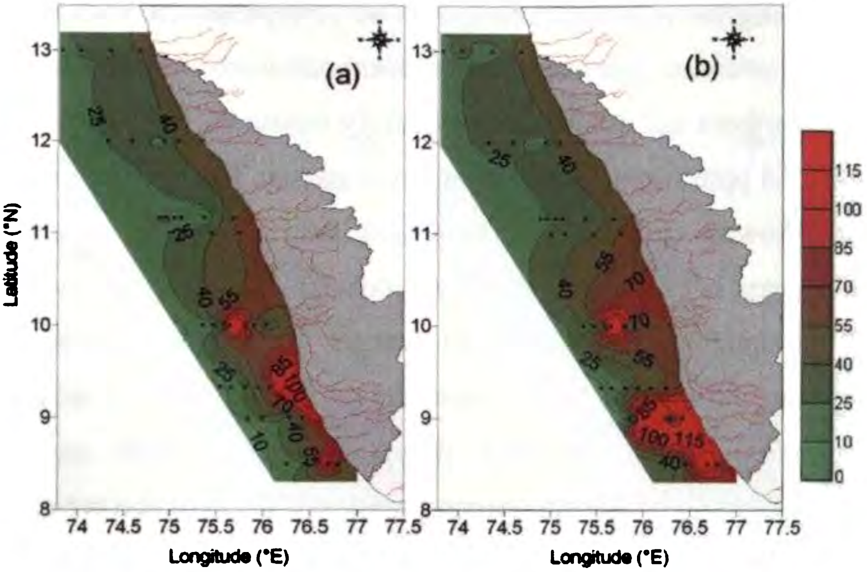

Figure 6.2 a&b. Distribution of cerium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

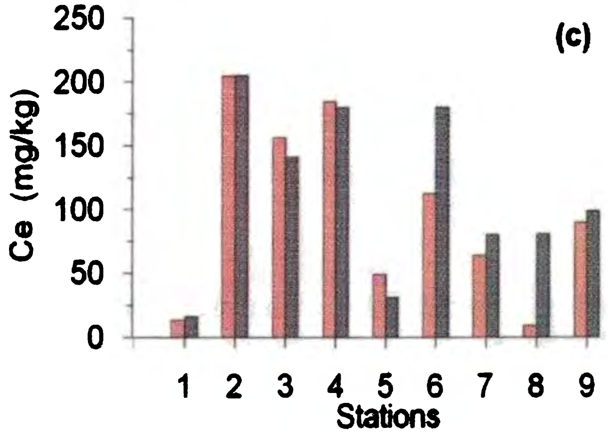

Figure 6.2 c. Distribution of cerium in the Cochin estuary during premonsoon (red) and monsoon (black).

It showed a premonsoon accumulation (average 65.5 ppm) compared to monsoon (average 48.3 ppm). Similar to lanthanum, it showed an accumulation towards the south compared to the northern zone. The average concentrations were 30.9 and 60.9 ppm along the northern and southern zones respectively during monsoon, whereas they were 34.3 and 93.7 ppm respectively during premonsoon. The seasonal variation was perceptible; premonsoon showed enrichment (average 65.5 ppm) compared to monsoon (average 48.3 ppm). Ce was high along the transects of Kollam and Kochi during both seasons. In Cochin estuary, Ce behaved similar to lanthanum with high values in the northern zone and also at station 6 during both seasons (Figure 6.2c). The average concentrations were 176.4 ppm and 164.3 ppm during monsoon and premonsoon respectively along the above stations, whereas the remaining stations showed an average of 61.5 ppm and 45.1 ppm during monsoon and premonsoon seasons respectively. The northern zone exhibited very high accumulation compared to the central and southern zones during both seasons. The average concentrations were 175.1, 75.9 and 86.6 ppm along the northern, central and southern zones respectively during monsoon, whereas they were 181.7, 58.3 and 54.3 ppm respectively during premonsoon. This high values observed along the northern estuary indicate point sources from industries and river inputs from Periyar, whereas the high concentration at station 6 might be due to the sediment input from Muvattupuzha River, especially during monsoon.

Praseodymium

Praseodymium is an abundant rare-earth element. It is four time more abundant than tin. The major commercial ores are monazite and bastnasite. Like all metals, praseodymium has low to moderate toxicity. Its soluble salts are mildly toxic by ingestion, but insoluble salts are non toxic. Praseodymium when inhaled can cause lung embolisms, especially during long-term exposure. Praseodymium is also introduced into the environment by refineries, which damages cell membranes, affects reproduction and nervous system. Praseodymium showed nearshore enrichment then a decrease, followed by a mid-depth high and a decrease towards deep in all the transects during both seasons (Figure 6.3 a & b).

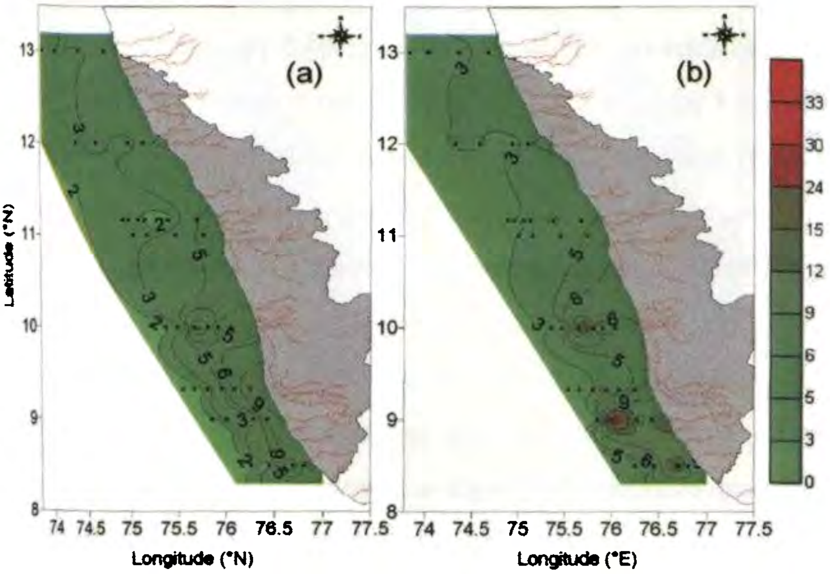

Figure 6.3 a&b. Distribution of praseodymium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

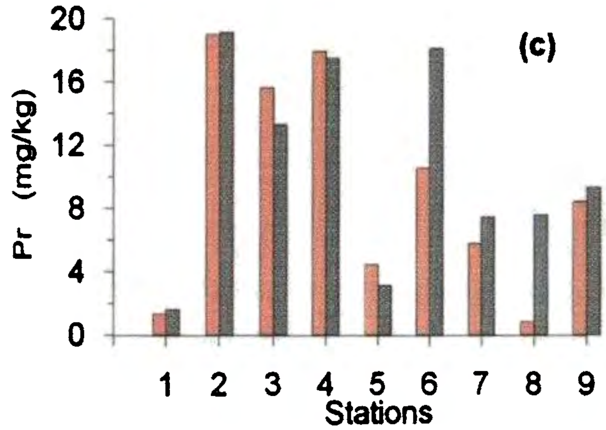

Figure 6.3 c. Distribution of praseodymium in the Cochin estuary during premonsoon (red) and monsoon (black).

It showed a seasonal accumulation with an average of 6.2 ppm during premonsoon and 4.7 ppm during monsoon. Similar to lanthanum and cerium, it also showed a southern enrichment compared to the northern zone during both seasons. The average values were 3.2 and 6.0 ppm along the northern and southern zones during monsoon, and 3.4 and 8.6 ppm respectively during premonsoon. In Cochin estuary, it showed very high values towards the north compared to the central and southern part of estuary during both seasons (Figure 6.3 c). The average concentrations were 16.6, 7.6 and 8.1 ppm along the northern, central and southern zones during monsoon, whereas the values were 17.5, 5.4 and 5.0 ppm respectively during premonsoon. The marginal monsoonal enrichment along the central and southern zones might be due the fluvial transport from rivers. The high concentrations in the northern stations could be from the industries and river inputs from Periyar.

Neodymium

Neodymium is the second most abundant of the rare-earth element and is almost as abundant as copper. It is found in all lanthanide minerals such as monazite and bastnasite. It quickly tarnishes in air, so it must be stored away from contact with air. It reacts slowly with cold water and rapidly with hot. The amount of neodymium in humans is quite small and, although the metal has no biological role: dust and salts are very irritating to the eyes. Ingested soluble Nd salts are slightly toxic. It is dumped in the environment in many different ways, mainly by petrol-producing industries. Neodymium will gradually accumulate in humans, animals and soil. With aquatic animals, neodymium causes damage to cell membranes, which has several negative influences on the reproduction and on the functions of the nervous system.

Neodymium showed a nearshore enrichment followed by a mid-depth increase and a decrease towards deep in all most all transects during both seasons (Figure 6.4 a & b).

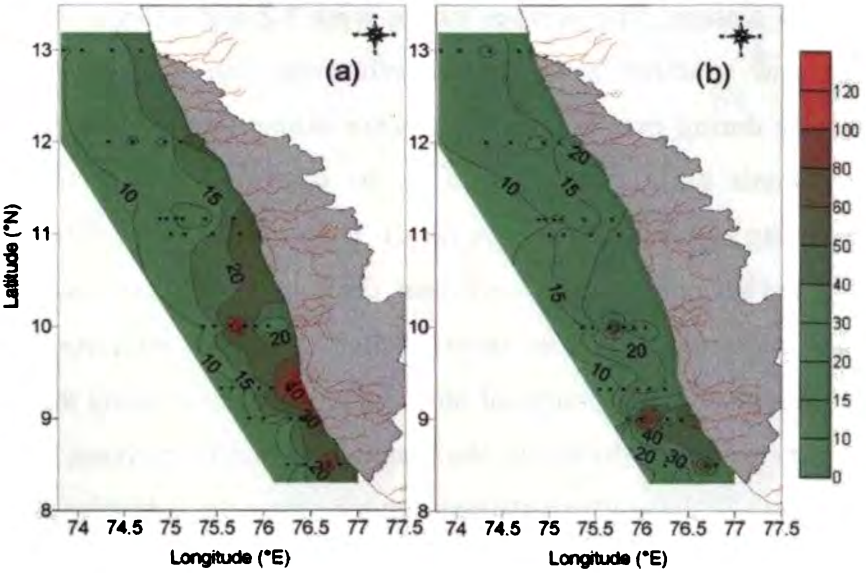

Figure 6.4 a&b. Distribution of neodymium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

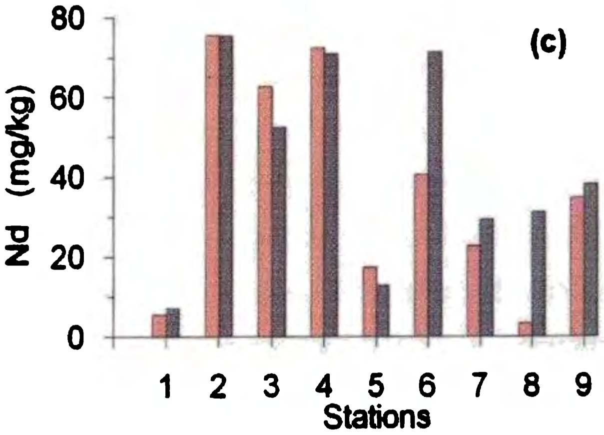

Figure 6.4 c. Distribution of neodymium in the Cochin estuary during premonsoon (red) and monsoon (black).

The average concentrations did not increase during premonsoon compared to monsoon (monsoon average 18.4 ppm; premonsoon average 24.4 ppm). There was a southern enrichment compared to the northern zone during both seasons. The average concentrations were 13.4 and 22.4 ppm along the northern and southern zones during monsoon, and they were 14.6 and 33.2 ppm respectively during the premonsoon. In Cochin estuary, high accumulation was observed in the northern zone during both seasons (Figure 6.4 c). The average concentrations were 70.3, 21.2 and 20.4 ppm along the northern, central and southern zones respectively during premonsoon, whereas they were 66.3, 30.5 and 33.0 ppm respectively during monsoon. Similar to praseodymium, it also showed enrichment at station 6 during monsoon (71.5 ppm), which could be due to the sediment load transported through Muvattupuzha River (Laluraj et al., 2008). In general, the average concentrations were high during monsoon (average 43.3 ppm) compared to the premonsoon (average 37.3 ppm), which might be due to the intense weathering and suspended sediments brought by rivers (Nath et al., 2000).

Samarium

Samarium is the fifth most abundant of the rare-earth elements and is almost four times the concentration of tin. It is found in mineral monazite, bastnasite and samarskite. Samarium has no biological role, but it has been noted to stimulate metabolism. Soluble samarium salts are mildly toxic because exposure to samarium causes skin and eye irritation. Samarium showed a nearshore and mid-depth accumulation followed by a decrease towards deep in almost all transects during both seasons (Figure 6.5 a & b).

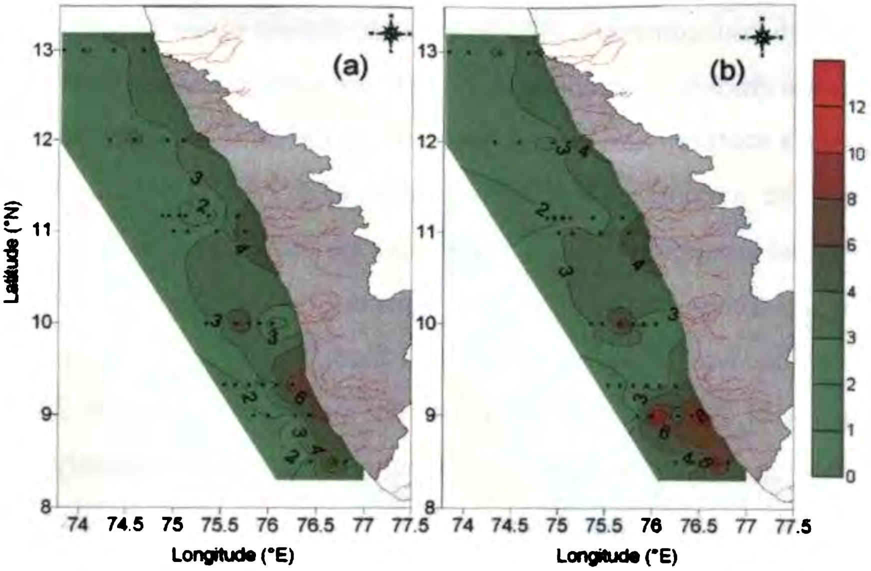

Figure 6.5 a&b. Distribution of samarium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

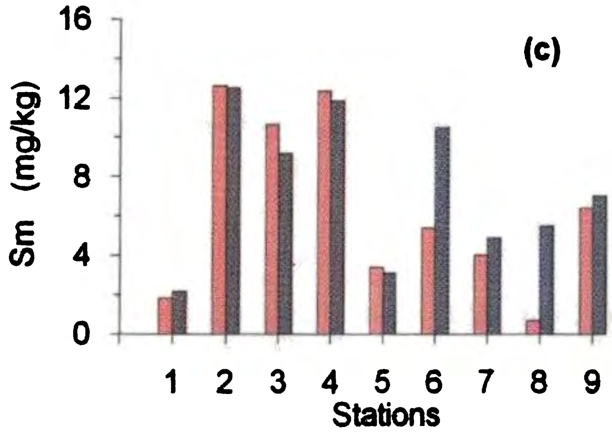

Figure 6.5 c. Distribution of samarium in the Cochin estuary during premonsoon (red) and monsoon (black).

The average concentrations were almost similar during both seasons (monsoon average 3.2 ppm; premonsoon average 3.8 ppm). It also showed a southern enrichment compared to the northern zone during both seasons. The average concentrations were 2.8 and 3.6 ppm along the northern and southern zones respectively during monsoon, whereas they were 2.9 and 4.8 ppm respectively during premonsoon. High concentrations of samarium were observed along Trivandrum, Kollam and Kochi transects during both seasons. In Cochin estuary, there was a northern enrichment compared to central and southern zones during both seasons (Figure 6.5 c). The average concentrations were 11.9, 3.5 and 3.7 ppm along the northern, central and southern zones respectively during premonsoon, whereas they were 11.2, 5.3 and 5.8 ppm respectively during monsoon. Similar to praseodymium and neodymium, this element also showed enrichment at station 6 during monsoon (10.5 ppm). It showed seasonal variations, with an average of 7.4 and 6.4 ppm during monsoon and premonsoon seasons respectively. This high concentration indicates the transport of metal from rivers during monsoon.

Europium

Europium is one of the less abundant rare-earth elements: it is almost as abundant as tin. It is never found in nature as the free element, but there are many elements that contains europium. It is the most reactive in the lanthanide group: it tarnishes quickly in air at room temperature, burns at about 150° to 180°C and reacts readily with water. It has no known biological role; however, its salts could be mildly toxic. Europium also showed a nearshore deposition, a mid-depth increase followed by a decrease towards deep in almost all transects during both seasons (Figure 6.6 a & b). The response was uniform along the study region during both seasons. The average concentrations were 0.63 and 0.68 ppm during monsoon and premonsoon periods respectively. It showed little accumulation along the northern zone compared to the southern zone. The average concentrations were 0.67 and 0.58 ppm along the northern and southern zones respectively during monsoon, whereas during premonsoon, the values were 0.70 and 0.66 ppm respectively. The coastal region of Kollam recorded high concentrations during both season.

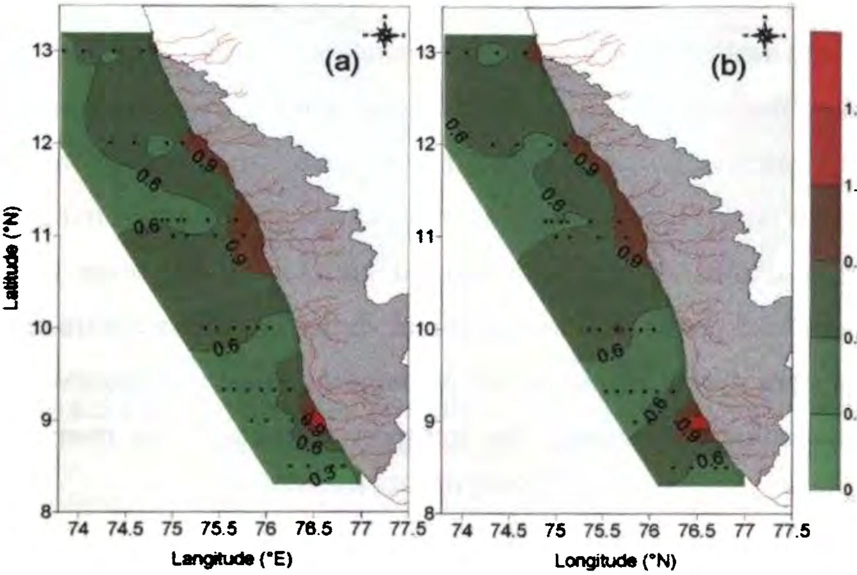

Figure 6.6 a&b. Distribution of europium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

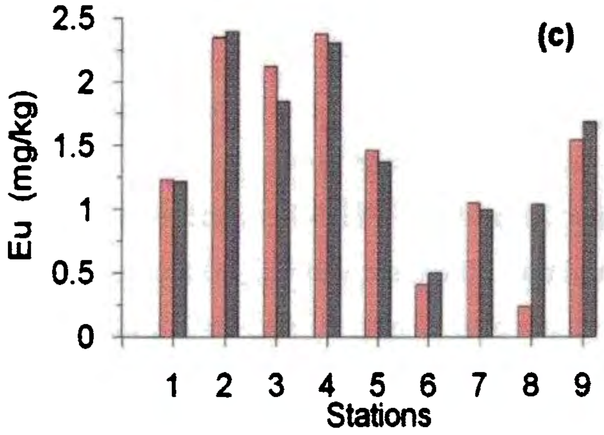

Figure 6.6 c. Distribution of europium in the Cochin estuary during premonsoon (red) and monsoon (black).

In Cochin estuary, there was high concentration along the northern stations compared to the central and southern zones during both seasons (Figure 6.6 c). The average concentrations were 2.2, 1.0 and 1.2 ppm along the northern, central and southern zones during monsoon, whereas the average values were 2.3, 1.0 and 0.94 ppm respectively during premonsoon. There was no distinct seasonal differences in the distribution of Eu; the average concentration was 1.4 ppm. The slight increase in concentration along the southern zone and a decrease at the northern zone during monsoon could be due to the high fresh water flux. The accumulated metals from the northern zone are transported by high water flux from Periyar River to enrich the central zone.

Gadolinium

Gadolinium is an abundant rare-earth element found in many minerals. Gd reacts slowly with water and dissolves in acids. Gadolinium, as other lanthanides, forms compounds of low to moderate toxicity. Gadolinium salts irritate skin and eyes and are suspected to be tumorigens. Gadolinium showed a nearshore increase, a mid-depth high followed by a decrease towards deep in almost all transects during both seasons (Figure 6.7 a & b). There was no marked difference in distribution during both seasons. The average concentrations were 2.8 and 3.3 ppm during monsoon and premonsoon respectively. There was accumulation along the southern zone compared to the northern zone during both seasons. The average concentrations were 2.4 and 2.8 ppm along the northern and southern zones during monsoon, whereas the recorded values were 2.5 and 4.04 ppm respectively during premonsoon. In Cochin estuary, gadolinium showed high accumulation along the northern zone compared to the central and southern zones (Figure 6.7 c). The average concentrations were 9.4, 3.8 and

4.9 ppm along the northern, central and southern zones during monsoon, whereas it was 9.8, 2.5 and 3.1 ppm respectively during premonsoon. During monsoon, the average concentrations were 6 and 5.1 respectively. The maximum concentration was observed at the station 2 (near to industrial zone) during both seasons.

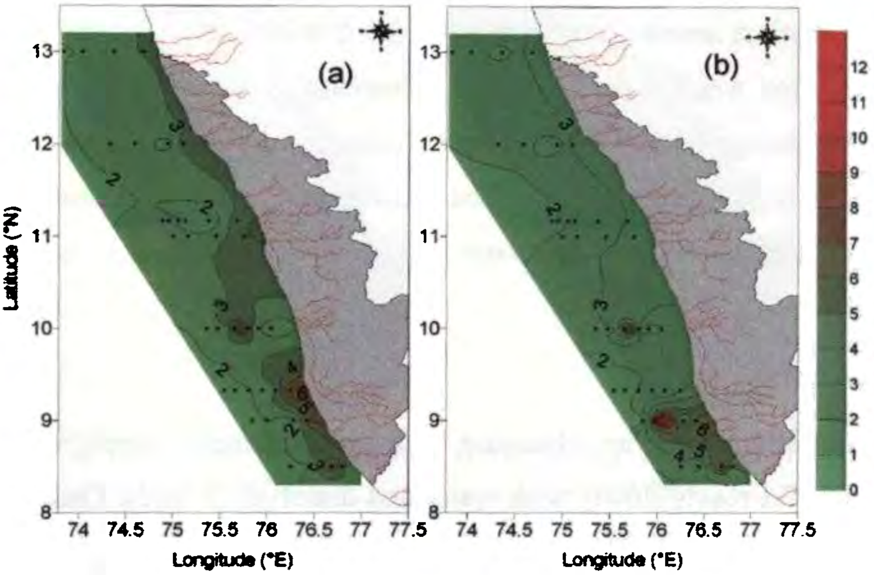

Figure 6.7 a&b. Distribution of gadolinium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

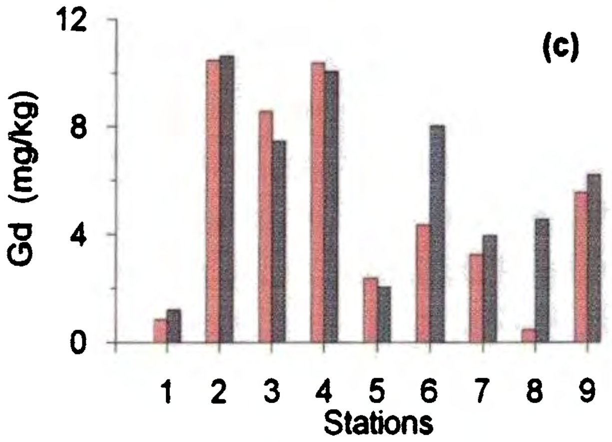

Figure 6.7 c. Distribution of gadolinium in the Cochin estuary during premonsoon (red) and monsoon (black).

The high concentrations along the northern zone clearly indicate some point sources. However, due to very high fresh water flux (Martin et al., 2008), the concentrations decreased in the northern zone, whereas along the central and southern zones, they gradually increased during monsoon.

Terbium

Terbium is one of the rarer rare-earth elements, although it is twice as common as silver on the earth's crust. It is never found in the nature as free element, but is contained in many minerals. The important ores are monazite, bastnasite and cerite. It is reasonably stable in air, but slowly oxidized and reacts with cold water. Tb has no biological role; it may be mildly toxic by ingestion. Tb powder and compounds are very irritating when they come into contact with skin and eyes. Terbium showed a nearshore and mid-depth enrichment followed by a decrease towards deep in almost all transects during both seasons (Figure 6.8 a & b). It showed almost uniform distribution pattern during both seasons, except a slight increase in the southern zone during premonsoon. The concentration was < 1 ppm along the study region with an average of 0.42 and 0.47 ppm during monsoon and premonsoon periods respectively. The average concentrations along the northern and southern zones were 0.42 and 0.41 ppm respectively during monsoon and 0.44 and 0.51 ppm during premonsoon. There was a slight accumulation of elements along Kollam and Trivandrum zones during premonsoon. In Cochin estuary, terbium showed very high concentrations at the northern zone compared to the central and southern zones during both seasons (Figure 6.8 c). The concentrations were > 1 ppm along the northern zone, whereas the other zones contained < 1 ppm during both seasons. The average concentrations were 1.3, 0.4 and 0.71 ppm along the northern, central and southern zones during monsoon, whereas they were 1.4, 0.3 and

0.5 ppm respectively during premonsoon. It showed an average of 0.82 and 0.72 ppm during monsoon and premonsoon.

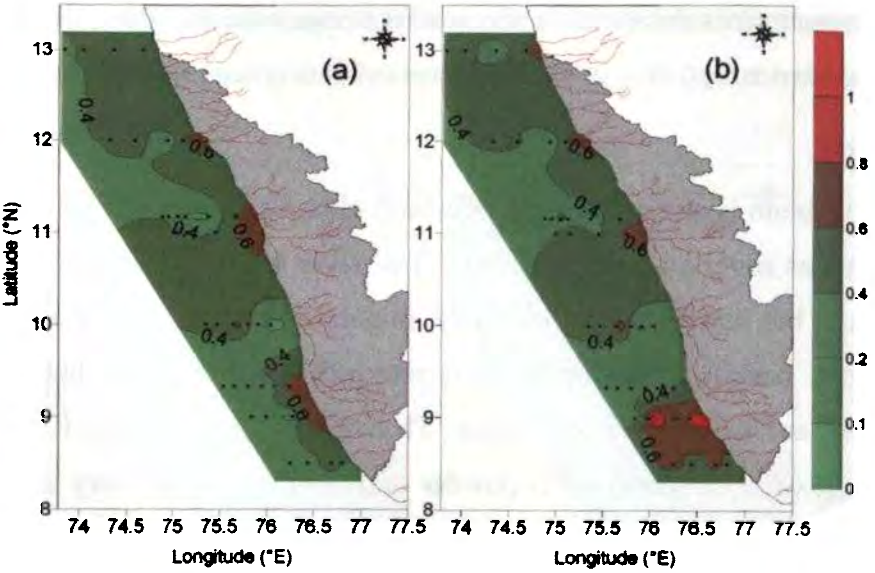

Figure 6.8 a&b. Distribution of terbium [mg/kg dry weight (ppm)] long the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

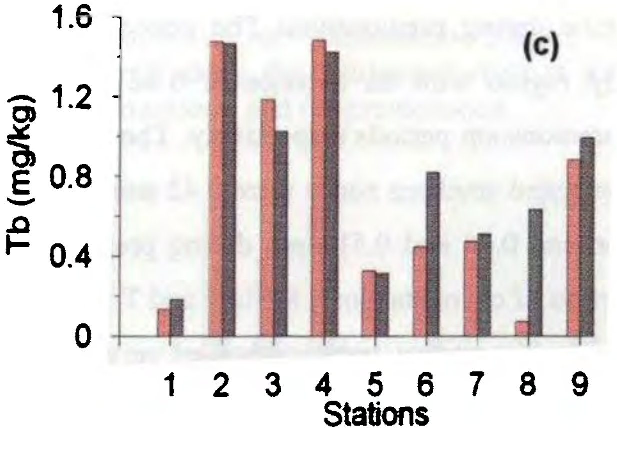

Figure 6.8 c. Distribution of terbium in the Cochin estuary during premonsoon (red) and monsoon (black).

The very high concentrations along the northern zone clearly indicate its origin either from industries or input from Periyar River.

Dysprosium

Dysprosium is an abundant lanthanide element, never encountered as the free element, but found in many minerals. The most important ores are monazite and bastnasite. It is stable at room temperature even if it is slowly oxydized. It reacts with cold water and rapidly dissolves in acids. Soluble dysprosium salts are mildly toxic, while insoluble salts are nontoxic. Dysprosium has no biological role. Dysprosium showed nearshore enrichment, a mid-depth high followed by a decrease towards deep in almost all transects during both seasons (Figure 6.9 a & b). The entire study region contained uniform concentration of Dy during both seasons, with an average of 2.1 and 2.4 ppm during monsoon and premonsoon periods respectively. The northern zone showed not much enrichment than the southern zone. The average concentrations were 2.4 and 1.9 ppm along the northern and southern zones during monsoon, whereas they were 2. 5 and 2.3 ppm respectively during premonsoon. The northern zone behaved almost uniformly in all stations except for the coastal enrichment. Whereas in southern zone, it was distributed mostly in coastal region, off Kollam and Alleppy transects showed the minimum values. In Cochin estuary, dysprosium was high along the northern zone and southernmost station (9) during both seasons (Figure 6.9 c). The average concentrations were 6.7, 1.8 and 3.7 ppm along the northern, central and southern zones during monsoon, whereas they were 7.2, 1.4 and 2.6 ppm respectively during premonsoon. The average concentrations were 3.7 and 4.1 ppm during premonsoon and monsoon respectively. The decrease in concentration along the northern zone during monsoon could be due to the high fresh water flux from Periyar River. Along the central and southern zones, the fresh water flow enriched the zone with these elements.

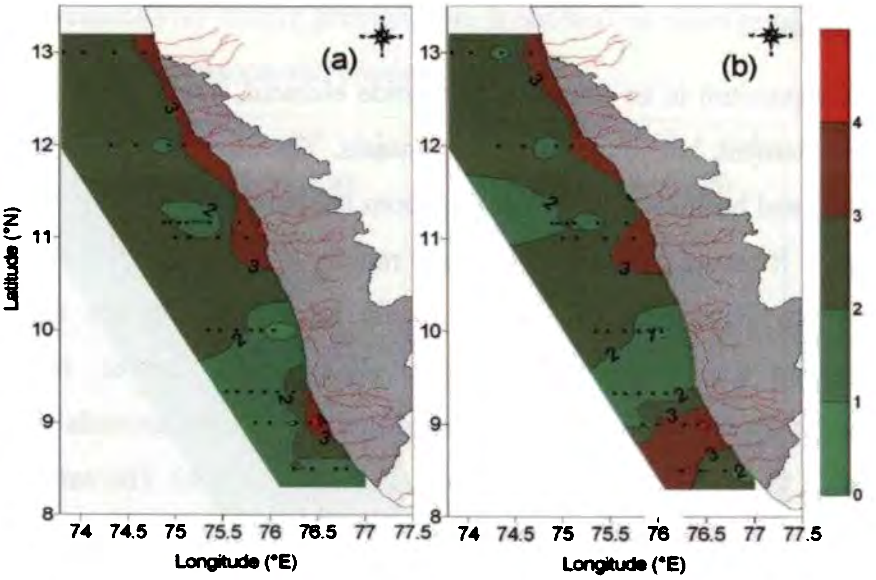

Figure 6.9 a&b. Distribution of dysprosium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

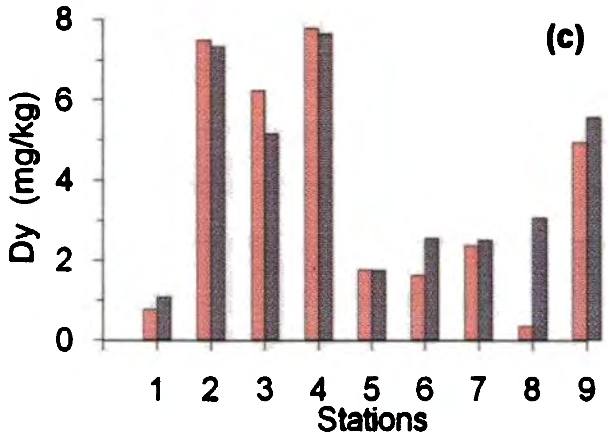

Figure 6.9 c. Distribution of dysprosium in the Cochin estuary during premonsoon (red) and monsoon (black).

Holmium

Holmium is a rare-earth element but, 20 times abundant than silver. Like all other rare-earths, holmium is not naturally found as free element. It is found in minerals such as monazite and bastanasite. It is slowly oxydized and dissolves in acids. It is stable at room temperature. Holmium has no biological role and it is considered as one of the least abundant elements present in human body. It has been noted that holmium stimulates metabolism, even though it has a mild toxicity.

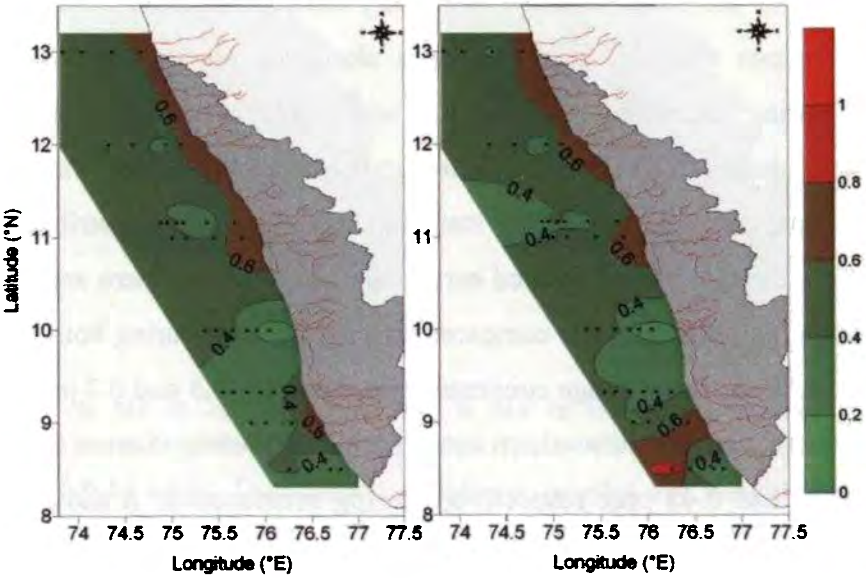

Figure 6.10 a&b. Distribution of holmium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

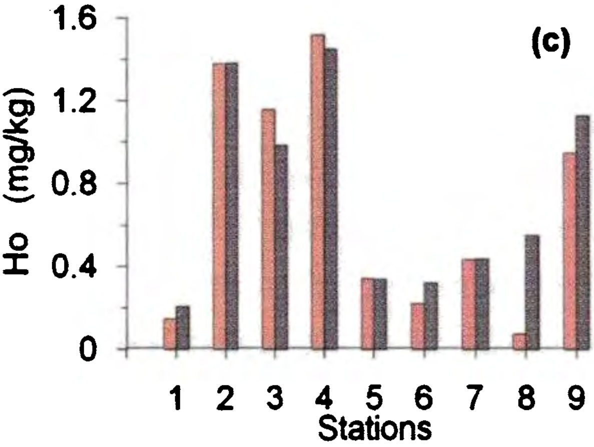

Figure 6.10 c. Distribution of holmium in the Cochin estuary during premonsoon (red) and monsoon (black).

Holmium showed an accumulation in the nearshore region and at 100 m, while all other depths showed minimum concentrations during both seasons (Figure 6.10 a & b). The average concentrations were 0.42 and 0.45 ppm during monsoon and premonsoon seasons. It showed a northern enrichment compared to the southern zone especially during monsoon. The average concentrations were 0.5 and 0.36 ppm along the northern and southern zones during monsoon, whereas 0.5 and 0.42 ppm respectively were recorded during premonsoon. The northern zone showed a coastal enrichment, while the remaining stations showed a normal distribution. In Cochin estuary, holmium showed enrichment along the northern zone and in the southernmost station (9) compared to other stations during both seasons (Figure 6.10 c). The average concentrations were 1.3, 0.3 and 0.7 ppm along the northern, central and southern zones during monsoon, whereas they were 1. 4, 0.23 and 0.48 ppm respectively during premonsoon. It showed little seasonal effect in the study region (monsoon average 0.75 ppm; premonsoon average 0.69 ppm).

Erbium

Erbium never exists free in nature. It is found in minerals of rare-earth elements. It is very stable in air; reacts very slowly with oxygen and water and, dissolves in acids. The most important ores are monazite and bastanite. Erbium has no biological role even if it has been noted that it stimulates metabolism. Erbium showed nearshore enrichment, a mid-depth increase followed by a decrease towards deep in all transects during both seasons (Figure 6.11 a & b). It was distributed uniformly during both seasons with an average of 1.2 and 1.3 ppm during monsoon and premonsoon periods. There was an enrichment in the north compared to the southern zone during both seasons. The average concentrations were 1.4 and 1.1 ppm along the northern and southern zones respectively during monsoon, whereas they were 1.4 and 1.3 ppm respectively during premonsoon.

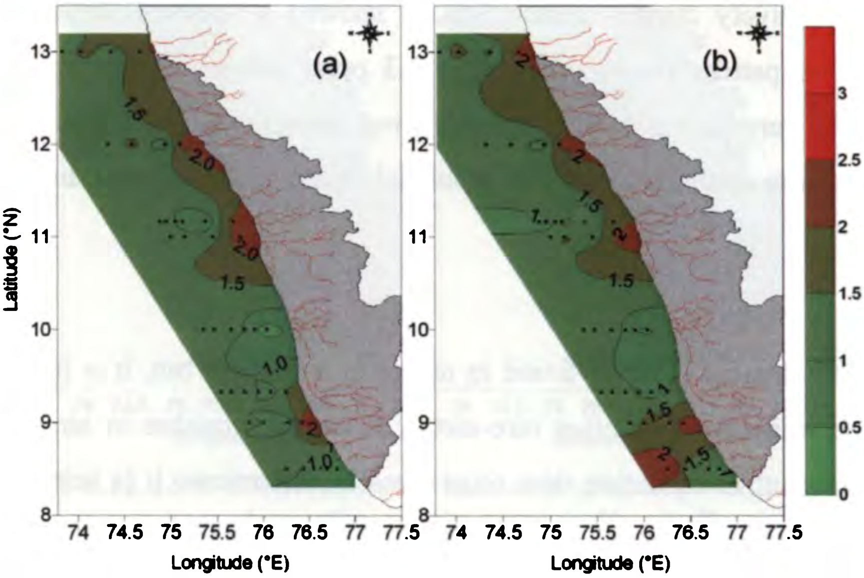

Figure 6.11 a&b. Distribution of erbium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

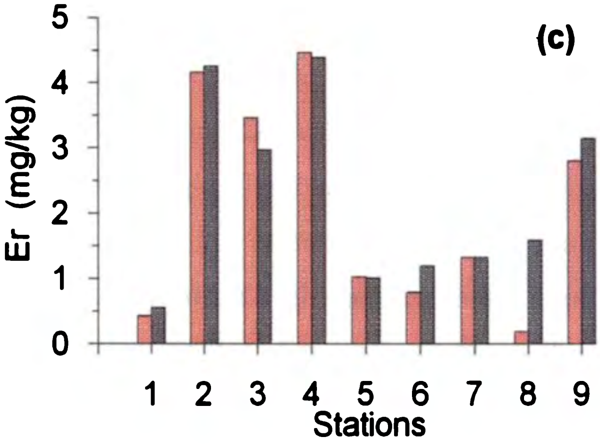

Figure 6.11 c. Distribution of erbium in the Cochin estuary during premonsoon (red) and monsoon (black).

In Cochin estuary, erbium showed enrichment along the northern zone and in the southernmost station (9) during both seasons (Figure 6.11 c). The average concentrations were 3.9, 0.92 and 2 ppm along the northern, central and southern zones during monsoon, whereas they were 4.0, 0.74 and 1.4 ppm respectively during premonsoon. It showed a seasonal variation in distribution pattern (monsoon average 2.3 ppm; premonsoon average 2.1 ppm). The very high concentrations observed along the northern zone might be due to the combined effect of industrial waste water disposal and river transport.

Thulium

The element is never found in nature in pure form but, it is found in traces in minerals with other rare-earths. It slowly tarnishes in air, but is more resistant to oxidation than most rare-earth elements. It is principally extracted from monazite, which contains about 0.007% of thulium and bastnasite. Soluble thulium salts are slightly toxic, but insoluble salts are non toxic. Thulium also showed nearshore and mid-depth maxima compared to all other stations during both seasons (Figure 6.12 a & b). There was no distinct seasonal variation between monsoon and premonsoon seasons (premonsoon average 0.18 and monsoon average 0.16 ppm). The northern and southern zones responded differently during two seasons. The average concentrations were 0.19 and 0.13 ppm along the northern and southern zones during monsoon, whereas 0.2 and 0.16 ppm respectively were recorded during premonsoon. In Cochin estuary, thulium showed enrichment along the northern zone and southern most station during both seasons (Figure 6.12 c). The average concentrations were 0.53, 0.11 and 0.28 ppm along the northern, central and southern zones during monsoon, whereas they were 0.56, 0.09 and 0.2 ppm respectively during premonsoon. The distributions generally showed little seasonal differences (monsoon average 0.31 ppm; premonsoon average 0.28 ppm).

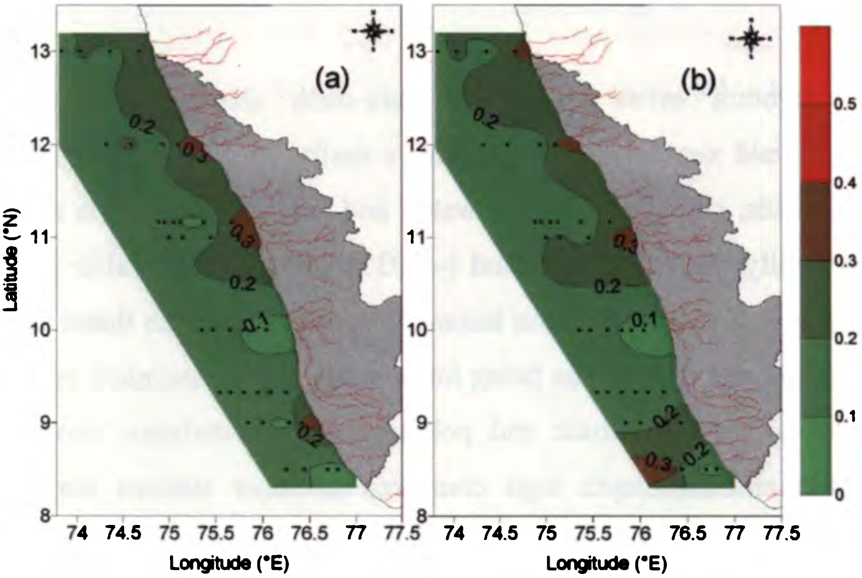

Figure 6.12 a&b. Distribution of thulium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

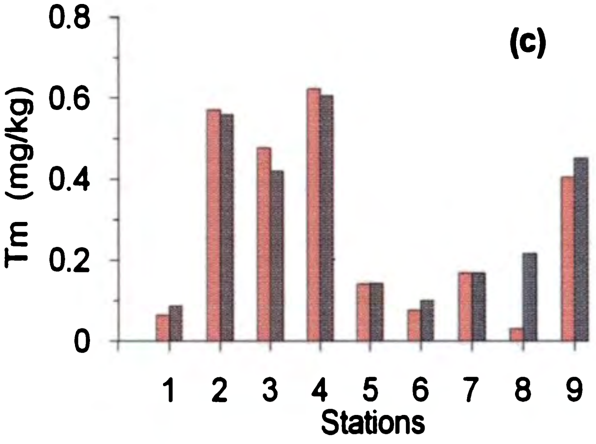

Figure 6.12c. Distribution of thulium in the Cochin estuary during premonsoon (red) and monsoon (black).

The higher concentrations along the northern zone indicates some point sources such as industrial waste disposal and river transport, whereas that in the southern most station might be due to the river transport by southerly encroaching rivers.

Ytterbium

Ytterbium exists with other rare-earth elements as gadolinite, monazite, and xenotime. The element is easily attacked and dissolved by mineral acids, slowly reacts with water, and oxidizes in air. It is recovered commercially from monazite sand (~0.03% ytterbium). Metallic ytterbium dust poses a fire and explosion hazard. Ytterbium poses no threat to plants and animals and its salts are being introduced into the chemical industry as catalysts in place of toxic and polluting ones. Ytterbium also showed nearshore and mid-depth high compared to other stations during both seasons (Figure 6.13 a & b). It was uniformly distributed with average concentrations of 0.94 and 1 ppm during monsoon and premonsoon periods respectively. It observed slight northern enrichment during both seasons. The average concentrations were 1.1 and 0.79 ppm along the northern and southern zones during monsoon, whereas they were 1.2 and 0.91 ppm respectively during premonsoon. In northern zone, most of the metals were concentrated along the coastal region, whereas it was accumulated along the coastal region of Kollam and outer regions of Trivandrum during premonsoon. In Cochin estuary, ytterbium showed enrichment along the stations at northern zone and southern most station (9) during both seasons (Figure 6.13 c). The average concentrations were 3.0, 0.61 and 1.6 ppm along the northern, central and southern zones during monsoon, whereas during premonsoon the values were 3.2, 0.53 and 1.2 ppm respectively. The seasonal averages were 1.7 ppm and 1.6 ppm during monsoon and premonsoon periods respectively. The high concentration along the northern zone could be from the point sources such as industrial waste disposal and river transport, whereas at the southern most station it might be due the river transport.

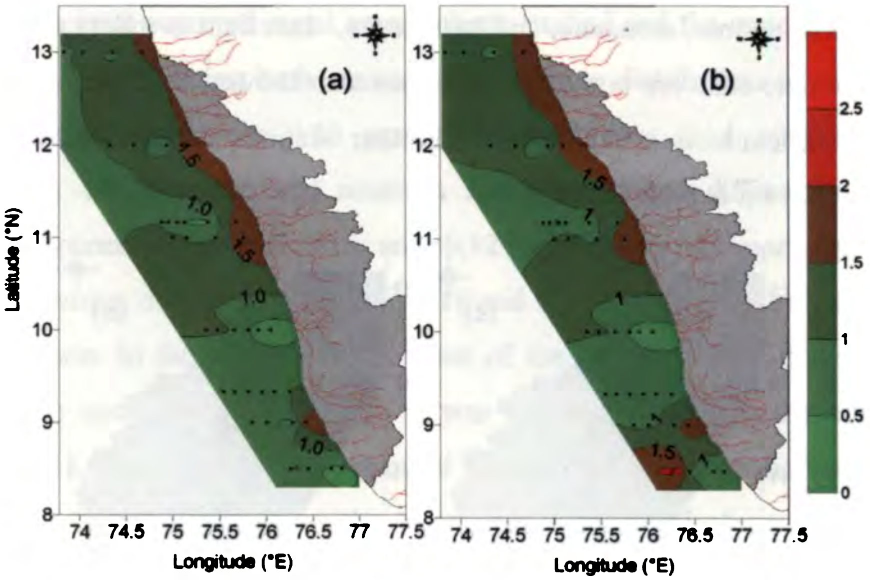

Figure 6.13 a&b. Distribution of ytterbium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

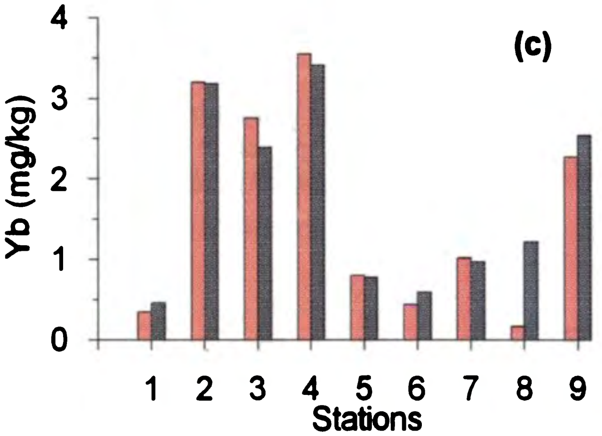

Figure 6.13 c. Distribution of ytterbium in the Cochin estuary during premonsoon (red) and monsoon (black).

Lutetium

Lutetium is the most expensive element and is very difficult to separate from other rare elements. This is largely because of the way it is found in nature. The lanthanides are found in nature in a number of minerals such as xenotime, monazite, and bastnaesite. Lutetium is mildly toxic, but its insoluble salts are non-toxic. Lutetium also showed nearshore and mid-depth enrichments compared to all other stations during both seasons (Figure 6.14 a & b).

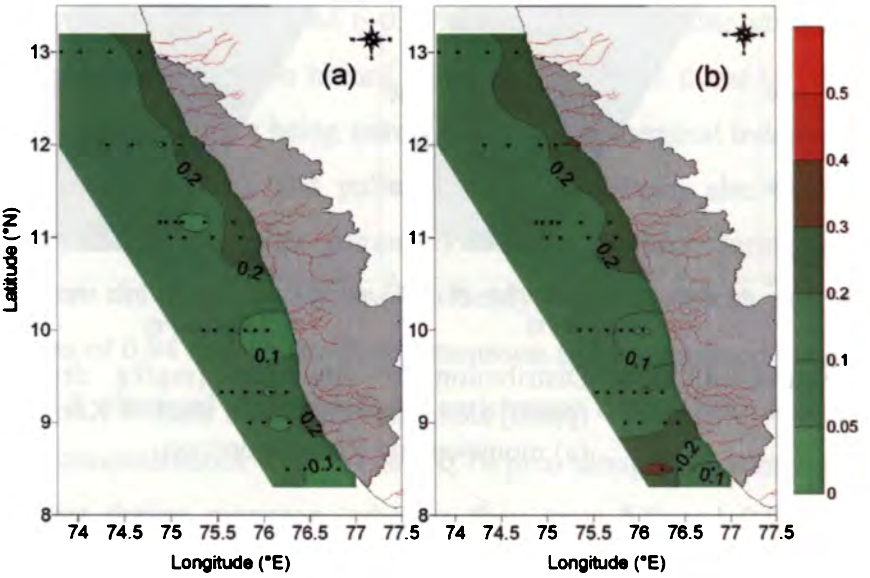

Figure 6.14 a&b. Distribution of lutetium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

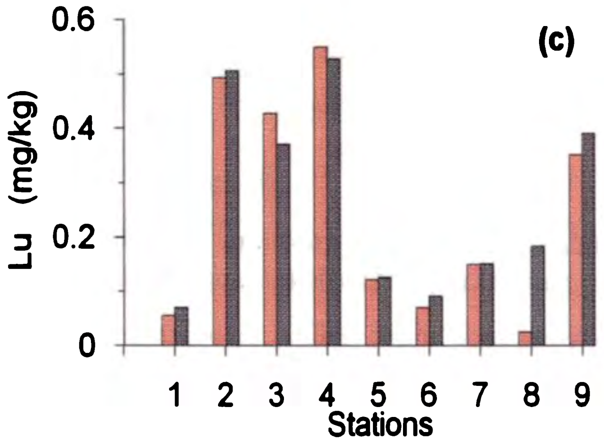

Figure 6.14 c. Distribution of lutetium in the Cochin estuary during premonsoon (red) and monsoon (black).

It was the least occurred metal among those studied and the concentrations were < 0.3 ppm during both seasons. The average distribution of element during premonsoon was 0.16 ppm, whereas it was 0.14 ppm during monsoon. The northern and southern zones responded differently with average concentrations of 0.16 and 0.12 ppm along the northern and southern zones during monsoon and 0.18 and 0.14 ppm respectively during premonsoon. In the northern zone, most of the elements were distributed along the coastal region, whereas it was accumulated along the coastal region of Kollam and offshore region of Trivandrum during premonsoon. In Cochin estuary, lutetium was the least distributed metal along the study region during both seasons; the concentration was < 0.5 ppm during both seasons at all stations (Figure 6.14 c). The average concentrations were 0.47, 0.1 and 0.24 ppm along the northern, central and southern zones during monsoon, whereas the recorded values were 0.49, 0.08 and 0.18 ppm respectively during premonsoon. The seasonal averages were 0.27 and 0.25 ppm during monsoon and premonsoon respectively. The high concentrations along the northern zone might be due to the companied effect of industrial waste water disposal and river transport.

Thorium

Thorium is surprisingly abundant in the earth's crust, being three times more abundant than uranium. Thorium occurs naturally in thorite, uranothorite, thorianite and is a major component of monazite. It is present in significant amounts in the minerals zircon, titanite, gadolinite and betafite. Thorium will slowly react with water, oxygen, and other compounds to form a wide variety of tungsten compounds. Thorium showed nearshore enrichment, a mid-depth increase followed by a decrease towards deep along all transects during both seasons (Figure 6.15 a & b).

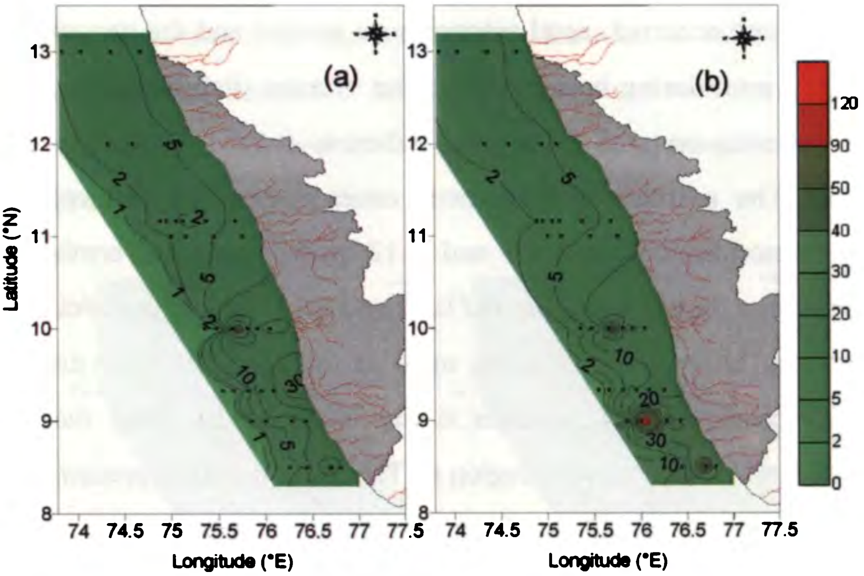

Figure 6.15 a&b. Distribution of thorium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

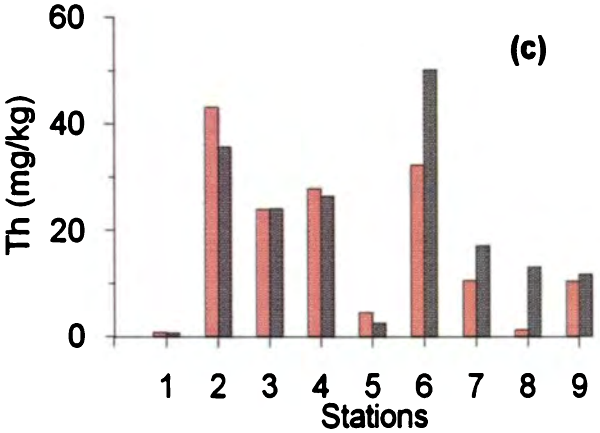

Figure 6.15 c. Distribution of thorium in the Cochin estuary during premonsoon (red) and monsoon (black).

It showed a premonsoon accumulation compared to monsoon, the average concentrations being 10.4 and 15.1 ppm during monsoon and premonsoon respectively. There was a drastic difference in distribution pattern along the northern and southern zones during both seasons. The average concentrations were 3.7 and 16.5 ppm along the northern and southern zones during monsoon, whereas they were 4.3 and 24.8 ppm respectively during premonsoon. The high accumulation of Th was observed at mid-depth stations of Cochin transect as well as along the Kollam and Trivandrum transects during both seasons. Among these, Kollam recorded the maximum concentration during both seasons. In Cochin estuary, thorium showed very high accumulations along the northern zone and at station 6 during both seasons (Figure 6.15 c). The average concentrations were 28.7, 17.7 and 13.9 ppm along the northern, central and southern zones during monsoon, whereas during premonsoon the recorded values were 31.6, 12.5 and 7.4 ppm respectively. The seasonal averages showed marginal enrichment during monsoon (monsoon average 20.1 ppm; premonsoon average 17.2 ppm). The high concentrations along the northern zone especially during the premonsoon could be due to the industrial wastes. The maximum concentration was observed at station 6 (50.1 ppm) during monsoon. The very high concentration observed at station 6 might be due to the very high sediment transport from inland through River Muvattupuzha during monsoon (Laluraj et al., 2008). The low value at barmouth is due to the swift currents at the barmouth (Srinivas et al., 2004), which restricts materials to settle down.

Uranium

Uranium is a radioactive material that is very reactive and not particularly rare. It is widely spread throughout the environment. Uranium is found naturally in rocks, soil, air and water. Uranium compounds dissolve in water to their own extends. The solubility of uranium compound determines its mobility and toxicity. Uranium also showed a coastal enrichment, a mid-depth increase followed by a decrease towards deep along all transects during both seasons (Figure 6.16 a & b).

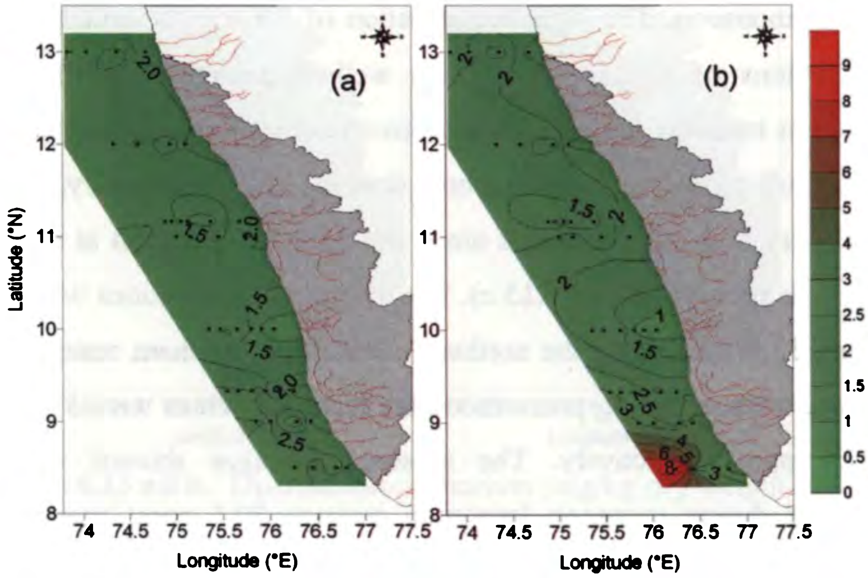

Figure 6.16 a&b. Distribution of uranium [mg/kg dry weight (ppm)] along the continental shelf of Kerala during (a) monsoon and (b) premonsoon.

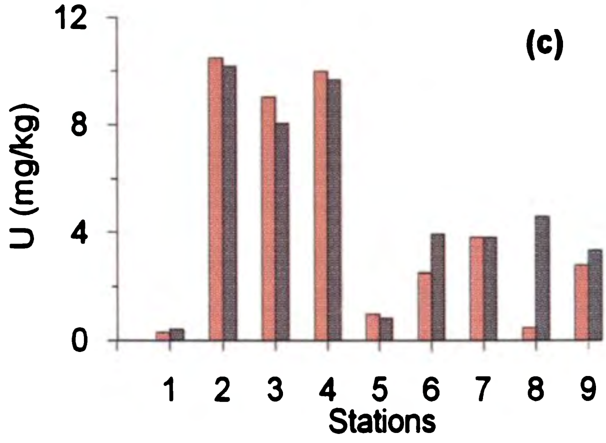

Figure 6.16 c. Distribution of uranium in the Cochin estuary during premonsoon (red) and monsoon (black).

Similar to thorium, it also showed premonsoon accumulation than monsoon (monsoon average 1.9 ppm and premonsoon average 2.2 ppm). The northern and southern zones responded differently during both seasons. The average concentrations were 1.6 and 2.1 ppm along the northern and southern zones during monsoon whereas the recorded values were 1.8 and 2.6 ppm respectively during premonsoon. In the northern zone, most of the elements were accumulated along the coastal region, whereas it was accumulated along the outer region of Alleppy, Kollam and Trivandrum transects. In Cochin estuary, uranium showed very high enrichment along the northern zone compared to the central and southern zones during both seasons (Figure 6.16 c). The average concentrations were 9.3, 1.7 and 3.9 ppm along the northern, central and southern zones during monsoon, whereas it was 9.8, 1.3 and 2.4 ppm respectively during premonsoon. The seasonal averages along the entire study region were 5 ppm and 4.5 ppm during monsoon and premonsoon respectively. The high concentrations along the northern zone could be due to the waste water disposal from the industrial zone.

6.2.2 Normalisation of rare-earth elements, thorium and uranium

The normalised values of rare-earth elements, thorium and uranium with respect to the global shale during both seasons, are given in (Table 6.1a & Table 6.1b). The normalisation factor (NF) < 1 refers to low contamination, 1 < NF < 3 means moderate contamination, 3 < NF< 6 indicates severe contamination, and NF > 6 indicates extreme contamination. REEs showed high NF along the southern zone compared to the northern zone with a marginal increase during premonsoon compared to monsoon season. The mid-depth stations of Cochin (75m) and Kollam (100m) showed severe contamination with LREEs such as La to Nd, whereas Sm showed moderate contamination during premonsoon. In addition, the mid-depth stations of Cochin (100m) and the nearshore stations of Kollam (20m) and Trivandrum (50m) showed moderate contamination for LREEs during premonsoon.

Table 6.1a. Shale normalised values of rare-earth elements along the study region during premonsoon.

Shelf																	
Transects	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
Manglore	20	0.6	0.6	0.5	0.6	0.7	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.5	0.9
	50	0.2	0.2	0.2	0.2	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.1	0.4
	100	0.4	0.4	0.4	0.4	0.5	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.2	0.6
	200	0.3	0.3	0.3	0.4	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.2	0.7
Kannoore	20	0.6	0.7	0.6	0.6	0.8	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.5	0.8
	50	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.3
	100	0.4	0.4	0.4	0.4	0.5	0.6	0.5	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.2	0.6
	200	0.4	0.4	0.4	0.4	0.5	0.6	0.5	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.3	0.6
Baypore	20	0.6	0.6	0.5	0.5	0.6	0.9	0.7	0.7	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.8
	50	0.3	0.3	0.3	0.3	0.4	0.6	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.2	0.4
	75	0.6	0.5	0.5	0.5	0.5	0.4	0.5	0.4	0.3	0.3	0.3	0.3	0.2	0.2	0.3	0.3
	100	0.5	0.5	0.4	0.5	0.6	0.7	0.6	0.6	0.5	0.5	0.5	0.4	0.4	0.3	0.3	0.5
	150	0.4	0.4	0.4	0.5	0.6	0.7	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.4	0.3	0.6
	200	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.1	0.3
Ponnani	20	0.7	0.8	0.6	0.7	0.8	1.0	0.8	0.9	0.9	0.8	0.8	0.8	0.7	0.7	0.5	0.8
	50	0.4	0.4	0.4	0.4	0.5	0.6	0.5	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.4	0.5
	100	0.5	0.5	0.5	0.5	0.6	0.8	0.7	0.7	0.7	0.6	0.6	0.5	0.4	0.4	0.2	0.8
	200	0.4	0.5	0.4	0.5	0.6	0.7	0.6	0.6	0.6	0.5	0.5	0.5	0.4	0.4	0.3	0.8
Cochin	20	1.0	0.8	0.6	0.6	0.4	0.3	0.4	0.3	0.2	0.1	0.2	0.1	0.1	0.1	0.9	0.2
	50	0.3	0.3	0.2	0.2	0.3	0.5	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.3	0.3
	75	5.6	4.3	3.3	3.1	2.0	1.0	2.2	1.3	0.7	0.5	0.6	0.4	0.3	0.3	5.5	0.6
	100	1.6	1.4	1.1	1.1	1.0	0.9	1.0	0.8	0.6	0.4	0.5	0.4	0.3	0.3	2.2	0.7
	150	0.5	0.6	0.5	0.6	0.6	0.7	0.7	0.6	0.5	0.5	0.5	0.4	0.4	0.3	0.5	0.6
	200	0.5	0.6	0.5	0.5	0.6	0.7	0.6	0.6	0.5	0.5	0.5	0.4	0.4	0.4	0.5	0.5
Alleppy	20	0.8	0.8	0.6	0.6	0.7	0.6	0.6	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.9	0.8
	50	0.7	0.6	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.3	0.2	0.2	0.2	0.9	0.6
	75	0.6	0.5	0.5	0.5	0.6	0.5	0.6	0.5	0.4	0.4	0.3	0.3	0.3	0.3	0.6	0.7
	100	1.1	0.9	0.7	0.7	0.6	0.5	0.6	0.5	0.4	0.3	0.4	0.3	0.3	0.3	1.1	0.7
	150	0.6	0.5	0.4	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.6	0.9
	200	0.4	0.3	0.3	0.3	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.9
Kollam	20	1.9	1.7	1.5	1.6	1.6	1.3	1.5	1.2	0.9	0.8	0.8	0.7	0.6	0.6	2.2	1.2
	50	0.4	0.4	0.4	0.4	0.6	0.7	0.6	0.6	0.6	0.5	0.5	0.5	0.5	0.4	0.3	0.7
	100	6.8	5.4	4.2	3.9	2.5	0.8	2.9	1.6	0.9	0.6	0.7	0.4	0.3	0.3	9.6	0.9
	200	0.3	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.9
Trivandrum	20	0.9	0.9	0.8	0.9	0.9	0.3	0.8	0.6	0.4	0.3	0.3	0.2	0.2	0.2	1.6	0.7
	50	2.3	2.3	2.1	2.2	1.9	0.4	1.6	1.0	0.5	0.3	0.4	0.2	0.2	0.2	4.7	1.0
	100	0.5	0.5	0.4	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.6	0.8
	200	0.5	0.4	0.4	0.5	0.6	0.8	0.7	0.8	0.9	0.9	0.9	0.9	0.8	0.8	0.4	2.8

Estuary																	
St.No.	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
1	3	0.2	0.2	0.1	0.2	0.3	1.1	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.1
2	5	2.8	2.6	2.2	2.2	2.3	2.2	2.2	1.9	1.6	1.4	1.5	1.4	1.1	1.1	3.0	3.4
3	3	2.2	2.0	1.8	1.9	1.9	2.0	1.8	1.5	1.3	1.2	1.2	1.2	1.0	1.0	1.6	2.9
4	ND	2.6	2.3	2.0	2.1	2.2	2.2	2.2	1.9	1.7	1.5	1.6	1.5	1.3	1.3	1.9	3.2
5	2	0.8	0.6	0.5	0.5	0.6	1.4	0.5	0.4	0.4	0.3	0.4	0.3	0.3	0.3	0.3	0.3
6	ND	1.6	1.4	1.2	1.2	1.0	0.4	0.9	0.6	0.3	0.2	0.3	0.2	0.2	0.2	2.2	0.8
7	6	0.9	0.8	0.7	0.7	0.7	1.0	0.7	0.6	0.5	0.4	0.5	0.4	0.4	0.3	0.7	1.2
8	4	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
9	9	1.2	1.1	1.0	1.0	1.2	1.4	1.2	1.1	1.1	1.0	1.0	1.0	0.8	0.8	0.7	0.9

Table 6.1b. Shale normalised values of rare-earth elements along the study region during monsoon.

Shelf																	
Transects	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
Manglore	20	0.5	0.6	0.5	0.5	0.7	0.8	0.7	0.7	0.7	0.7	0.7	0.7	0.6	0.6	0.4	0.8
	50	0.3	0.3	0.3	0.3	0.4	0.5	0.5	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.4
	100	0.4	0.4	0.4	0.4	0.6	0.7	0.6	0.7	0.6	0.6	0.6	0.6	0.5	0.5	0.3	0.6
	200	0.2	0.3	0.3	0.3	0.4	0.5	0.4	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.5
Kannoore	20	0.6	0.7	0.6	0.6	0.7	0.9	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.7	0.5	0.7
	50	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.3
	100	0.5	0.5	0.4	0.5	0.6	0.8	0.6	0.7	0.6	0.6	0.6	0.6	0.5	0.5	0.3	0.7
	200	0.3	0.3	0.3	0.4	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.2	0.5
Baypore	20	0.6	0.7	0.6	0.6	0.8	1.0	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.6	0.5	0.7
	50	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2
	75	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.3
	100	0.4	0.3	0.3	0.4	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.4
	150	0.3	0.3	0.3	0.3	0.4	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.3	0.3	0.1	0.5
	200	0.3	0.3	0.3	0.4	0.4	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.3	0.3	0.2	0.6
Ponnani	20	0.7	0.7	0.6	0.7	0.8	1.0	0.8	0.9	0.8	0.8	0.8	0.8	0.7	0.7	0.5	0.7
	50	0.5	0.5	0.4	0.5	0.5	0.6	0.5	0.5	0.5	0.4	0.4	0.4	0.3	0.3	0.4	0.4
	100	0.3	0.3	0.3	0.4	0.5	0.6	0.5	0.5	0.5	0.4	0.4	0.4	0.3	0.3	0.2	0.6
	200	0.3	0.3	0.3	0.3	0.5	0.6	0.5	0.6	0.5	0.5	0.5	0.4	0.4	0.4	0.2	0.6
Cochin	20	0.5	0.4	0.3	0.3	0.2	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.5	0.2
	50	1.0	0.8	0.7	0.7	0.7	0.7	0.7	0.5	0.3	0.3	0.3	0.2	0.2	0.2	1.1	0.4
	75	4.2	3.2	2.4	2.2	1.4	0.7	1.7	1.0	0.6	0.4	0.5	0.3	0.3	0.3	6.8	0.7
	100	1.5	1.3	1.0	1.0	0.9	0.9	0.9	0.7	0.5	0.4	0.5	0.4	0.3	0.3	1.5	0.7
	150	0.5	0.6	0.5	0.5	0.7	0.8	0.7	0.7	0.6	0.5	0.5	0.5	0.4	0.4	0.4	0.5
	200	0.4	0.5	0.4	0.5	0.6	0.7	0.6	0.6	0.5	0.5	0.4	0.4	0.4	0.3	0.4	0.5
Alleppy	20	2.0	1.8	1.6	1.6	1.4	0.8	1.4	1.0	0.6	0.5	0.6	0.4	0.4	0.4	2.6	0.9
	50	1.0	0.8	0.6	0.6	0.5	0.4	0.5	0.4	0.3	0.2	0.2	0.2	0.2	0.2	1.2	0.4
	75	0.7	0.6	0.5	0.5	0.5	0.4	0.5	0.4	0.4	0.3	0.4	0.3	0.3	0.3	0.7	0.7
	100	0.9	0.8	0.7	0.7	0.6	0.4	0.7	0.5	0.4	0.3	0.4	0.3	0.3	0.3	0.9	1.1
	150	0.3	0.3	0.3	0.3	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.8
	200	0.3	0.3	0.3	0.3	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.8
Kollam	20	1.0	1.0	0.9	0.9	1.1	1.3	1.1	1.0	0.9	0.9	0.9	0.9	0.7	0.7	0.8	0.9
	50	0.3	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.3	0.2
	100	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.7	0.8
	200	0.3	0.2	0.2	0.3	0.3	0.4	0.3	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.2	1.0
Trivandrum	20	0.5	0.5	0.5	0.5	0.6	0.2	0.6	0.4	0.3	0.2	0.2	0.2	0.2	0.1	0.8	0.6
	50	1.7	1.6	1.4	1.5	1.4	0.4	1.2	0.7	0.4	0.2	0.3	0.2	0.2	0.1	2.5	1.1
	100	0.3	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.3	0.6
	200	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.4	0.4	0.5	0.5	0.4	0.4	0.3	1.0
Estuary																	
St.No.	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
1	3	0.3	0.2	0.2	0.2	0.4	1.1	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.0	0.1
2	5	2.8	2.6	2.2	2.2	2.3	2.2	2.3	1.9	1.6	1.4	1.5	1.4	1.1	1.2	2.4	3.3
3	3	1.9	1.8	1.5	1.6	1.7	1.7	1.6	1.3	1.1	1.0	1.0	1.0	0.8	0.9	1.6	2.6
4	ND	2.5	2.3	2.0	2.1	2.1	2.1	2.2	1.8	1.6	1.5	1.5	1.5	1.2	1.2	1.8	3.1
5	2	0.5	0.4	0.4	0.4	0.6	1.3	0.4	0.4	0.4	0.3	0.4	0.4	0.3	0.3	0.2	0.3
6	ND	2.3	2.3	2.1	2.1	1.9	0.5	1.7	1.1	0.5	0.3	0.4	0.2	0.2	0.2	3.4	1.3
7	6	1.1	1.0	0.8	0.9	0.9	0.9	0.8	0.7	0.5	0.4	0.5	0.4	0.3	0.3	1.2	1.2
8	4	1.0	1.0	0.9	0.9	1.0	1.0	1.0	0.8	0.7	0.6	0.6	0.5	0.4	0.4	0.9	1.5
9	9	1.3	1.2	1.1	1.1	1.3	1.6	1.3	1.3	1.2	1.1	1.1	1.1	0.9	0.9	0.8	1.1

The MREEs such as Gd and Tb showed moderate contamination along the mid-depth stations of Cochin (75m) and Kollam (20 & 100m) during premonsoon. Eu showed moderate contamination at the mid-depths (75 m) of Cochin, whereas Gd showed moderate contamination at the mid-depth of Trivandrum during premonsoon. Whereas during monsoon, the coastal stations of Alleppy (20m), the mid-depth stations of Cochin (75m) and Kollam (50m) showed moderate contamination for LREEs and Gd. However, low contamination was observed for all REEs along the northern zone and HREEs along the entire shelf region during both seasons. Th showed moderate contamination along the few coastal and mid-depth stations of southern zone during both seasons. An extreme contamination was observed for Th at the mid-depths of Kollam during premonsoon. U showed low contamination except at a few stations along the southern zone during both seasons. In Cochin estuary, the northern zone and southern most station (station no.9) showed moderate contamination for all REEs (except Yb and Lu at station no.3) as well as Th & U during both seasons. In addition, along the central zone (station no.6) observed moderate contamination for LREEs during both seasons. Moderate enrichment is seen along the northern zone and stations 6 & 7 during monsoon. During monsoon, the entire estuary (except station nos 1 & 5) showed moderate contamination for U, indicates the influence of river inflow to estuary which acted as a carrier for U from inland.

Nath et al. (2000) has plotted shale normalized patterns of charnockites and gneisses based on data presented in Allen et al. (1985) and the present study is similar to that pattern indicating gneissic source for these sediments. The degree of rare-earth fractionation between the sub-environments varies, but can be easily explained by the difference in provenance characteristic of the drainage areas. Nath (2000) observed the estuarine zone and the rivers, which are encroaching to the estuary, were originating from the similar source terranes. Rivers leading to the estuarine zone of the Cochin estuary originated from gneissic terranes, which are not the case in southern rivers (Nath et al., 2000). However, the observed shale normalised patterns indicate that sediment recycling homogenizes the signature of sediment provenances. This could be the reason for the observed normalisation values of the present study.

6.2.3 Metal enrichment factor

Metal enrichment factor is used for the determination of level of metal contamination in sediments. The enrichment factors calculated for each element based on Al and Fe concentrations are furnished here (Table 6.2a & Table 6.2b and Table 6.3a & Table 6.3b). The southern zone (south of 10°N) showed high enrichment for all REEs, Th and U during both seasons. The differences in the enrichments generally reflected the geochemical reactivity of these elements in the marine environment. Similar to the normalisation factor, the enrichment factor (EF) < 1 refers to low enrichment, 1 < EF < 3 means moderate enrichment, 3 < EF< 6 indicates severe enrichment, and EF > 6 indicates extreme enrichment.

6.2.3.1 Enrichment with respect to aluminium

Enrichment factor with respect to aluminum varied between southern and northern zones during both seasons (Table 6.2a & Table 6.2b). The enrichment was in the order LREEs>MREEs>HREEs along the study region during both seasons. The enrichment factor revealed a premonsoon upsurge. Along the southern zone, extreme enrichment was observed for LREEs along the mid-depth stations of Cochin (75m) and Trivandrum (50m) transects during monsoon and along the nearshore and mi-depth stations of Cochin (75m), Kollam (100m) and Trivandrum (20 & 50m) transects during premonsoon.

Table 6.2a. Enrichment factors (rare-earth elements) with respect aluminium along the study region during premonsoon.

Shelf																	
Transects	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
Manglore	20	0.5	0.5	0.4	0.5	0.6	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.7
	50	1.0	0.9	0.9	1.1	1.4	1.8	1.5	1.6	1.5	1.5	1.5	1.5	1.2	1.2	0.6	1.8
	100	1.1	1.2	1.1	1.3	1.7	2.2	1.9	2.0	2.0	2.0	1.9	1.9	1.6	1.5	0.7	2.0
	200	0.7	0.8	0.8	0.9	1.2	1.5	1.2	1.4	1.3	1.3	1.3	1.2	1.0	1.0	0.6	1.8
Kannoore	20	0.5	0.5	0.4	0.5	0.6	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.3	0.6
	50	0.7	0.8	0.7	0.7	0.8	1.0	0.9	0.9	0.8	0.8	0.9	0.8	0.8	0.8	0.6	1.4
	100	1.0	0.9	0.9	1.0	1.2	1.6	1.3	1.4	1.3	1.3	1.3	1.2	1.1	1.0	0.6	1.4
	200	1.0	1.0	1.0	1.0	1.3	1.6	1.4	1.5	1.3	1.3	1.3	1.3	1.1	1.0	0.7	1.4
Baypore	20	0.5	0.5	0.5	0.5	0.6	0.8	0.6	0.6	0.6	0.5	0.6	0.5	0.5	0.4	0.4	0.7
	50	0.8	0.7	0.7	0.7	0.9	1.3	0.9	0.9	0.9	0.8	0.9	0.8	0.6	0.7	0.4	0.9
	75	2.2	2.1	1.8	1.9	1.9	1.7	2.0	1.7	1.4	1.2	1.2	1.1	0.9	0.9	1.2	1.3
	100	1.4	1.4	1.3	1.5	1.7	2.0	1.8	1.8	1.6	1.5	1.4	1.3	1.1	1.1	0.8	1.6
	150	1.3	1.4	1.3	1.5	1.9	2.3	1.9	2.1	2.0	1.8	1.8	1.7	1.4	1.4	0.9	1.9
	200	0.9	0.9	0.9	1.0	1.2	1.4	1.2	1.3	1.3	1.2	1.2	1.2	1.0	1.0	0.7	1.5
Ponnani	20	0.5	0.6	0.5	0.5	0.6	0.8	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.6
	50	1.3	1.3	1.2	1.3	1.5	1.7	1.5	1.4	1.3	1.1	1.2	1.1	0.9	0.9	1.2	1.5
	100	2.1	2.3	2.1	2.5	3.0	3.8	3.1	3.3	3.0	2.7	2.6	2.5	2.0	1.9	1.0	3.5
	200	0.9	1.0	0.9	1.0	1.2	1.5	1.3	1.3	1.3	1.1	1.1	1.1	0.9	0.9	0.7	1.7
Cochin	20	5.7	4.6	3.5	3.2	2.3	1.6	2.4	1.6	1.1	0.8	0.9	0.7	0.6	0.5	5.0	1.3
	50	1.1	0.9	0.8	0.8	0.9	1.5	0.8	0.7	0.6	0.6	0.6	0.6	0.4	0.4	0.8	0.9
	75	13.9	10.6	8.2	7.8	4.9	2.6	5.4	3.2	1.8	1.2	1.5	0.9	0.8	0.7	13.6	1.4
	100	3.1	2.6	2.1	2.1	1.9	1.8	1.9	1.4	1.1	0.9	0.9	0.8	0.7	0.6	4.3	1.4
	150	1.5	1.7	1.4	1.6	1.8	1.9	1.8	1.8	1.5	1.4	1.3	1.2	1.0	0.9	1.4	1.6
	200	1.3	1.4	1.2	1.3	1.5	1.8	1.5	1.5	1.3	1.2	1.2	1.1	0.9	0.9	1.1	1.2
Alleppy	20	1.5	1.4	1.2	1.2	1.3	1.2	1.2	1.0	0.8	0.7	0.8	0.7	0.6	0.6	1.7	1.5
	50	2.7	2.2	1.8	1.7	1.5	1.5	1.6	1.3	1.1	0.9	1.0	0.9	0.7	0.7	3.5	2.3
	75	2.1	1.9	1.7	1.8	2.0	1.9	2.0	1.8	1.4	1.3	1.2	1.2	0.9	1.0	2.3	2.5
	100	6.7	5.5	4.3	4.2	3.3	2.7	3.5	2.7	2.2	1.9	2.1	1.9	1.6	1.5	6.6	4.3
	150	2.1	1.8	1.6	1.7	1.8	1.8	1.8	1.7	1.5	1.4	1.4	1.4	1.1	1.1	2.2	3.1
	200	1.4	1.2	1.1	1.3	1.5	1.9	1.6	1.6	1.5	1.5	1.4	1.5	1.2	1.2	1.1	3.3
Kollam	20	1.8	1.7	1.5	1.6	1.6	1.3	1.5	1.1	0.9	0.8	0.8	0.7	0.6	0.6	2.2	1.1
	50	1.0	1.1	1.0	1.1	1.5	1.8	1.6	1.6	1.6	1.4	1.4	1.4	1.2	1.1	0.8	1.8
	100	25.0	20.1	15.6	14.5	9.3	3.1	10.7	6.0	3.4	2.1	2.7	1.5	1.2	1.3	35.4	3.3
	200	1.5	1.2	1.2	1.4	1.6	2.0	1.8	1.9	1.9	1.9	1.8	1.9	1.5	1.6	1.1	4.3
Trivandrum	20	7.9	7.8	7.2	7.6	7.8	2.7	7.0	5.0	3.3	2.5	2.6	2.0	1.8	1.6	13.6	6.3
	50	13.7	13.7	12.6	13.3	11.1	2.4	9.6	5.8	2.9	1.6	2.1	1.1	1.1	1.1	27.6	6.0
	100	3.2	2.8	2.5	2.5	2.6	2.5	2.8	2.5	2.3	2.2	2.2	2.2	1.7	1.7	3.7	4.6
	200	2.1	1.8	1.9	2.3	2.8	3.5	3.3	3.7	4.0	3.9	3.9	4.0	3.4	3.4	2.0	12.6

Estuary																	
St.No.	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
1	3.0	0.3	0.2	0.2	0.2	0.4	1.3	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.1
2	4.5	1.3	1.3	1.1	1.1	1.1	1.1	1.1	0.9	0.8	0.7	0.7	0.7	0.6	0.6	1.4	1.7
3	2.5	1.3	1.2	1.0	1.1	1.1	1.2	1.1	0.9	0.8	0.7	0.7	0.7	0.6	0.6	1.0	1.7
4	ND	1.3	1.2	1.0	1.1	1.1	1.1	1.1	1.0	0.8	0.8	0.8	0.8	0.6	0.6	0.9	1.6
5	1.5	0.7	0.5	0.4	0.4	0.5	1.1	0.4	0.4	0.3	0.3	0.3	0.3	0.2	0.2	0.3	0.3
6	ND	7.2	6.5	5.5	5.5	4.5	1.7	4.3	2.6	1.6	1.0	1.3	0.9	0.7	0.7	10.1	3.7
7	5.5	1.2	1.1	0.9	0.9	1.0	1.3	1.0	0.8	0.7	0.6	0.6	0.6	0.5	0.5	1.0	1.7
8	4.0	0.9	0.8	0.7	0.7	0.8	1.5	0.7	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.6	1.1
9	8.5	0.7	0.7	0.6	0.6	0.7	0.9	0.7	0.7	0.7	0.6	0.6	0.6	0.5	0.5	0.4	0.6

Table 6.2b. Enrichment factors (rare-earth elements) with respect aluminium along the study region during monsoon.

Shelf																	
Transects	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
Manglore	20	0.5	0.5	0.5	0.5	0.6	0.8	0.6	0.7	0.7	0.6	0.6	0.6	0.5	0.5	0.4	0.7
	50	1.4	1.4	1.3	1.5	2.1	2.3	2.1	2.3	2.1	1.9	1.9	1.7	1.4	1.3	0.8	1.7
	100	1.2	1.2	1.2	1.4	1.9	2.2	1.9	2.2	2.1	2.0	2.0	1.9	1.6	1.5	0.9	2.0
	200	0.8	0.9	0.9	1.0	1.4	1.7	1.5	1.6	1.5	1.5	1.4	1.4	1.2	1.1	0.7	1.7
Kannoore	20	0.5	0.5	0.4	0.5	0.6	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.6
	50	1.1	1.1	1.0	1.1	1.4	1.3	1.4	1.4	1.2	1.1	1.0	0.9	0.8	0.7	0.9	1.5
	100	1.0	0.9	0.9	1.0	1.3	1.6	1.3	1.4	1.3	1.3	1.2	1.2	1.0	1.0	0.6	1.5
	200	0.9	1.0	0.9	1.0	1.4	1.7	1.4	1.5	1.4	1.4	1.3	1.3	1.1	1.0	0.7	1.5
Baypore	20	0.5	0.5	0.4	0.5	0.6	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.3	0.5
	50	0.6	0.6	0.6	0.6	0.8	1.2	0.7	0.8	0.7	0.7	0.6	0.6	0.5	0.5	0.4	0.9
	75	0.8	0.8	0.8	0.8	1.0	1.4	1.1	1.1	1.0	1.1	1.1	1.0	0.8	0.8	0.5	1.5
	100	1.7	1.6	1.6	1.7	2.2	2.6	2.3	2.3	2.1	2.0	1.9	1.7	1.4	1.3	0.9	1.7
	150	2.1	2.2	2.2	2.5	3.3	4.2	3.6	3.7	3.5	3.3	3.3	3.1	2.5	2.4	1.0	3.8
	200	0.8	0.9	0.8	0.9	1.2	1.4	1.2	1.3	1.2	1.2	1.1	1.1	0.9	0.8	0.6	1.6
Ponnani	20	0.5	0.5	0.4	0.5	0.6	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.3	0.5
	50	1.1	1.1	1.0	1.1	1.2	1.5	1.3	1.2	1.1	1.0	1.0	1.0	0.8	0.7	0.8	1.0
	100	1.7	1.8	1.7	2.0	2.5	3.2	2.7	2.8	2.6	2.4	2.4	2.3	1.9	1.7	0.8	3.2
	200	1.9	2.1	2.0	2.3	3.2	4.2	3.5	3.8	3.5	3.4	3.2	2.9	2.5	2.4	1.0	3.7
Cochin	20	2.7	2.0	1.5	1.4	1.3	1.7	1.3	0.9	0.6	0.5	0.6	0.5	0.4	0.4	2.4	1.0
	50	2.5	2.1	1.7	1.7	1.7	1.8	1.7	1.2	0.9	0.7	0.7	0.5	0.4	0.4	2.6	1.0
	75	14.3	10.9	8.3	7.3	4.7	2.3	5.7	3.4	1.9	1.3	1.7	1.0	1.0	0.9	23.0	2.3
	100	2.9	2.4	1.9	1.8	1.6	1.7	1.7	1.3	1.0	0.8	0.9	0.8	0.7	0.6	2.9	1.3
	150	1.0	1.2	1.0	1.2	1.4	1.6	1.4	1.4	1.2	1.1	1.1	1.0	0.8	0.7	0.9	1.1
	200	0.9	1.1	0.9	1.0	1.2	1.5	1.2	1.2	1.1	1.0	0.9	0.9	0.7	0.7	0.8	1.0
Alleppy	20	3.2	2.9	2.6	2.6	2.3	1.2	2.2	1.6	1.0	0.8	0.9	0.7	0.6	0.6	4.3	1.5
	50	3.7	3.0	2.3	2.1	1.7	1.4	1.8	1.3	0.9	0.8	0.9	0.7	0.6	0.6	4.5	1.3
	75	2.5	2.2	1.8	1.8	1.7	1.5	1.8	1.5	1.3	1.2	1.3	1.1	0.9	0.9	2.4	2.3
	100	7.2	6.1	5.2	5.2	5.1	3.2	5.3	4.2	3.1	2.7	2.9	2.6	2.3	2.2	7.3	8.4
	150	1.3	1.3	1.2	1.3	1.5	1.8	1.6	1.6	1.5	1.5	1.5	1.4	1.2	1.1	1.2	3.2
	200	1.0	1.0	1.0	1.1	1.3	1.7	1.4	1.4	1.3	1.3	1.3	1.2	1.0	1.0	0.8	2.7
Kollam	20	0.8	0.8	0.7	0.7	0.8	1.0	0.8	0.8	0.7	0.7	0.7	0.7	0.6	0.5	0.6	0.7
	50	1.6	1.4	1.3	1.2	1.3	1.5	1.2	0.9	0.8	0.7	0.7	0.6	0.6	0.5	1.9	1.5
	100	2.4	2.1	1.8	1.8	1.8	2.0	1.8	1.6	1.3	1.3	1.3	1.2	1.0	1.0	2.7	2.8
	200	1.3	1.1	1.1	1.3	1.5	2.0	1.7	1.8	1.7	1.7	1.7	1.6	1.4	1.4	0.9	4.7
Trivandrum	20	4.7	4.9	4.8	5.1	5.8	2.3	5.3	4.2	2.7	1.9	2.0	1.7	1.4	1.3	7.4	5.3
	50	9.2	8.8	8.0	8.1	7.6	2.0	6.7	4.1	2.1	1.2	1.6	0.9	0.9	0.7	13.9	5.9
	100	2.7	2.6	2.4	2.6	2.9	2.9	3.1	2.8	2.7	2.7	2.7	2.5	2.1	2.1	3.0	5.4
	200	1.4	1.3	1.3	1.5	1.8	2.1	2.1	2.2	2.2	2.1	2.2	2.2	1.8	1.8	1.6	4.7
Estuary																	
St.No	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
1	3.0	0.3	0.2	0.2	0.2	0.4	1.2	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.0	0.1
2	4.5	1.3	1.2	1.0	1.0	1.0	1.0	1.0	0.9	0.7	0.6	0.7	0.6	0.5	0.5	1.1	1.5
3	2.5	1.3	1.2	1.0	1.1	1.1	1.2	1.1	0.9	0.8	0.7	0.7	0.7	0.6	0.6	1.1	1.8
4	ND	1.2	1.1	1.0	1.0	1.1	1.1	1.1	0.9	0.8	0.7	0.8	0.7	0.6	0.6	0.9	1.5
5	1.5	0.4	0.3	0.3	0.3	0.5	1.1	0.4	0.4	0.3	0.3	0.3	0.3	0.2	0.3	0.2	0.2
6	ND	10.9	10.5	9.5	9.8	8.8	2.1	8.0	4.9	2.5	1.5	1.9	1.1	1.0	1.0	15.9	5.9
7	5.5	1.3	1.2	1.0	1.1	1.1	1.1	1.0	0.8	0.7	0.5	0.6	0.5	0.4	0.4	1.4	1.5
8	4.0	1.3	1.2	1.0	1.1	1.2	1.2	1.2	1.0	0.8	0.7	0.7	0.6	0.5	0.5	1.1	1.8
9	8.5	0.7	0.7	0.6	0.6	0.7	0.8	0.7	0.7	0.6	0.6	0.6	0.6	0.5	0.5	0.4	0.6

In addition, extreme enrichment was observed along the mid-depth stations (100m) of Alleppy transect for La and Ce during monsoon and for La during premonsoon. Also, LREEs observed severe enrichment along the nearshore stations along the Trivandrum transect during monsoon. The remaining stations in the southern zone observed moderate enrichment for almost all LREEs and MREEs during both seasons. The entire outer shelf observed moderate enrichment for all the MREEs and HREEs during both seasons. Th observed very high enrichment along the southern zone during both seasons. Similar to Th, U also observed southern enrichment, especially along the Kollam and Trivandrum transects. In Cochin estuary, moderate enrichment was observed for LREEs along the northern zone during both seasons; whereas it was observed extreme enrichment during monsoon and sever enrichment during premonsoon at station 6. Thus, station 6 showed maximum enrichment but, minimum enrichment was observed at station 1 for all REEs during both seasons. Similar to REEs, Th and U also showed the similar pattern of enrichment during both seasons.

6.2.3.2 Enrichment with respect to iron

The enrichment factor with respect to iron is less compared to aluminium along the shelf region during both seasons and the entire northern zone was found low enrichment during both seasons (Table 6.3a & Table 6.3b). The enrichment factor revealed that there was southern enrichment during both seasons. The order of enrichment was LREEs>MREEs>HREEs along the study region during both seasons. LREEs observed extreme and sever enrichment along the mid-depth stations of Kollam and Trivandrum during premonsoon. Apart from this, the coastal and mid-depth stations found moderate contamination for LREEs along the southern zone.

Table 6.3a. Enrichment factors (rare-earth elements) with respect iron along the study region during premonsoon.

Shelf																	
Transects	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
Manglore	20	0.4	0.4	0.4	0.4	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.3	0.6
	50	0.5	0.5	0.5	0.5	0.7	0.9	0.7	0.8	0.7	0.7	0.7	0.7	0.6	0.6	0.3	0.9
	100	0.3	0.3	0.3	0.3	0.4	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.2	0.5
	200	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.1	0.4
Kannoore	20	0.4	0.4	0.4	0.4	0.5	0.6	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.3	0.6
	50	0.5	0.5	0.4	0.4	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.3	0.8
	100	0.6	0.5	0.5	0.6	0.7	0.9	0.8	0.8	0.8	0.8	0.7	0.7	0.6	0.6	0.3	0.8
	200	0.4	0.3	0.3	0.4	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.2	0.5
Baypore	20	0.5	0.5	0.4	0.5	0.6	0.8	0.6	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.4	0.7
	50	0.5	0.5	0.4	0.5	0.6	0.8	0.6	0.6	0.6	0.5	0.5	0.5	0.4	0.4	0.3	0.6
	75	1.2	1.1	1.0	1.0	1.0	0.9	1.1	1.0	0.8	0.7	0.7	0.6	0.5	0.5	0.7	0.7
	100	0.5	0.5	0.5	0.5	0.6	0.7	0.6	0.6	0.6	0.5	0.5	0.5	0.4	0.4	0.3	0.6
	150	0.2	0.2	0.2	0.3	0.3	0.4	0.3	0.4	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.3
	200	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.3
Ponnani	20	0.5	0.5	0.4	0.5	0.5	0.7	0.6	0.6	0.6	0.5	0.5	0.6	0.5	0.5	0.3	0.5
	50	0.7	0.7	0.6	0.7	0.8	0.9	0.8	0.7	0.7	0.6	0.6	0.6	0.5	0.5	0.6	0.8
	100	0.5	0.5	0.5	0.6	0.7	0.9	0.7	0.8	0.7	0.6	0.6	0.6	0.5	0.5	0.2	0.8
	200	0.2	0.3	0.2	0.3	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.4
Cochin	20	4.4	3.6	2.7	2.4	1.8	1.3	1.9	1.2	0.8	0.6	0.7	0.6	0.4	0.4	3.9	1.0
	50	1.2	1.0	0.8	0.8	0.9	1.6	0.8	0.8	0.7	0.6	0.6	0.6	0.5	0.5	0.9	0.9
	75	7.5	5.8	4.5	4.2	2.7	1.4	2.9	1.7	1.0	0.6	0.8	0.5	0.4	0.4	7.4	0.8
	100	2.4	2.0	1.6	1.6	1.4	1.3	1.4	1.1	0.8	0.6	0.7	0.6	0.5	0.5	3.2	1.1
	150	0.2	0.3	0.2	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.3
	200	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.2
Alleppy	20	1.3	1.2	1.0	1.0	1.0	1.0	1.0	0.8	0.7	0.6	0.6	0.6	0.5	0.5	1.4	1.3
	50	1.5	1.3	1.0	0.9	0.8	0.9	0.9	0.7	0.6	0.5	0.5	0.5	0.4	0.4	2.0	1.3
	75	1.2	1.1	1.0	1.1	1.2	1.1	1.2	1.0	0.8	0.8	0.7	0.7	0.5	0.6	1.3	1.4
	100	2.9	2.3	1.9	1.8	1.4	1.1	1.5	1.2	0.9	0.8	0.9	0.8	0.7	0.6	2.8	1.9
	150	0.7	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.8	1.1
	200	0.5	0.4	0.4	0.5	0.5	0.7	0.6	0.6	0.6	0.5	0.5	0.5	0.4	0.4	0.4	1.2
Kollam	20	1.6	1.5	1.3	1.4	1.4	1.1	1.3	1.0	0.8	0.7	0.7	0.6	0.6	0.5	1.9	1.0
	50	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.3	0.2	0.4
	100	8.5	6.8	5.3	4.9	3.2	1.0	3.6	2.1	1.2	0.7	0.9	0.5	0.4	0.4	12.0	1.1
	200	0.7	0.6	0.6	0.6	0.8	1.0	0.8	0.9	0.9	0.9	0.8	0.9	0.7	0.8	0.5	2.0
Trivandrum	20	2.2	2.1	2.0	2.1	2.1	0.7	1.9	1.4	0.9	0.7	0.7	0.6	0.5	0.4	3.7	1.7
	50	6.8	6.7	6.2	6.5	5.5	1.2	4.8	2.8	1.4	0.8	1.1	0.5	0.5	0.5	13.6	3.0
	100	1.6	1.4	1.2	1.3	1.3	1.2	1.4	1.2	1.1	1.1	1.1	1.1	0.8	0.8	1.8	2.3
	200	0.3	0.2	0.2	0.3	0.4	0.5	0.4	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.3	1.7

Estuary																	
St.No	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
1	3.0	0.9	0.7	0.6	0.7	1.4	4.7	0.7	0.7	0.7	0.6	0.6	0.6	0.5	0.5	0.2	0.4
2	4.5	1.2	1.1	0.9	0.9	1.0	0.9	1.0	0.8	0.7	0.6	0.6	0.6	0.5	0.5	1.2	1.4
3	2.5	0.9	0.8	0.7	0.7	0.8	0.8	0.7	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.7	1.2
4	ND	1.1	1.0	0.9	0.9	1.0	1.0	1.0	0.8	0.7	0.7	0.7	0.7	0.6	0.6	0.8	1.4
5	1.5	1.4	1.2	0.9	1.0	1.1	2.5	1.0	0.8	0.7	0.6	0.7	0.7	0.5	0.5	0.6	0.6
6	ND	4.0	3.6	3.1	3.1	2.5	1.0	2.4	1.5	0.9	0.6	0.7	0.5	0.4	0.4	5.7	2.1
7	5.5	1.0	0.9	0.7	0.8	0.8	1.1	0.8	0.7	0.6	0.5	0.5	0.5	0.4	0.4	0.8	1.4
8	4.0	0.8	0.8	0.6	0.6	0.8	1.4	0.6	0.6	0.5	0.5	0.4	0.5	0.4	0.4	0.5	1.0
9	8.5	0.7	0.6	0.5	0.6	0.7	0.8	0.7	0.6	0.6	0.5	0.6	0.6	0.5	0.5	0.4	0.5

Table 6.3b. Enrichment factors (rare-earth elements) with respect iron along the study region during monsoon.

Shelf																	
Transects	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
Manglore	20	0.4	0.4	0.4	0.4	0.5	0.6	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.3	0.6
	50	0.7	0.7	0.7	0.8	1.1	1.2	1.1	1.2	1.0	1.0	1.0	0.8	0.7	0.7	0.4	0.9
	100	0.3	0.3	0.3	0.3	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.2	0.5
	200	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.1	0.3
Kannoore	20	0.4	0.5	0.4	0.4	0.5	0.7	0.5	0.6	0.5	0.5	0.5	0.5	0.5	0.5	0.3	0.5
	50	0.8	0.8	0.7	0.8	1.0	0.9	1.0	1.0	0.9	0.7	0.7	0.7	0.6	0.5	0.6	1.1
	100	0.6	0.6	0.6	0.6	0.8	1.0	0.8	0.9	0.8	0.8	0.8	0.7	0.6	0.6	0.4	0.9
	200	0.3	0.3	0.3	0.3	0.4	0.5	0.4	0.5	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.4
Baypore	20	0.4	0.4	0.4	0.4	0.5	0.7	0.5	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.3	0.4
	50	0.5	0.5	0.4	0.5	0.6	0.9	0.6	0.6	0.6	0.5	0.5	0.5	0.4	0.4	0.3	0.7
	75	0.5	0.5	0.4	0.5	0.6	0.8	0.6	0.6	0.6	0.6	0.6	0.6	0.5	0.5	0.3	0.9
	100	0.8	0.7	0.7	0.8	1.0	1.2	1.0	1.0	0.9	0.9	0.8	0.8	0.6	0.6	0.4	0.8
	150	0.4	0.4	0.4	0.5	0.7	0.8	0.7	0.7	0.7	0.7	0.6	0.6	0.5	0.5	0.2	0.7
	200	0.2	0.2	0.2	0.2	0.3	0.4	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.4
Ponnani	20	0.4	0.5	0.4	0.4	0.5	0.7	0.5	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.3	0.4
	50	0.6	0.6	0.6	0.6	0.7	0.8	0.7	0.7	0.6	0.6	0.6	0.5	0.4	0.4	0.5	0.6
	100	0.5	0.5	0.5	0.6	0.7	0.9	0.8	0.8	0.7	0.7	0.7	0.6	0.5	0.5	0.2	0.9
	200	0.3	0.3	0.3	0.3	0.4	0.6	0.5	0.5	0.5	0.5	0.4	0.4	0.3	0.3	0.1	0.5
Cochin	20	2.9	2.2	1.7	1.6	1.4	1.9	1.4	1.0	0.6	0.5	0.6	0.5	0.4	0.4	2.7	1.1
	50	2.2	1.9	1.6	1.6	1.5	1.6	1.5	1.1	0.8	0.6	0.6	0.5	0.4	0.4	2.4	0.9
	75	5.7	4.3	3.3	2.9	1.9	0.9	2.3	1.3	0.7	0.5	0.7	0.4	0.4	0.4	9.1	0.9
	100	2.4	2.0	1.6	1.5	1.3	1.4	1.4	1.0	0.8	0.7	0.7	0.6	0.5	0.5	2.4	1.1
	150	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2
	200	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.2
Alleppy	20	2.6	2.3	2.0	2.0	1.8	1.0	1.7	1.2	0.8	0.6	0.7	0.6	0.5	0.5	3.4	1.2
	50	2.1	1.7	1.3	1.2	0.9	0.8	1.0	0.8	0.5	0.4	0.5	0.4	0.3	0.3	2.6	0.8
	75	1.4	1.2	1.0	1.0	1.0	0.9	1.0	0.9	0.7	0.7	0.7	0.6	0.5	0.5	1.3	1.3
	100	2.2	1.9	1.6	1.6	1.6	1.0	1.6	1.3	0.9	0.8	0.9	0.8	0.7	0.7	2.2	2.6
	150	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.3	0.4	0.3	0.3	0.3	0.3	0.8
	200	0.3	0.3	0.3	0.3	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.2	0.7
Kollam	20	0.7	0.6	0.6	0.6	0.7	0.8	0.7	0.6	0.6	0.6	0.6	0.6	0.5	0.4	0.5	0.6
	50	1.1	1.0	0.9	0.9	0.9	1.1	0.8	0.7	0.6	0.5	0.5	0.5	0.4	0.4	1.3	1.1
	100	1.5	1.3	1.1	1.1	1.1	1.2	1.1	1.0	0.8	0.8	0.8	0.7	0.6	0.6	1.7	1.8
	200	0.6	0.5	0.5	0.6	0.7	0.9	0.7	0.8	0.8	0.8	0.8	0.7	0.7	0.6	0.4	2.1
Trivandrum	20	1.1	1.1	1.1	1.1	1.3	0.5	1.2	0.9	0.6	0.4	0.5	0.4	0.3	0.3	1.7	1.2
	50	4.9	4.7	4.3	4.3	4.1	1.1	3.6	2.2	1.1	0.7	0.8	0.5	0.5	0.4	7.4	3.2
	100	1.0	0.9	0.8	0.9	1.0	1.0	1.1	1.0	1.0	0.9	1.0	0.9	0.8	0.7	1.0	1.9
	200	0.2	0.2	0.2	0.2	0.3	0.4	0.3	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.3	0.8

Estuary																	
St.No	**Depth (m)**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Th**	**U**
1	3.0	4.1	3.2	2.9	3.3	6.2	17.9	4.1	3.8	3.6	3.3	3.1	3.4	2.6	2.6	0.6	2.1
2	4.5	5.2	4.8	4.1	4.2	4.2	4.1	4.3	3.5	2.9	2.6	2.8	2.6	2.1	2.2	4.6	6.1
3	2.5	3.7	3.4	2.9	3.0	3.2	3.3	3.1	2.6	2.1	1.9	2.0	2.0	1.6	1.7	3.2	5.0
4	ND	5.0	4.5	4.0	4.2	4.3	4.3	4.3	3.7	3.3	2.9	3.1	3.0	2.4	2.5	3.6	6.3
5	1.5	3.7	3.0	2.7	2.9	4.3	9.8	3.4	3.1	2.9	2.6	2.7	2.7	2.1	2.2	1.3	2.0
6	ND	27.5	26.6	24.1	24.8	22.3	5.4	20.3	12.5	6.4	3.8	4.9	2.9	2.5	2.5	40.3	14.9
7	5.5	5.4	5.2	4.4	4.5	4.5	4.8	4.4	3.4	2.7	2.3	2.4	2.1	1.8	1.8	6.0	6.3
8	4.0	4.6	4.5	3.8	4.1	4.4	4.3	4.4	3.7	2.9	2.5	2.5	2.4	1.9	1.9	4.0	6.6
9	8.5	2.9	2.8	2.4	2.6	2.9	3.5	3.0	2.9	2.7	2.6	2.5	2.5	2.0	2.1	1.8	2.4

The lighter MREEs observed moderate enrichment along the nearshore and mid-depth stations of southern zone during both seasons. However, HREEs observed low enrichment along the shelf during both seasons. Th and U were found a similar enrichment pattern as that of enrichment with respect to aluminum during both seasons. In estuary, the iron enrichment factor was found higher that that of enrichment with respect to aluminum; however, the pattern was similar to that of enrichment factor with respect to aluminum. The estuary observed a very high monsoonal enrichment compared to premonsoon. The entire estuary was enriched with all the REEs during monsoon; could be due to the inflow of water and sediment from rivers (Laluraj et al., 2008), which carrying the REEs to the estuary during monsoon. Th and U also were highly enriched along the entire estuary during monsoon. Station 6 was observed a very high enrichment for almost all the REEs including Th and U during both seasons which might be due to the sediment transport from Muvattupuzha River during monsoon (Laluraj et al., 2008). LREEs enrichment and steep HREEs patterns are attributed to felsic source characteristics (Nath et al., 2000). The U enrichment in sediments can be used as a tool for inferring suboxic to anoxic conditions (Wignall and Myers, 1988; Calvert and Pedersen, 1993).

6.2.4 Elemental excess

The elemental excess represents elements bound to detrital component compared to that element in the sediment. Element excess showed high values indicating sources other than REEs which are not PAAS like. The calculated elemental excess along the study region are given in table (Table 6.4a & Table 6.4b). Premonsoon showed high values of El_{ex} compared to monsoon.

Table 6.4a. Elemental excess (rare-earth elements) along the study region during premonsoon.

Shelf

Transects	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Manglore	20	-26.5	-53.1	-6.6	-23.9	-3.1	-0.4	-2.4	-0.4	-2.4	-0.5	-1.5	-0.2	-1.7	-0.3	-11.2	-1.2
	50	-0.3	-1.0	-0.1	0.6	0.5	0.2	0.4	0.1	0.5	0.1	0.3	0.0	0.1	0.0	-1.3	0.5
	100	1.8	4.0	0.4	3.4	1.3	0.4	1.3	0.2	1.5	0.3	0.8	0.1	0.5	0.1	-1.3	1.0
	200	-4.1	-7.1	-0.8	-1.5	0.4	0.2	0.4	0.1	0.5	0.1	0.3	0.0	0.0	0.0	-2.4	1.0
Kannoore	20	-27.3	-54.6	-6.8	-24.4	-3.2	-0.4	-2.6	-0.4	-2.7	-0.6	-1.6	-0.2	-1.8	-0.3	-12.7	-1.5
	50	-2.4	-4.6	-0.8	-2.5	-0.3	0.0	-0.1	0.0	-0.2	0.0	-0.1	0.0	-0.2	0.0	-1.6	0.3
	100	-0.8	-1.9	-0.4	0.0	0.6	0.3	0.6	0.1	0.6	0.1	0.3	0.0	0.1	0.0	-2.5	0.5
	200	0.1	0.1	-0.1	0.6	0.7	0.3	0.7	0.1	0.6	0.1	0.3	0.0	0.1	0.0	-1.8	0.5
Baypore	20	-19.2	-41.4	-5.2	-18.7	-2.5	-0.2	-2.0	-0.3	-2.3	-0.5	-1.4	-0.2	-1.6	-0.3	-9.6	-1.0
	50	-4.0	-8.9	-1.3	-4.3	-0.2	0.1	-0.1	0.0	-0.3	-0.1	-0.2	0.0	-0.4	-0.1	-3.6	-0.1
	75	11.8	20.9	1.8	7.4	1.2	0.2	1.1	0.1	0.5	0.1	0.2	0.0	-0.1	0.0	0.8	0.2
	100	4.9	10.9	0.9	5.1	1.3	0.4	1.2	0.2	0.9	0.1	0.4	0.0	0.1	0.0	-0.9	0.6
	150	3.5	10.2	0.8	5.0	1.5	0.4	1.3	0.3	1.4	0.2	0.7	0.1	0.3	0.1	-0.5	0.9
	200	-1.2	-1.8	-0.3	-0.3	0.2	0.1	0.2	0.1	0.3	0.0	0.1	0.0	0.0	0.0	-1.1	0.3
Ponnani	20	-24.7	-47.8	-6.5	-22.5	-3.0	-0.4	-2.4	-0.4	-2.3	-0.5	-1.6	-0.2	-1.8	-0.3	-12.2	-1.8
	50	4.1	8.7	0.5	3.1	0.9	0.2	0.7	0.1	0.5	0.0	0.2	0.0	-0.1	0.0	1.0	0.5
	100	9.2	22.3	2.1	10.6	2.4	0.6	2.1	0.4	2.0	0.4	1.0	0.1	0.6	0.1	0.0	1.7
	200	-1.2	-0.8	-0.5	0.1	0.6	0.3	0.6	0.1	0.6	0.1	0.1	0.0	-0.2	0.0	-1.9	0.9
Cochin	20	32.0	51.3	3.9	13.0	1.3	0.1	1.2	0.1	0.1	0.0	0.0	0.0	-0.2	0.0	10.5	0.2
	50	0.9	-2.1	-0.7	-2.4	-0.3	0.2	-0.3	-0.1	-0.6	-0.1	-0.4	-0.1	-0.5	-0.1	-0.8	-0.1
	75	198.1	308.9	25.7	93.1	8.7	0.7	8.3	0.7	1.6	0.1	0.6	0.0	-0.3	0.0	74.2	0.5
	100	42.8	67.8	5.2	18.9	2.6	0.4	2.1	0.2	0.2	-0.1	-0.2	0.0	-0.5	-0.1	25.1	0.7
	150	7.1	19.3	1.3	6.8	1.6	0.4	1.4	0.2	0.9	0.1	0.3	0.0	0.0	0.0	1.9	0.7
	200	4.0	14.1	0.7	4.3	1.1	0.3	1.0	0.2	0.6	0.1	0.2	0.0	-0.1	0.0	0.9	0.2
Alleppy	20	11.1	18.2	1.0	3.8	0.8	0.1	0.5	0.0	-0.5	-0.2	-0.4	-0.1	-0.6	-0.1	5.2	0.9
	50	17.4	25.9	1.7	6.1	0.7	0.2	0.7	0.1	0.1	0.0	0.0	0.0	-0.2	0.0	9.7	1.1
	75	11.9	20.2	1.7	7.6	1.6	0.3	1.3	0.2	0.6	0.1	0.2	0.0	-0.1	0.0	5.1	1.2
	100	37.2	60.8	5.0	18.4	2.2	0.3	2.0	0.2	1.0	0.1	0.5	0.1	0.3	0.0	13.9	1.8
	150	11.4	17.6	1.5	6.8	1.2	0.3	1.1	0.2	0.7	0.1	0.3	0.0	0.1	0.0	4.9	1.9
	200	4.0	4.7	0.3	2.4	0.7	0.3	0.7	0.1	0.7	0.1	0.4	0.1	0.1	0.0	0.5	2.0
Kollam	20	32.2	56.9	4.5	20.1	3.2	0.3	2.2	0.1	-0.5	-0.2	-0.6	-0.1	-1.1	-0.2	17.1	0.4
	50	0.6	3.0	0.1	1.9	1.0	0.3	1.0	0.2	1.0	0.2	0.4	0.1	0.2	0.0	-1.1	0.9
	100	247.8	410.1	34.8	123.9	12.5	0.6	12.2	1.1	3.1	0.3	1.3	0.1	0.2	0.0	135.5	1.9
	200	3.6	3.3	0.4	2.5	0.7	0.2	0.7	0.1	0.9	0.2	0.5	0.1	0.3	0.1	0.3	2.1
Trivandrum	20	30.7	63.2	6.3	26.1	4.4	0.2	3.3	0.4	1.3	0.2	0.5	0.0	0.3	0.0	21.4	1.9
	50	82.2	170.7	17.4	70.4	9.5	0.2	6.8	0.6	1.5	0.1	0.6	0.0	0.0	0.0	65.8	2.6
	100	14.4	24.2	2.2	8.8	1.5	0.3	1.4	0.2	1.0	0.2	0.6	0.1	0.3	0.0	6.7	1.9
	200	9.4	14.9	1.8	9.5	2.3	0.6	2.4	0.5	3.1	0.7	1.9	0.3	1.5	0.2	3.1	8.1

Estuary

St. No.	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
1	3.0	-24.6	-56.0	-6.4	-23.9	-3.0	0.3	-3.2	-0.5	-3.3	-0.7	-2.1	-0.3	-2.1	-0.3	-11.9	-2.4
2	4.5	27.3	41.3	0.9	6.1	1.3	0.1	0.9	-0.1	-2.1	-0.7	-1.7	-0.3	-2.6	-0.4	13.2	4.1
3	2.5	19.8	21.5	0.7	5.3	1.2	0.3	0.7	-0.1	-1.7	-0.5	-1.4	-0.2	-2.0	-0.3	-0.9	3.8
4	ND	22.1	24.4	0.1	4.3	1.2	0.2	1.0	-0.1	-1.6	-0.5	-1.3	-0.2	-2.1	-0.3	-1.6	3.8
5	1.5	-15.6	-44.3	-5.9	-22.4	-3.1	0.2	-3.1	-0.6	-3.7	-0.8	-2.3	-0.3	-2.5	-0.4	-12.6	-2.7
6	ND	51.4	94.8	8.6	33.2	4.2	0.2	3.3	0.3	0.6	0.0	0.2	0.0	-0.2	0.0	29.1	1.8
7	5.5	6.0	6.1	-0.6	-1.9	0.0	0.3	-0.1	-0.1	-1.0	-0.3	-0.8	-0.1	-1.0	-0.2	-0.1	1.6
8	4.0	-0.8	-2.2	-0.4	-1.6	-0.1	0.1	-0.2	0.0	-0.3	-0.1	-0.2	0.0	-0.2	0.0	-0.9	0.0
9	8.5	-16.7	-37.0	-5.6	-19.0	-2.4	-0.2	-1.9	-0.3	-2.5	-0.6	-1.7	-0.2	-2.2	-0.3	-12.8	-2.2

Table 6.4b. Elemental excess (rare-earth elements) along the study region during monsoon.

Shelf																	
Transects	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Manglore	20	-20.4	-40.7	-5.1	-18.6	-2.3	-0.3	-1.8	-0.3	-1.8	-0.4	-1.1	-0.2	-1.4	-0.2	-9.3	-0.9
	50	3.1	6.0	0.6	3.8	1.3	0.3	1.1	0.2	1.0	0.2	0.5	0.1	0.2	0.0	-0.5	0.4
	100	2.5	5.7	0.6	3.8	1.5	0.4	1.4	0.3	1.5	0.3	0.9	0.1	0.6	0.1	-0.6	1.0
	200	-1.7	-2.0	-0.3	0.3	0.6	0.2	0.6	0.1	0.7	0.1	0.3	0.0	0.1	0.0	-1.3	0.6
Kannoore	20	-25.1	-49.1	-6.3	-22.5	-2.9	-0.4	-2.3	-0.3	-2.2	-0.5	-1.4	-0.2	-1.7	-0.3	-11.8	-1.7
	50	0.4	1.0	0.0	0.9	0.5	0.1	0.4	0.1	0.2	0.0	0.0	0.0	-0.1	0.0	-0.4	0.3
	100	-0.6	-1.9	-0.3	0.3	0.8	0.3	0.7	0.1	0.7	0.1	0.3	0.0	0.0	0.0	-2.5	0.7
	200	-1.1	-1.0	-0.2	0.6	0.7	0.3	0.7	0.1	0.6	0.1	0.3	0.0	0.1	0.0	-1.7	0.6
Baypore	20	-27.2	-53.7	-6.8	-24.6	-3.3	-0.4	-2.6	-0.4	-2.7	-0.6	-1.6	-0.2	-2.0	-0.3	-13.1	-2.1
	50	-4.0	-9.0	-1.1	-3.9	-0.4	0.1	-0.3	0.0	-0.4	-0.1	-0.3	0.0	-0.4	-0.1	-2.5	-0.1
	75	-1.2	-3.1	-0.4	-1.3	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	-0.1	0.0	-1.5	0.3
	100	5.7	9.9	1.1	5.3	1.4	0.4	1.3	0.2	1.1	0.2	0.5	0.1	0.3	0.0	-0.3	0.5
	150	5.4	12.5	1.3	6.5	1.7	0.4	1.6	0.3	1.5	0.3	0.8	0.1	0.5	0.1	0.0	1.1
	200	-2.4	-3.4	-0.5	-0.9	0.4	0.2	0.4	0.1	0.3	0.1	0.1	0.0	-0.1	0.0	-2.1	0.8
Ponnani	20	-28.5	-56.0	-7.1	-25.4	-3.4	-0.4	-2.8	-0.4	-2.8	-0.6	-1.7	-0.3	-2.1	-0.3	-14.1	-2.3
	50	1.7	4.3	0.0	1.0	0.6	0.2	0.5	0.1	0.1	0.0	0.0	0.0	-0.3	-0.1	-1.0	0.0
	100	4.7	11.9	1.2	6.2	1.5	0.4	1.5	0.3	1.3	0.3	0.7	0.1	0.4	0.1	-0.4	1.3
	200	5.0	13.2	1.4	6.7	1.8	0.5	1.8	0.3	1.8	0.4	1.0	0.1	0.6	0.1	0.1	1.3
Cochin	20	11.7	15.4	0.9	2.6	0.3	0.1	0.2	0.0	-0.4	-0.1	-0.2	0.0	-0.3	0.0	3.9	0.0
	50	22.2	34.3	2.6	9.9	1.6	0.3	1.2	0.1	-0.2	-0.1	-0.3	-0.1	-0.6	-0.1	9.6	0.1
	75	149.8	233.2	19.0	63.1	6.1	0.4	6.5	0.5	1.2	0.1	0.6	0.0	0.0	0.0	94.8	1.2
	100	38.4	59.3	4.4	14.8	1.9	0.4	1.7	0.1	-0.1	-0.1	-0.2	-0.1	-0.5	-0.1	14.9	0.6
	150	0.0	7.4	0.1	2.4	1.0	0.3	0.9	0.1	0.4	0.0	0.1	0.0	-0.3	-0.1	-0.9	0.2
	200	-2.0	1.9	-0.3	0.1	0.5	0.2	0.5	0.1	0.2	0.0	-0.1	0.0	-0.4	-0.1	-1.2	0.0
Alleppy	20	52.6	94.7	8.5	32.7	4.5	0.2	3.5	0.3	0.0	-0.1	-0.1	-0.1	-0.7	-0.1	29.4	0.9
	50	27.8	42.7	3.2	10.5	1.0	0.1	1.0	0.1	-0.1	-0.1	-0.1	0.0	-0.3	0.0	14.1	0.3
	75	16.5	26.4	2.1	7.4	1.2	0.2	1.1	0.1	0.4	0.1	0.2	0.0	-0.1	0.0	5.6	1.1
	100	29.8	51.5	4.7	18.0	2.9	0.3	2.6	0.3	1.2	0.2	0.7	0.1	0.5	0.1	11.7	2.9
	150	3.3	5.5	0.4	2.4	0.7	0.2	0.7	0.1	0.6	0.1	0.4	0.0	0.1	0.0	0.6	1.7
	200	0.0	-1.1	-0.1	0.6	0.6	0.2	0.6	0.1	0.4	0.1	0.2	0.0	0.0	0.0	-0.9	1.6
Kollam	20	-10.1	-22.8	-3.5	-11.9	-1.2	0.0	-1.0	-0.2	-1.6	-0.4	-1.1	-0.2	-1.5	-0.3	-7.8	-1.3
	50	3.7	5.5	0.4	1.2	0.3	0.1	0.1	0.0	-0.2	-0.1	-0.1	0.0	-0.2	0.0	2.1	0.2
	100	14.2	22.5	1.9	6.9	1.2	0.3	1.0	0.1	0.4	0.1	0.2	0.0	0.0	0.0	6.5	1.5
	200	2.3	1.3	0.3	1.9	0.6	0.2	0.6	0.1	0.7	0.1	0.4	0.1	0.3	0.0	-0.3	2.4
Trivandrum	20	15.2	33.4	3.6	14.6	2.8	0.2	2.1	0.3	0.9	0.1	0.3	0.0	0.1	0.0	10.0	1.4
	50	56.7	111.5	11.1	43.3	6.6	0.2	4.8	0.4	0.9	0.0	0.3	0.0	-0.1	0.0	34.0	2.7
	100	6.9	13.7	1.3	5.6	1.1	0.2	1.0	0.1	0.8	0.2	0.5	0.1	0.3	0.1	3.0	1.4
	200	3.1	4.8	0.6	3.2	0.9	0.2	1.0	0.2	1.1	0.2	0.7	0.1	0.4	0.1	1.9	2.3

Estuary																	
St.No.	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
1	12	-25.7	-57.9	-6.6	-24.4	-3.0	0.2	-3.1	-0.5	-3.3	-0.7	-2.1	-0.3	-2.2	-0.3	-13.0	-2.5
2	4.5	22.8	31.9	0.0	1.8	0.5	0.0	0.5	-0.2	-2.8	-0.8	-1.9	-0.3	-2.9	-0.4	4.0	3.5
3	2.5	17.7	24.3	0.3	2.9	1.1	0.3	0.6	-0.1	-1.7	-0.5	-1.2	-0.2	-1.7	-0.3	2.6	3.5
4	1	18.1	18.7	-0.3	2.4	0.6	0.1	0.6	-0.1	-1.8	-0.6	-1.4	-0.2	-2.3	-0.3	-3.1	3.4
5	3	-25.1	-59.1	-6.9	-25.7	-3.2	0.1	-3.2	-0.6	-3.6	-0.8	-2.2	-0.3	-2.4	-0.4	-14.1	-2.7
6	2.5	81.1	162.9	16.2	64.2	9.3	0.3	7.0	0.7	1.5	0.1	0.6	0.0	0.0	0.0	46.9	3.3
7	5.5	9.3	15.4	0.3	1.8	0.4	0.1	0.2	-0.1	-1.3	-0.4	-1.0	-0.2	-1.3	-0.2	5.1	1.3
8	13	7.9	15.2	0.3	3.3	0.9	0.1	0.7	0.0	-0.8	-0.3	-0.8	-0.1	-1.1	-0.2	0.9	2.0
9	8.5	-22.1	-47.2	-6.9	-23.9	-3.1	-0.3	-2.3	-0.4	-3.0	-0.7	-2.1	-0.3	-2.6	-0.4	-15.1	-2.4

The southern zone showed high values for El_{ex} compared to the northern zone during both seasons. Similar to enrichment and normalisation factors, the El_{ex} follows the order of LREEs>MREEs>HREEs during both seasons. However, most of the HREEs, El_{ex} was very low or negative during both seasons. The maximum El_{ex} for LREEs, MREEs and Th was observed along the Kollam transect during premonsoon. Th and U observed a very high El_{ex} along the southern zone. The mid-depth stations showed high El_{ex} for almost all the REEs including Th and U compared to other depths during both seasons. In Cochin estuary, high El_{ex} was observed for LREEs along the northern zone and station 6 during both seasons. However, MREEs and HREEs were very low or negative along the estuary during both seasons.

The samples beneath the oxygen minimum zone showed high values compared to the coastal samples, which are consistent with the observation of Nath et al. (1997). He found high content of U_{ex} (82-91%) for the samples falling in OMZ. Uranium is mobilized as U^{+6} under oxic conditions and precipitated as U^{+4} in reducing environments, whereas Th is relatively immobile in aqueous solution (Anderson et al., 1983; Wright et al., 1984; Jernstrüom et al., 2001). Yang et al. (1995) have suggested that an increase in productivity-driven carbon flux raises the redox boundary closer to the sediment–water interface leading to an increased flux of U into the subsurface anoxic sediments. High U concentrations in these suboxic sediments are consistent with the estimate of Klinkhammer and Palmer (1991) that 75% of U supplied to the oceans has been removed by diffusion onto suboxic sediments (Nath et.al, 1997). The reason for the excess values especially for the southern transects (Trivandrum, Kollam and Kochi) would be the presence of heavy minerals, which are dominantly present in these areas (Stefan et al., 2008).

6.2.5 Ce and Eu anomaly

The seasonal anomalies in Ce and Eu are presented in Table 6.5. Cerium anomalies showed no temporal variations among the seasons, while Eu showed minor anomalies. The entire shelf had Ce anomalies >1, except at 200 m along the Kollam and Trivandrum transects. Eu anomalies showed low values along the southern zone compared to the northern zone during both seasons. Along the 20 and 100 m, the values of Eu anomalies were low (<1) along the southern zone during both seasons (except Kochi and Kollam during monsoon). These sediments are characterized by gneissic provenance (Rao and Rao, 1995). One of the reasons for Th high Eu anomaly may be attributed to the heavy minerals present in these sediments. In Cochin estuary, Ce and Eu anomalies showed high values (>1) for almost all stations during both seasons (except station 1 for Ce and station 6 for Eu). There was no seasonal variation on anomalies. Ce anomaly helps to focus on the redox-controlled reactions of Ce by comparing its concentration with neighbors which are stable towards redox reactions (Pattan et al., 2005). Ce anomalies along the coastal stations are close to unity suggesting the influence of terrigenous inputs. As the sedimentation in these areas is influenced by coastal inputs and along shore currents, no relation was observed between dissolved oxygen levels and Ce anomalies (Table 6.5). Negative Ce anomaly is characteristic of seawater and positive Ce anomaly is associated with manganese nodules (Hole et al., 1984). Liu et.al (1988), Wang et.al (1986) and Ahmed Saif (2008) have suggested that Ce anomaly in ancient sedimentary sequences can be used as a paleo-redox proxy. But many factors control the Ce distribution 1) depositional environment (Murray et al., 1990) 2) source areas (Murray et al., 1991) 3) redox conditions in sediments (Murray et al., 1992) 4) lithological and diagenetic controls (Nath et al., 1992) and 5) carbonate content (Nath et al., 1992).

Table 6.5. Cerium anomaly, europium anomaly and authigenic uranium in sediments along the study region.

Shelf									
Station		Monsoon				Premonsoon			
Transects	Depth (m)	Ce ano.	Eu ano.	DO (ml/l)	Authigenic U	Ce ano.	Eu ano.	DO (ml/l)	Authigenic U
Manglore	20	1.1	1.2	1.76	1.0	1.1	1.2	3.709	0.3
	50	1.0	1.1	2.35	0.9	1.0	1.2	3.433	0.6
	100	1.0	1.2	0.30	1.0	1.0	1.2	0.562	0.9
	200	1.0	1.2	0.28	1.1	1.0	1.3	0.226	1.2
Kannoore	20	1.1	1.2	1.37	1.0	1.1	1.2	3.868	0.3
	50	1.0	0.9	0.52	0.8	1.1	1.2	2.124	0.4
	100	1.0	1.2	0.26	1.0	1.0	1.2	0.751	0.6
	200	1.0	1.2	0.29	1.1	1.0	1.2	0.269	0.4
Baypore	20	1.1	1.3	2.54	1.0	1.0	1.4	3.281	0.2
	50	1.0	1.6	0.42	1.5	1.0	1.4	3.188	0.3
	75	1.0	1.3	0.40	1.2	1.0	0.9	1.523	0.0
	100	1.0	1.2	0.39	1.0	1.1	1.2	0.66	0.4
	150	1.0	1.2	0.28	1.1	1.1	1.2	0.277	0.5
	200	1.1	1.2	0.23	1.0	1.1	1.2	0.317	0.3
Ponnani	20	1.1	1.2	1.38	1.0	1.1	1.2	2.925	
	50	1.1	1.2	0.56	1.0	1.1	1.1	3.52	
	100	1.1	1.2	0.31	1.1	1.1	1.2	0.708	1.3
	200	1.1	1.2	0.30	1.1	1.1	1.2	0.343	0.7
Cochin	20	1.0	1.4	0.25	1.3	1.0	0.7	3.246	
	50	1.0	1.0	0.73	0.8	1.0	1.8	2.701	
	75	1.0	0.4	0.40		1.0	0.5	1.607	
	100	1.0	1.0	0.46	0.7	1.0	0.9	0.401	
	150	1.2	1.1	0.31	0.9	1.1	1.1	0.478	
	200	1.2	1.2	0.27	1.0	1.2	1.2	0.401	
Alleppy	20	1.0	0.5	1.29	0.1	1.0	1.0	2.427	
	50	1.0	0.8	0.52	0.7	1.0	1.0	2.132	
	75	1.0	0.9	0.59	0.7	1.0	0.9	0.968	
	100	1.0	0.6	0.38	0.4	1.0	0.8	0.722	
	150	1.0	1.1	0.27	1.0	1.0	1.0	0.512	
	200	1.0	1.2	0.26	1.1	1.0	1.2	0.405	1.3
Kollam	20	1.0	1.2	0.54	0.8	1.0	0.8	2.276	
	50	1.0	1.3	0.42	1.2	1.1	1.2	2.179	0.6
	100	1.0	1.1	0.38	0.9	1.0	0.3	0.606	
	200	0.9	1.2	0.30	1.1	0.9	1.2	0.385	1.6
Trivandrum	20	1.0	0.4	0.82	0.2	1.0	0.4	2.448	
	50	1.0	0.3	0.68		1.0	0.2	2.164	
	100	1.0	1.0	0.71	0.9	1.0	0.9	1.103	
	200	0.9	1.1	0.29	0.9	0.9	1.1	0.466	6.6

Estuary									
Station		Monsoon				Premonsoon			
St.No.	Depth	Ce ano.	Eu ano.	D.O (ml/l)	Authigenic U	Ce ano.	Eu ano.	D.O (ml/l)	Authigenic U
1	3.0	0.9	4.5	4.49	0.2	0.9	4.5	3.10	0.0
2	4.5	1.0	1.0	5.03		1.0	1.0	3.20	
3	2.5	1.0	1.0	4.38	0.0	1.0	1.0	5.06	1.1
4	ND	1.0	1.0	5.05	0.9	1.0	1.0	3.31	0.7
5	1.5	1.0	2.4	4.81	0.0	1.0	2.4	2.95	
6	ND	1.0	0.4	5.23		1.0	0.4	6.03	
7	5.5	1.0	1.4	4.72		1.0	1.4	4.60	0.3
8	4.0	1.1	2.0	4.56	0.2	1.1	2.0	5.89	0.1
9	8.5	1.1	1.2	5.16		1.1	1.2	5.08	

However, Nath et al. (1997) observed REEs along the Arabian Sea sediments beneath the intense OMZ (<0.2ml/l) and away from the OMZ (1-2 ml/l) with no dramatic variations in Ce anomalies. However, the present observation, the Ce anomaly at certain locations along the shelf was not responded to redox conditions of the overlying water column. This could be due to the high sedimentation and dynamic nature of shelf. Eu anomalies are observed in waters affected by eolian input (Elderfield, 1988) or in hydrothermal solutions and the sediments resulting from high T-basalt alteration along the mid-ocean ridges and back-arc spreading centers (Michard et al., 1983; Nath et al., 1997). The present samples are not affected by these potential inputs, and so terrestrial influence may be the reason for positive Eu anomaly.

6.2.6 Authigenic uranium

The calculated authigenic U in the study region is presented in Table 6.5. Along the shelf, Trivandrum transect showed greater than 2 during premonsoon. Authigenic uranium (at 2 ppm), a parameter based on U and Th concentrations has been suggested as an index of anoxia and ancient sedimentary sequences (Nath et al, 1997; Wignall and Myers, 1988). Moderate to high concentrations of authigenic uranium in margin sediments makes this basin one of the potential sites for removal of U from seawater (Borole et al., 1982; Nath et al., 1997; Pailler et al., 2002). Based on the study of uranium distribution in a sediment core in the southeastern Arabian Sea, Sarkar et al. (1993) had inferred that anoxic conditions prevailed in this region during the last glacial period. From the elevated concentrations of authigenic uranium in sediments from various regions of the Arabian Sea, Borole et al. (1982), Sarkar et al. (1993), and Balakrishna et al. (2001) reported that this oceanic region is a sink for seawater uranium. However, Cerium enrichment was observed along the oxygen poor stations and the Ce anomalies clearly indicate the relation to low oxygen values. Redox reactions lead to the preferential removal of Ce under oxidizing conditions and its preferential enrichment under reducing conditions (De Baar et al., 1988; Pattan et al., 2005). Hence, the distribution of Ce can be compared with that of other lanthanides to distinguish redox from other transport processes (Moffett, 1994; Pattan et al., 2005). Ce anomalies are well known in the marine environment. Negative Ce anomaly is characteristic of seawater and positive Ce anomaly is associated with manganese nodules (Elderfield, 1988; Piepgras and Jacobsen, 1992; Pattan et al., 2005). Nath et al. (1994) reported that oceanic waters resulting from the oxidation-reduction reactions are associated with Ce depletion. Variations in Ce fractionation have been found across the redox boundaries in Cariaco Trench (De Baar et al., 1988), oxygen deficient Chesapeake bay (Sholkovitz et al., 1992) and the OMZ of northwestern Indian Ocean (German et al., 1990). How much of this is reflected in the sediments impinged by low oxygenated waters is not known. Liu et al. (1988), Pattan et al. (2005) and others have suggested that Ce anomaly in ancient sedimentary sequences can be used as a paleo-redox-proxy.

Uranium and Th are geochemically coherent due to the similarities in oxidation states and ionic radius (Huglund, 1972; Chabaux et al., 2003). The present study observed slight higher values at the outer shelf stations than previous depth station, where low oxygen was observed. The distributions of certain minor and trace elements in marine sediments provide evidence for determining the redox conditions during deposition (Calvert and Pedersen, 1993). The stable form of U in oxygenated waters is U^{+6}. Carbonate ions complex with dissolved U in seawater produce

$[UO_2(CO_3)_3]^{4-}$, which dominates in most natural waters (Barnes and Cochran, 1990). Klinkhammer and Palmer (1991) and James et al. (2006) reported that in anoxic basins, organic-rich shelves and hemipelagic sediments are sites for authigenic U deposition. Uranium behaves as a nearly conservative element in oxygenated seawater, but is precipitated under reducing conditions in sediments underlain by oxygen deficient waters or receiving high fluxes of particulate organic carbon (Zheng et al., 2002). The Arabian Sea, because of its characteristic chemical and biological properties, is an interesting basin to study the geochemical behavior of uranium. Oceanic waters contain a relatively uniform amount of saturated U, but in continental waters, it shows wide ranges due to the nature of the rocks forming the drainage basin. The important minerals of U are: uranite (UO_2), pitchblende (variety of UO_2), uranothorite [(Th,U) SiO_4] etc., (Huglund, 1972). Thorium was found richly deposited in sand along the Kerala coast, especially southern zone as monazite sand. U/Th ratio is used as a redox indicator by many geochemists (Wright et al., 1984; Jones and Manning, 1994; Stefan et al., 2008). Since Th is immobile at low temperature, the ratio is sensitive to changes in U supplied from seawater. In turn, U variation depends on the redox state of seawater with low valency U under reducing conditions. Hence, both oxygen concentration and temperature played a major role in the observed distribution of U and Th along the shelf region. Low values were probably because of the dilution effects of calcium carbonate, supported by the negative correlation between $CaCO_3$ and elements.

Estuaries are biogeochemical reactors modifying the composition of REEs delivered by rivers to the ocean. The important processes in estuaries are: coagulation of river-borne colloids, adsorption/desorption/remobilization of river particles and bottom sediments, diagenesis of sediments. The significant one is the removal of dissolved REEs and yttrium in the estuary. On a global scale, riverine shale-normalised REEs patterns are diverse and display different types of (light, middle, or heavy REEs) enrichments (LREEs, MREEs, and HREEs) covering three orders of magnitude (Elderfield and Greaves, 1982; Sholkovitz, 1992; Michael and Kamber, 2006.). Despite particle reactivity and short residence time (Tachikawa et al., 2003), REEs have remained robust over geological periods. Considering the short oceanic residence times, the resilience of the marine REEs patterns are quite remarkable, implying that fundamental processes (salt-induced coagulation) are responsible for their distribution.

The chemical properties of sediments can be influenced by physicochemical conditions in estuaries. Salinity is the most variable parameter in the estuary and is significantly influenced by freshwater discharges from rivers and tidal action from the sea (Kurup, 1982; Martin et al., 2008). During the premonsoon period, the entire estuary was saline (5 PSU to 25 PSU), which changed to freshwater during monsoon (Figure 3.2 c). Salinity has a profound influence on the chemistry of dissolved, colloidal and suspended materials in coastal and estuarine zone (Sholkovitz, 1993; Balachandran et al., 2005). Extensive removal of dissolved REEs in low salinity region is a key feature common to all previous studies (Martin et al., 1976; Elderfield et al., 1990; Sholkovitz et al., 1993; Michael and Kamber, 2006). Salt induced coagulation of river colloids has been established as a mechanism responsible for removal of dissolved REEs (Sholkovitz, 1976; Sholkovitz and Elderfield, 1988; Sholkovitz et al., 1992; Michael and Kamber, 2006). In addition to removal, extensive fractionation among the REEs was also noticed with changing salinity. In most of the estuaries, salt induced coagulation led to fractionation in the order, LREEs >

MREEs > HREEs (Sholkovitz and Elderfield, 1988; Sholkovitz et al., 1992; Zhong and Liu, 2008). The present study also followed the same order on distribution of REEs as LREEs > MREEs > HREEs during both seasons. In addition, estuarine reactions reduce the effective fluxes of dissolved REEs to the ocean from rivers and modify the relative REEs abundance of dissolved pool through the estuary to the ocean (Sholkivitz, 1993; Zhong and Liu, 2008).

REEs are found to be mobile during weathering and diagenetic process and fractionation takes place (Nesbitt, 1979; Awwiller, 1994; Johan et al., 2000). The large scale removal of the dissolved REEs pool from the estuaries could be a net gain for the particulate or bedload clays. It is therefore necessary to distinguish the REEs distribution and fractionation derived from the source rock and that which results from estuarine mixing or weathering. During monsoon, the salinity is mostly zero in estuarine zone, and the REEs removal process may not be active and leading, contribution from dissolved phase is zero, especially HREEs. In addition, removal of LREEs from dissolved phases is usually linked to REEs complexation. Complexation as $Ln(CO_3)^{2-}$ (carbonates of lanthanides or REEs) produce strong enrichment of HREEs over LREEs and relative affinity of REEs (III) for binding to surface decrease from La to Lu (Turner et al., 1981; Byrne and Kim, 1990; Luke et al., 2004). This suggested that the REEs signature is derived mainly from the source/detrital components in estuary.

The estuarine sediments have much lower Th/U ratios, probably because of enrichment of U released during redox processes and their subsequent adsorption onto organic matter (Ben Othman et al., 1989; Vroon et al., 1995; Chabaux et al., 2003). The sediments from estuary have high organic matter content as cited with finer-grained sediments and many samples when collected revealed a hydrogen peroxide smell (Table 6.6).

Table 6.6. Pearson correlation for rare-earth elements with biogeochemical parameters along the estuarine sediments (metals are in ppm).

Premonsoon																									
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	Al (%)	Fe(%)	Silt %	Clay %	Sand %	D.O(ml/l)	Sal	Org.C (%)	$CaCO_3$ (%)
La	1																								
Ce	1.00	1																							
Pr	1.00	1.00	1																						
Nd	1.00	1.00	1.00	1																					
Sm	0.98	0.98	0.99	0.99	1																				
Eu	0.76	0.76	0.76	0.78	0.85	1																			
Gd	0.98	0.98	0.99	0.99	1.00	0.83	1																		
Tb	0.95	0.96	0.96	0.97	0.99	0.87	0.99	1																	
Dy	0.92	0.92	0.93	0.94	0.97	0.90	0.98	1.00	1																
Ho	0.89	0.90	0.91	0.92	0.96	0.91	0.96	0.99	1.00	1															
Er	0.91	0.91	0.92	0.93	0.96	0.90	0.97	0.99	1.00	1.00	1														
Tm	0.88	0.89	0.89	0.91	0.95	0.91	0.95	0.98	1.00	1.00	1.00	1													
Yb	0.88	0.89	0.89	0.91	0.95	0.91	0.96	0.98	1.00	1.00	1.00	1.00	1												
Lu	0.88	0.89	0.90	0.91	0.95	0.91	0.96	0.98	1.00	1.00	1.00	1.00	1.00	1											
Th	0.92	0.92	0.91	0.90	0.84	0.50	0.84	0.78	0.72	0.67	0.69	0.66	0.66	0.66	1										
U	0.95	0.95	0.95	0.95	0.97	0.82	0.96	0.96	0.94	0.93	0.93	0.92	0.92	0.92	0.80	1									
Al (%)	0.75	0.75	0.75	0.77	0.84	0.98	0.84	0.88	0.91	0.93	0.92	0.93	0.93	0.93	0.48	0.79	1								
Fe(%)	0.87	0.88	0.89	0.90	0.94	0.88	0.94	0.97	0.98	0.97	0.98	0.97	0.98	0.98	0.65	0.92	0.90	1							
Silt %	0.22	0.19	0.23	0.24	0.30	0.43	0.26	0.27	0.30	0.32	0.31	0.32	0.32	0.33	0.00	0.33	0.34	0.29	1						
Clay %	0.34	0.34	0.33	0.31	0.20	-0.17	0.20	0.09	0.01	-0.03	-0.01	-0.05	-0.06	-0.05	0.61	0.10	-0.19	-0.11	-0.03	1					
Sand %	-0.41	-0.39	-0.40	-0.39	-0.32	-0.05	-0.30	-0.21	-0.15	-0.12	-0.13	-0.10	-0.10	-0.11	-0.55	-0.25	0.01	-0.04	-0.45	-0.88	1				
D.O(ml/l)	-0.19	-0.18	-0.17	-0.17	-0.26	-0.64	-0.23	-0.27	-0.29	-0.32	-0.31	-0.32	-0.32	-0.32	-0.03	-0.25	-0.58	-0.21	-0.32	0.18	0.00	1			
Sal	-0.54	-0.57	-0.57	-0.58	-0.58	-0.34	-0.60	-0.62	-0.62	-0.60	-0.60	-0.60	-0.60	-0.60	-0.50	-0.64	-0.39	-0.70	0.12	0.16	-0.20	-0.38	1		
Org.C (%)	0.45	0.43	0.46	0.45	0.41	0.17	0.38	0.30	0.26	0.23	0.24	0.22	0.22	0.23	0.49	0.40	0.09	0.23	0.67	0.60	-0.86	0.09	-0.05	1	
$CaCO_3$(%)	-0.45	-0.42	-0.43	-0.43	-0.46	-0.56	-0.41	-0.38	-0.36	-0.36	-0.36	-0.35	-0.35	-0.35	-0.37	-0.56	-0.41	-0.32	-0.60	-0.11	0.38	0.64	-0.07	-0.54	1

Monsoon																									
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	Al (%)	Fe(%)	Silt %	Clay %	Sand %	D.O(ml/l)	Sal	Org.C(%)	$CaCO_3$ (%)
La	1																								
Ce	1.00	1																							
Pr	1.00	1.00	1																						
Nd	1.00	1.00	1.00	1																					
Sm	1.00	0.99	0.99	0.99	1																				
Eu	0.47	0.43	0.39	0.40	0.51	1																			
Gd	0.98	0.98	0.97	0.98	0.99	0.56	1																		
Tb	0.91	0.91	0.89	0.90	0.94	0.72	0.97	1																	
Dy	0.79	0.77	0.74	0.76	0.83	0.85	0.87	0.97	1																
Ho	0.71	0.69	0.66	0.67	0.75	0.89	0.81	0.93	0.99	1															
Er	0.76	0.74	0.72	0.73	0.80	0.88	0.85	0.95	1.00	1.00	1														
Tm	0.68	0.66	0.63	0.64	0.73	0.91	0.78	0.91	0.99	1.00	0.99	1													
Yb	0.69	0.67	0.64	0.65	0.74	0.91	0.80	0.92	0.99	1.00	0.99	1.00	1												
Lu	0.69	0.67	0.64	0.66	0.74	0.91	0.80	0.92	0.99	1.00	0.99	1.00	1.00	1											
Th	0.89	0.90	0.92	0.91	0.85	0.02	0.81	0.64	0.42	0.31	0.38	0.27	0.29	0.29	1										
U	0.88	0.86	0.84	0.84	0.88	0.71	0.91	0.93	0.89	0.85	0.88	0.84	0.85	0.86	0.60	1									
Al (%)	0.41	0.38	0.34	0.35	0.46	0.97	0.53	0.71	0.85	0.90	0.88	0.92	0.91	0.92	-0.04	0.64	1								
Fe(%)	0.65	0.63	0.60	0.61	0.69	0.87	0.75	0.87	0.94	0.96	0.95	0.97	0.97	0.97	0.27	0.85	0.87	1							
Silt %	0.85	0.83	0.84	0.85	0.84	0.42	0.82	0.75	0.64	0.56	0.62	0.53	0.54	0.55	0.74	0.70	0.35	0.38	1						
Clay %	0.74	0.76	0.77	0.78	0.77	0.26	0.76	0.72	0.60	0.55	0.58	0.51	0.52	0.52	0.70	0.44	0.32	0.46	0.61	1					
Sand %	-0.86	-0.87	-0.88	-0.89	-0.88	-0.36	-0.87	-0.80	-0.68	-0.61	-0.65	-0.58	-0.58	-0.59	-0.79	-0.59	-0.37	-0.47	-0.83	-0.95	1				
D.O(ml/l)	0.52	0.54	0.56	0.56	0.53	0.09	0.53	0.48	0.39	0.34	0.36	0.29	0.30	0.30	0.54	0.18	0.19	0.14	0.62	0.81	-0.82	1			
Sal	-0.53	-0.55	-0.54	-0.54	-0.53	-0.17	-0.55	-0.54	-0.48	-0.44	-0.46	-0.42	-0.43	-0.43	-0.46	-0.49	-0.21	-0.47	-0.26	-0.41	0.40	-0.40	1		
Org.C (%)	0.79	0.80	0.79	0.80	0.84	0.60	0.86	0.89	0.85	0.83	0.84	0.80	0.80	0.80	0.59	0.67	0.66	0.75	0.65	0.91	-0.90	0.68	-0.40	1	
$CaCO_3$(%)	-0.23	-0.17	-0.16	-0.16	-0.20	-0.47	-0.17	-0.16	-0.18	-0.17	-0.21	-0.21	-0.21	-0.22	-0.06	-0.40	-0.28	-0.18	-0.39	0.26	-0.02	0.33	-0.28	0.09	1

Both of these characters are indicators of lower redox conditions in the sediments and might control the uranium distribution and U/Th ratios in present study.

The high values of normalisation, enrichment factor and elemental excess for REEs, U and Th observed along the southern shelf reflect their high deposition. The southwest coast of India is rich in placer deposits of economic importance (Stefan et al., 2008). The heavy minerals occur as assemblages of ilmenite, rutile, leucoxene, monazite, zircon and sillimanite in layers and patches along the beaches (Rao and Wagle, 1997). These minerals are of the world class found between Neendakara and Kayamkulam and, are commonly known as *Chavara deposit.* It covers a total area of 22 x 8 km^2 in the northern side and 22 x 6 km^2 in the southern side. The Chavara deposits are estimated to contain 127 million tonnes of heavy minerals (lmenite 80 million tonnestones). Between Kayamkulam and Thottappally, heavy minerals estimated to the order of 17 million tonnes with ilmenite content of 9 million tonnes from the raw sand of 242 million tonnes. Highest concentration of radioactive heavy minerals occurs in the beaches of south Kerala (Chavara- Manavalakurichi). This could be the reason for high REEs deposition along the southern zone, especially along the Kollam and Trivandrum transects. However, the monsoonal accumulation of all REEs, Th and U in the estuary could be due to the river inputs.

The concentrations of REEs reported from some of the coastal and estuarine region are furnished in Table 6.7. A comparison of these values with the average values for Kerala shelf region revealed that the sediments of shelf do not indicate any sign of pollution. However, the high values for LREEs along the estuarine sediments hints towards enrichment by fractional deposition and weathering process.

Table 6.7. Comparison of rare-earth elemental levels in the study region to that of other Indian and globally impacted coastal systems [mg/kg dry weight (ppm)].

Region	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	References
Andaman Backarc basin	33.6	67.8	7.2	29.7	6.4	1.54	5.17	0.92	5.35	1.11	3.29	0.48	2.84	0.44			Kurian et al., 2008
Irrawaddy shelf	44.7	89.1	9.5	39.5	8.01	1.8	6.39	1.11	6.18	1.22	3.53	0.51	3.1	0.46			Kurian et al., 2008
Mae Klong estuary, Thailand	34.1	38.9	3.6	15.7	3.38	0.64	2.85	0.5	2.88	0.57	1.49	0.25	1.46	0.22			Censi et al., 2007
Marabasco Estuary, Mexico	32.1	60.8	6.98	26.3	6.59	1.59	7.3	1.08	6.1	1.32	3.6	0.51	2.72	0.43			Marmolejo et al., 2007
Bohai Bay, China	32.3	71.1	7.38	27.5	5.39	1.21	5.32	0.68	3.5	0.69	1.88	0.29	1.79	0.268	10.9	1.67	Zhang et al., 2002b
Pearl River, China	58.9	114	13.2	50.1	9.38	1.7	8.95	1.19	5.99	1.19	3.25	0.50	2.66	0.47	25.7	6.33	Zhang and Wang, 2001
Odiel Estuary, Spain	18.92	45.79	5.46	20.84	4.59	0.99	4.24	0.59	3.09	0.57	1.53		1.25	0.17	4.63		Borrego et al., 2004
Florida Bay, Gulf of Mexico	17.8	33.4	4.5	17.8	3.2	0.86	3.2	0.52	3.1	0.7	2	0.26	1.6	0.19			Caccia and Millero, 2007
Shelf of Kerala	30.2	56.9	5.4	21.4	3.5	0.66	3.1	0.95	2.5	0.43	1.3	0.17	0.44	0.15	12.8	2.1	Present study
Cochin Estuary	54.9	103.4	10.1	40.3	6.8	1.5	5.6	0.78	3.9	0.72	2.2	0.29	1.7	0.26	18.7	4.7	Present study

6.3.1 Statistical approach

6.3.1.1 Multiple regression analysis

Multiple regression is an extension of bivariate regression in which several independent variables are combined to predict the depended variable. The combined effects of all the variables act on the dependent variable, for a net, combined effect. The resulting r^2 value provides an indication of the goodness of fit of the model. Here, multiple regression analysis is applied using metals as the dependent variable and direct and first order interaction effects of the independent variables such as Al, Fe, silt, clay, temperature, dissolved oxygen, organic carbon and $CaCO_3$, to examine the controlling role of any particular parameter or group of parameters on metal distribution. The significance of the regression coefficients is tested using ANOVA and the percentage of variability was measured using r^2. Similar analysis was done separately for both seasons along the continental shelf and are presented in Table 6.8. In this study, only the significant correlation ($p<0.01$) explaining the variability of Al, Fe, silt, clay, dissolved oxygen, temperature, organic carbon and $CaCO_3$ are considered.

In general, the number of REEs having significant correlations increased from premonsoon (6) to monsoon (8), whereas there was no such correlation in the estuary during both seasons. Along the shelf sediments, the multiple correlation was significant for Er, Dy, Ho, Tm, Yb, Tb, Lu and Eu ($p<0.001$) during monsoon. The regression generally explains the variability in the data. Al is the major predictor for REEs such as Er, Dy, Ho, Tm, Yb and Eu during both seasons. In addition, silt and $CaCO_3$ are also predictors for Er, Ho, Tm, Yb and Lu during monsoon.

Table 6.8. Multiple regression model for rare-earth elements along the shelf sediments.

Metal	Fitted regression equation	Anova	% variability	Significant positive variable	Significant negative variable
	Premonsoon				
Er	Er=-0.304+0.119 Al+0.06461 Fe-0.00008417 Silt-0.004045Clay – 0.276D.O +0.05309 Temp+ 0.04351Org.C+ 0.0189$CaCO_3$	P<0.001	64.1	Al	Temp
Dy	Dy=-0.782+0.204 Al+0.119Fe-0.002271Silt-0.009928Clay – 0.697D.O +0.13Temp+ 0.04351 Org.C+ 0.0189 $CaCO_3$	P<0.01	56.4	Al	D.O
Ho	Ho=-0.169+0.0416Al+0.02538Fe-0.0001209 Silt-0.001255Clay – 0.07933 D.O +0.01735 Temp+ 0.0204Org.C+ 0.0219$CaCO_3$	P<0.001	73.2	Al, Fe	
Tm	Tm=-0.06425+0.0201Al+0.00787 Fe-0.0001187 Silt-0.0004325Clay – 0.01869D.O +0.004695 Temp+ 0.007734Org.C+ 0.008026$CaCO_3$	P<0.001	79.4	Al, $CaCO_3$	
Yb	Yb=-0.408+0.109 Al+0.05239Fe+ 0.000289 Silt-0.00165Clay – 0.106 D.O +0.02921 Temp+ 0.05329Org.C+ 0.03912$CaCO_3$	P<0.001	77.6	Al	
Eu	Eu=-279+0.08674 Al-0.016233Fe-0.001316 Silt-0.004953Clay – 0.213D.O +0.03899 Temp+ 0.002557Org.C+ 0.0128$CaCO_3$	P<0.001	73.2	Al, Temp	D.O
	Monsoon				
Er	Er=0.536+0.124 Al+0.006277Silt-0.006293 Clay +0.171D.O -0.01745 Temp -2.584 Org.C+ 0.04473 $CaCO_3$+0.01535 Fe	P<0.001	88.4	Al, Silt, $CaCO_3$	Temp
Dy	Dy=0.981+0.187 Al+0.01022Silt-0.01538 Clay +0.341D.O -0.0229 Temp +0.01522 Org.C+ 0.05924 $CaCO_3$+0.04836 Fe	P<0.001	84.6	Al, Silt,	
Ho	Ho=0.2110.03773Al+0.02665Silt-0.00173 Clay +0.06177D.O -0.007585 Temp +0.0002 Org.C+ 0.01485 $CaCO_3$+0.009221 Fe	P<0.001	91.3	Al, Silt, $CaCO_3$, D.O	
Lu	Lu=0.07141+0.01494Al+0.08649Silt-0.000151Clay +0.01835 D.O -0.003026 Temp -0.0003177 Org.C + 0.005527 $CaCO_3$+0.001314 Fe	P<0.001	94.5	Al, Silt, $CaCO_3$. D.O	
Tb	Tb=0.08246+0.03618Al+0.000886Silt-0.005505Clay +0.06634D.O +0.004449 Temp +0.0008922 Org.C+0.0105$CaCO_3$+0.008893Fe	P<0.001	56.8	Al	
Tm	Tm=0.0715+0.1804Al+0.0009301Silt-0.0005289Clay +0.0217D.O -0.003166Temp +0.00243Org.C+ 0.0063 $CaCO_3$+0.002084 Fe	P<0.001	93.2	Al, Silt, $CaCO_3$	
Yb	Yb=0.459+0.09368Al+0.006266 Silt-0.0008015Clay +0.108D.O -0.0183Temp +0.00519Org.C+ 0.03316 $CaCO_3$+0.01535 Fe	P<0.001	93.4	Al, Silt, $CaCO_3$	
Eu	Eu=0.524+0.0881Al+0.001548Silt-0.007647Clay +0.03309D.O -0.0147Temp -0.008596Org.C+ 0.01539 $CaCO_3$-0.006546 Fe	P<0.001	85.1	Al	Clay

This reveals that Al is a major element controlling the distribution of elements along the shelf of Kerala. This was confirmed by their observed enrichment with respect to aluminium compared to iron. In addition, silt and $CaCO_3$ co-varied with certain REEs during monsoon. The cooling caused by monsoon upwelling seems to negatively influence most of the REEs. However, during premonsoon, the bottom oxygen concentration controls the distribution of Dy and Eu. The inclusion of silt as a positive variable indicates the restitution of REEs in sediments during monsoon. These associations are generally in agreement with the nature of sediment and the relative enrichment or depletion of elements over the shelf, suggesting well-defined carriers of these elements to the sediment.

6.4 Summary

1. The enrichment of REEs in the coastal sediments indicates their influence from terrigenous inputs, while the mid depth enrichment may be due to the monazite sand, especially along the southern zone. In Cochin estuary, the high accumulations of all REEs in the northern zone during both seasons indicate external input, possibly from industries.
2. Ce is the most abundant element among the REEs, whereas Lu is the least abundant element.
3. The inconsistency in the relation between dissolved oxygen and Ce anomalies observed along some transects may be due to the deposition of terrigenous matter transported by the along shore currents.
4. The Eu anomaly and accumulation of Th and U along the southern zone are characteristic features of the region enriched in heavy minerals.

5. The shelf sediments are generally rich in REEs during premonsoon, whereas the estuary showed a monsoonal accumulation indicating the influence of seasonal factors in the distribution of elements.
6. Al enrichment is higher than Fe enrichment along the shelf sediments, whereas it is in the reverse order in Cochin estuary during both seasons. This is probably due to the different geochemical reactivity of Al and Fe in these two environments.
7. The premonsoonal accumulation in the self sediments was higher than monsoonal accumulation, in contrast to Cochin estuary, indicting the differential response of seasons on the two regions.
8. Most of the rare-earth elements were present in excess and exhibited high normalisation values towards the southern stations, indicating that the sediments along the southern continental shelves are rich in heavy mineral sources.
9. Trivandrum transects showed authigenic uranium of 2 ppm, indicative of the anoxia and ancient sedimentary sequences along the region.
10. Multiple regression models revealed that Al acted as a major scavenger for REEs along the shelf sediment whereas in estuary such mechanism was absent.
11. The results of premonsoon and monsoon metal data revealed that tsunami has no effect on the distribution of rare-earth elements along the shelf and estuary.

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Summary

The main aim of the present study is to understand the geochemical processes in the shelf and adjacent estuaries along the southwest coast of India based on the texture, rare-earth and heavy metal concentrations in the sediments. The importance of this study lies on the fact that there has not been a proper evaluation of the impact of the Great Tsunami of 2004 on the coastal areas of the south India. Besides, the Arabian Sea is a vulnerable region because of its sub-surface oxygen deficiency and associated denitrification. The coastal sediments influence in regulating the anthropogenic inputs into the sea. In view of this, a study on the composition of sediment and elements was undertaken from the southwest coast of India for two seasons. A similar study was also carried out from the Cochin estuary to understand the impact of estuarine anthropogenic activities on the coastal region.

The thesis is presented in six chapters as per the scheme outlined in the preface. The results and discussions are made in respective chapters and major findings are summarized at the end of each chapter. The statistical techniques used in this study are also incorporated at the end of each chapter. The salient findings emerging from the study are summarised below.

1. The coastal processes such as southwest monsoon upwelling associated with the annually reversing coastal currents play major roles in the geochemical and granulometric properties of sediments along the southwest continental shelf, whereas the dynamics of tidal currents and freshwater flow are the contributing factors in the Cochin Estuary.

2. The organic enrichment in the shelf sediments are probably oxygen deficient and controls the distribution of redox sensitive elements such as V, Cr, Mn, Fe, Co, Ni, Zn, Mo, Pb, Ce and U through adsorption/desorption processes. The fresh water dominated Cochin Estuary during monsoon was progressively transforming into a tidal estuary during post and premonsoon seasons, which modified the adsorption/desorption mechanism of metals in the estuary.
3. The enrichment factor based on Al was higher than that based on Fe in the shelf sediments, but lower in the estuarine sediments. This may be due to the different geochemical affinity of Al and Fe in the two regions.
4. In Cochin Estuary, the concentrations of Ga and Pr are reported for the first time, which are high, whereas the concentrations of Dy, Ho and Er are lower than the other coastal environments.
5. The metals generally showed higher normalisation, enrichment and excess along the southern part of the shelf and in the northern parts of Cochin Estuary, indicating the influence of environmental characteristics on the shelf region and anthropogenic influence in the estuary.
6. A comparison of the biogeochemical properties of sediments, before and after the December 2004 tsunami, reveals that the study region was either not significantly affected by the tsunami or recovered immediately without any alteration.

Processes controlling the geochemical distribution of elements in the sediments along the southwest continental shelf and an adjacent estuary: a comparison

When metals enter the estuaries, they are exposed to intense chemical and physical changes such as weathering and alteration. The most important estuarine processes are precipitation, adsorption, desorption and uptake by organisms. Aluminium and iron are precipitated as hydroxides, which scavenge other metals before settling into sediments. Thus, with more than 90 % of riverine particulate matter deposited in estuaries and coastal zones, only a small fraction reach the sea. Hence, the ultimate sink of most of the elements in the aquatic environment is the sediment and an evaluation of their geochemical composition on a long term will provide information on the role of anthropogenic activities and natural processes. Geochemical studies from this region have shown that, on moving from river to the shelf environment, coarser illites and kaolinites (formed from leaching of laterites) are replaced by fine-grained montmorrilonites (Nath et al., 2000). These montmorrilonites in the coastal environments are hence, responsible for greater accumulation of organic matter due to their larger surface area.

In the present study, surface sediments collected from the continental shelf of southwest coast of India and from the Cochin Estuary were examined for their geochemical properties to identify the processes leading to the deposition of elements. The study area generally showed wide variation in the depositional patterns of elements, which can be better represented by a three-way process (Figure S1). The flowchart denotes that the metal deposition in coastal environment is controlled by natural processes such as diffusion by coastal currents (including monsoon upwelling) and normalization through bio-mediated, geochemical and anthropogenic activities induces inorganic precipitation of elements under the fluctuating ionic conditions. Another observation is that aluminium is primarily controlling the elemental deposition in the shelf sediments, whereas scavenging of elements through iron complexation (inorganic) is the principal mechanism in the estuarine sediments. This is reflected in the enrichment ratios of elements in these two environments. The release of industrial effluents into the flow-restricted Cochin Estuary favors the metal deposition. In the coastal environment, upwelling induced productivity has a major influence on the biogeochemical cycling of metals.

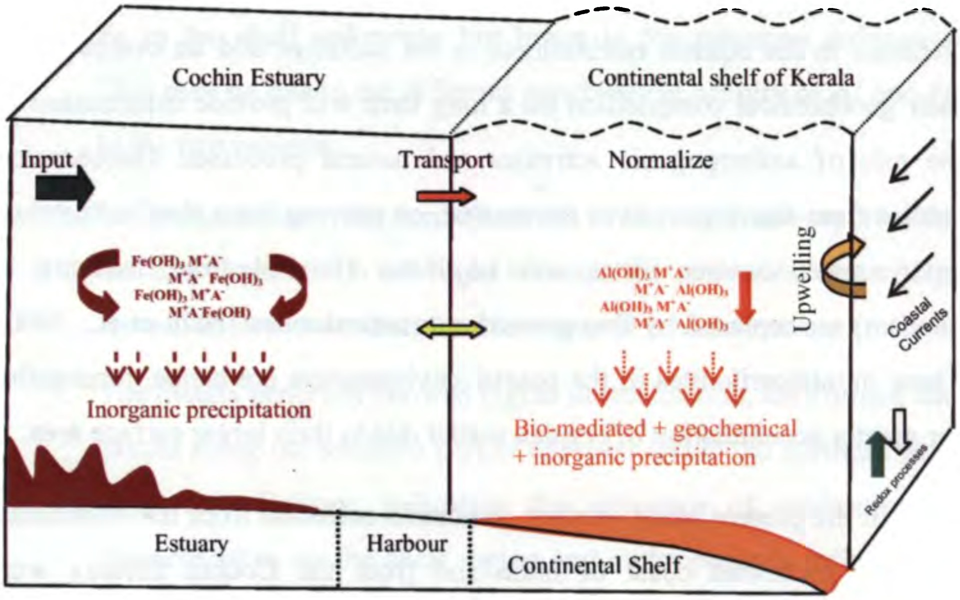

Figure S1. Schematic representation showing the geochemical processes in Cochin Estuary and along the adjoining shelf sediments.

The retention of metals in the shelf area (chemical process) is mainly through scavenging by Fe and Mn on to the particulate state and then to sediments. The shelf edge sediments are relatively organic rich and hence, susceptible to early diagenesis. As a result, metals incorporated into the sediments under reducing environment get released easily into the overlying sediments under reducing environment get released easily into the overlying waters; via diffusion or pore water seepage during sediment resuspension. In addition, temporary retention of metals can occur during upwelling associated high primary production, which elute metals into the water column by sediment diffusion. In estuary, the early flocculation of Fe followed by scavenging other metals at low salinity is found to accumulate other elements. The possible mechanism appears to be estuarine coagulation-flocculation of elements as colloids in association with hydrous iron oxides under fluctuating salinity. Inadequate flushing of pollutants released into a flow restricted estuary can also promote coagulation or co-precipitation of metals under the prevailing ionic (salinity) condition.

Seasonality in the texture and geochemical properties of coastal sediments along the southwest coast of India: a comparison with Cochin Estuary

A long term comparison has been made on the geochemical composition of elements in the southwest coastal sediments as well as the sediments of Cochin estuary since 1981 (Table S1 & Table S2). The earlier data from the shelf region was taken from Nath et al (1997; 2000), Shajan (2001) and Siby (2005). The present study was additionally useful in collecting geochemical data from the southwest coastal environment before (July 2004) and after (March 2005) the Great Tsunami 2004 event. This has been accordingly used to evaluate the impact of tsunami on the western continental shelf of India. For the Cochin estuary, the works carried out by Nath et al. (2000) and Shajan (2001) were taken. However, due to the difference in sediment fractions (0.2 μm) analyzed by Nath et al. (2000) and Shajan (2001), the comparison was mainly based on the information from Siby (2004).

Table S1. Long-term changes in the concentration of elements in the surficial sediments along the continental shelf [(all in ppm, except Al and Fe (% dry weight)].

Metal	Nath et al, 2000	Shajan, 2001	Siby, 2005		Present study	
			Northern	Southern	Northern	Southern
Be	—	1.5	—	—	0.9 (0.8)	0.7 (0.8)
Al	20.15	16.33	9.9	4.16	5.3 (5.0)	3.3 (3.4)
Ga	—	—	10.45	4.76	5.6 (5.4)	4.1 (3.8)
Rb	85.6	22	36.79	18.63	18.6 (17.7)	14.5 (12.5)
Sr	250	204	529.1	910.6	730.6 (743.7)	877.9 (895.7)
Cs	4.04	—	2.26	0.51	1.1 (1.1)	0.4 (0.4)
Ba	268	—	120.17	270.9	96.7 (78.7)	228.3 (158.8)
Pb	—	516	15.51	16.22	10.1 (9.7)	10.6 (11.7)
Sc	22.8	43.54	11.03	6.63	6.9 (6.6)	4.7 (4.7)
V	150	96.23	70.31	39.61	47.8(46.5)	38.6 (36.8)
Cr	252	203.4	160.9	91.85	97.9 (91.3)	80.2 (71.8)
Mn	330	400.0	363.3	212.5	304.9 (282.9)	195.9 (174.9)
Fe	9.81	8.8	6.33	3.54	5.0 (4.4)	3.8 (3.7)
Co	17.5	16.24	9.78	4.51	6.9 (6.2)	4.4 (4.1)
Ni	—	81.47	58.58	22.8	44.4 (41.5)	32.9 (31.7)
Cu	—	34.45	26.5	14.06	17.9 (17.2)	14.1 (14.0)
Zn	415	152.4	76.03	55.23	64.2 (53.7)	75.3 (72.4)
Y	—	19.24	20.25	11.66	14.3 (14.0)	12.9 (10.6)
Zr	—	109.4	74.15	50.26	39.1 (34.1)	52.3 (37.6)
Nb	—	33.47	5.66	5.02	3.3 (3.1)	8.9 (6.4)
Mo	—	5.14	—	—	1.0 (1.1)	0.9 (1.2)
Hf	—	1.99	2.05	1.32	1.2 (1.0)	1.5 (1.2)
Ta	—	1.43	0.44	0.25	0.3 (0.3)	0.6 (0.5)
La	19.6	55	23.96	25.48	16.1 (14.3)	52.4 (40.0)
Ce	41.7	128	50.35	45.95	34.3 (30.9)	93.7 (63.9)
Pr	4.6	—	4.93	4.45	3.4 (3.2)	8.6 (6.1)
Nd	17.7	57	20.33	17.02	14.6 (13.4)	33.2 (22.9)
Sm	3.6	9.36	4.10	2.93	2.9 (2.8)	4.7 (3.6)
Eu	0.88	2.08	1.01	0.62	0.7 (0.7)	0.7 (0.6)
Gd	3.1	—	3.42	2.29	2.5 (2.4)	4.1 (3.1)
Tb	0.46	1.19	0.59	0.34	0.4 (0.4)	0.5 (0.4)
Dy	2.9	—	3.37	1.82	2.5 (2.4)	2.4 (1.9)
Ho	0.57	—	0.68	0.36	0.5 (0.5)	0.4 (0.4)
Er	1.71	—	1.91	1.04	1.4 (1.4)	1.2 (1.1)
Tm	0.22	—	0.27	0.14	0.19 (0.19)	0.15 (0.13)
Yb	1.46	2.45	1.65	0.85	1.2 (1.1)	0.9 (0.8)
Lu	0.21	0.42	0.24	0.13	0.18 (0.16)	0.14 (0.12)
Th	4.25	14.1	6.27	8.87	4.3 (3.7)	24.8 (16.9)
U	4.12	3.7	2.1	1.62	1.8 (1.6)	2.5 (2.1)

Table S2. Long-term changes in the concentration of elements in the surficial sediments in the Cochin estuary [(all in ppm, except Al and Fe (% dry weight)].

Metal	Nath et al., 2000	Shajan, 2001			Present study		
		Northern	Central	Southern	Northern	Central	Southern
Be	---	1.5	1.2	1.1	2.3 (2.2)	0.9 (0.9)	1.1(1.4)
Al	22.6	14.4	16	8.7	19.2 (18.9)	7.6 (7.6)	8.2(11.6)
Ga	---	---	---	---	23.5 (23.3)	7.8 (8.1)	9.3(12.8)
Rb	82.3	24.3	29.6	11.2	77.3 (79.2)	27.5(27.8)	32.8 44.2)
Sr	204.3	336.7	208.1	188.4	261.4(240.8)	353.4 (318.4)	143.2 (148.2)
Cs	4.08	---	---	---	2.2(2.0)	0.3 (0.3)	1.4(1.9)
Ba	320.4	1016.7	386.2	540.2	991.5 (966.2)	942.5 (892.3)	318.4 (376.8)
Pb	---	41.3	28.1	16.6	209.3 (39.7)	73.4 (10.7)	33.6 (10.9)
Sc	22.8	28.3	15.3	4.3	22.8(21.9)	5.4(6.1)	9.3(12.6)
V	180.1	69.4	76.3	47.3	153.9 (149.8)	37.2(42.1)	61.2(74.1)
Cr	520.2	115.3	158.4	66.7	225.4 (222.8)	49.9(57.8)	102.9 (126.4)
Mn	420.4	460.2	500.2	330.2	528.7 (519.1)	216.7 (244.5)	381.1 (479.3)
Fe	12.5	6.1	8.7	3.4	10.8(10.7)	1.8(1.9)	4.5(5.9)
Co	28.4	13.2	15.8	7.6	18.7(18.7)	4.3 (4.6)	10.1(14.2)
Ni	---	41.3	66.4	21.5	74.1(72.9)	15.3(15.2)	42.2(52.1)
Cu	---	29.6	24.3	10.3	64.3(62.9)	12.3(12.7)	21.7(26.9)
Zn	396.5	685.4	94.5	33.3	983.8 (959.3)	84.7(85.9)	100.6 (112.7)
Y	---	17.6	14.6	4.3	44.6 (42.7)	6.9 (8.5)	14.7(20.8)
Zr	---	139.6	70.3	87.3	84.3(70.8)	51.1(40.4)	45.7(64.3)
Nb	---	28.1	18.4	14.6	15.2(15.1)	11.2(11.7)	9.7(10.9)
Mo	---	1.3	2.6	2.3	1.4(1.3)	0.5(0.4)	0.9 (1.2)
Hf	2.27	2.4	1.9	2.7	2.5(2.1)	1.3(1.1)	1.3(1.8)
Ta	0.85	0.8	0.95	0.7	1.1(1.0)	0.7(0.7)	0.6(1.1)
La	61.2	---	---	---	96.3 (91.6)	32.6(39.2)	27.54(42.6)
Ce	123.4	---	---	---	181.7 (175.1)	58.2 (75.9)	54.3 (86.6)
Pr	---	---	---	---	17.5 (16.6)	5.4 (7.6)	5.1 (8.1)
Nd	58.3	---	---	---	70.3 (66.3)	21.2 (30.5)	20.4 (32.9)
Sm	9.27	---	---	---	11.9 (11.2)	3.5 (5.3)	3.7 (5.8)
Eu	1.85	---	---	---	2.3 (2.2)	1.03 (1.01)	0.9 (1.2)
Gd	---	---	---	---	9.8 (9.4)	2.5 (3.6)	3.1 (4.9)
Tb	1.02	---	---	---	1.4 (1.3)	0.3 (0.4)	0.5 (0.7)
Dy	---	---	---	---	7.2 (6.7)	1.4 (1.8)	2.6 (3.7)
Ho	---	---	---	---	1.3 (1.3)	0.2 (0.3)	0.5 (0.7)
Er	---	---	---	---	4.1 (3.9)	0.7 (0.9)	1.4 (2.01)
Tm	---	---	---	---	0.6 (0.5)	0.1 (0.1)	0.2 (0.3)
Yb	2.31	---	---	---	3.2 (2.9)	0.5 (0.6)	1.1 (1.6)
Lu	0.39	---	---	---	0.5 (0.5)	0.1 (0.1)	0.2 (0.2)
Th	15.1	---	---	---	31.5 (28.7)	12.5 (17.7)	7.4 (13.9)
U	7.8	---	---	---	9.8 (9.3)	1.3 (1.7)	2.4 (3.9)

It can be seen that a long-term variation in the geochemical distribution of elements is insignificant in the coastal sediments, although variations associated with sediment restitution are recurring with respect to seasons. Cochin Estuary, especially in the northern parts showed very high accumulation of heavy metals in sediments during the present observation compared to earlier studies. This is expected since an annual loading of approximately 63 Mm^3 of effluents from 247 chemical industries situated upstream of the River Periyar could lead to a gross metal pollution. The metal contamination is however, not seen in the central or south part of the estuary.

The present study also examined the distributional character of the elements along the south western continental shelf of India and an adjoining estuary (Cochin) over two seasons. The estuarine sediments showed a greater inter-element correlation indicating their common source from effluents. Since the Fe-hydroxide depositions of elements are detrimental, the estuary seems to be under stress. It is therefore assumed that the geochemical behavior of the estuary is controlled by anthropogenic processes, whereas the shelf environment remains free from contaminants as the metals are rapidly removed by the coastal currents and biogenic associations, which normalize the elemental accumulation in sediments.

The present study has importance in that it gave an opportunity to examine the impact of the Great Tsunami 2004 caused on the coastal environment. Fortunately, the first sampling cruise was conducted prior to the tsunami event and the second cruise was soon after the tsunami. The sediment characteristics during post-tsunami did not show much variation from that during pre-tsunami periods. The texture, organic content and elemental concentrations in sediments generally remained unaltered during the two observations. This shows that tsunami has not significantly altered the sedimentary environment of the study region. While disasters like tsunami are expected to destroy the entire oceanic realm, the results from this study is quite encouraging, as it categorically states that tsunami waves do not impinge the texture or its geochemical composition of sediments in the two environments.

In conclusion, metals do not seem to constitute a threat to the marine environment other than in estuaries. The difference between the natural concentration and that at which, acute effects are observable, is normally several orders of magnitude. Though the use of metals has declined over the years, their remaining uses are unlikely to find substitutes in the foreseeable future. However, the metals are natural constituents of the earth and man's input on these geological cycles is relatively small. Consequently, the release of metals into the coastal zone through anthropogenic activities is adequately dealt by the sea's natural control mechanisms resulting in minimal biological impact.

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Annexure

Annexure-I

Source, abundance and residence time of selected non-transition elements.

Element	At. weight	Abundance/Sources in environment	Oceanic residence time (years)/Toxicity
Be	9.01	Earth's Crust: 2.6 $\mu g.g^{-1}$ Seawater/ppm: 20 $pmol.kg^{-1}$ Found mostly in minerals like beryl [$AlBe_3(Si_6O_{18})$] and chrysoberyl (Al_2BeO_4). Total world production per year is around 364 tons. Its ability to absorb large amounts of heat makes it useful in spacecraft, missiles, aircraft, smelting industry and computer parts.	63×10^4 Beryllium and its salts are toxic and should be handled with great care. Beryllium is a potential occupational carcinogen (lung cancer).
Al	26.98	Earth's Crust: 82000 $\mu g.g^{-1}$ Seawater: 0.5 $\mu g.l^{-1}$ Deep sea clay: 95000 $\mu g.g^{-1}$ Most plentiful metal in earth's crust (8%), but never occurs in free form. Obtained by electrolysis from bauxite (Al_2O_3). Total world production is around 15,000,000 tons per year. Application: Kitchen utensils, building decorations, electrical transmission (not conductive as copper, but cheaper). Alloys containing copper, magnesium, silicon, manganese and other metals are much stronger and more durable than aluminum, making aluminum useful in the manufacture of aircraft and rockets.	6.2×10^2 It is non toxic in nature but its high exposure affects eyes, skin, respiratory system.
Ga	69.72	Earth's Crust: 18 $\mu g.g^{-1}$ Seawater: 0.03 $\mu g.l^{-1}$ Deep sea clay: 20$\mu g.g^{-1}$ Found throughout the crust in minerals like bauxite, germanite and coal. Is produced as a by-product of zinc and copper refining. Around 30 tons per year are produced world wide.Used in semiconductor production, quartz thermometers, laser diodes and used to locate tumors.	9.0×10^3 Non-toxic
Rb	85.46	Earth's Crust: 90 $\mu g.g^{-1}$ Seawater: 120 $\mu g.l^{-1}$ Deep sea clay: 110 $\mu g.g^{-1}$ Occurs abundantly, but so widespread that production is limited. Usually obtained from lithium production. Has limited commercial use. Primarily used for research purposes.	3.0×10^6 Toxic
Sr	87.62	Earth's Crust: 370 Seawater: 8000 $\mu g.l^{-1}$ Seawater: 7.6 $\mu g.g^{-1}$ Deep sea clay: 250 $\mu g.g^{-1}$ Found in minerals celestite and strontianite. Annual production is around 137,000 tons. Used in flares and fireworks for crimson color. Also used in nuclear batteries in buoys and phosphorescent paint	5.1×10^6 Non toxic
Cs	132.91	Earth's Crust: 3 $\mu g.g^{-1}$ Seawater: 0.4 $\mu g.l^{-1}$ Deep sea clay: 5 $\mu g.g^{-1}$ Found in pollucite [$(Cs_4Al_4Si_9O_{26}).H_2O$] and lepidolite. World production is around 20 tons per year. Used as a 'getter' to remove air traces in vacuum tubes. Since it ionizes readily, it is used as an ion rocket motor propellant. Also used in photoelectric cells, atomic clocks, infra-red lamps.	3.3×10^5 Cesium can have very serious effects on the body if taken in excess
Ba	137.33	Earth's Crust: 500 $\mu g.g^{-1}$ Seawater: 20 $\mu g.l^{-1}$ Deep sea clay: 1500 $\mu g.g^{-1}$ Found in barytine ($BaSO_4$) and witherite ($BaCO_3$), never found in pure form due to its reactivity. Total annual world production estimated around 6,000,000 tons. Used in sparkplugs, vacuum tubes, fireworks, fluorescent lamps. Insoluble barium sulfate is used for body imaging.	8.8×10^3 Soluble barium salts are highly toxic.
Pb	207.2	Earth's Crust: 14 $\mu g.g^{-1}$ Seawater: 0.003 $\mu g.l^{-1}$ Deep sea clay: 200 $\mu g.g^{-1}$ Found most often in ores called galena. Also found in pyromorphite, boulangerite and cerussite ores. World wide production of lead is around 2,800,000 tons per year. Used in solder, shielding against radiation, in batteries and ammunition. Still used in gasoline in some areas of the world, but this use is being phased out.	8.1×10^1 Lead is extremely toxic, but its effects are accumulative and most often develop after extended exposure.

Annexure-II

Source, abundance and residential time of selected transition elements.

Element	Atomic weight	Sources in environment	Residence time (years)/Toxicity
Sc	44.96	Earth's Crust.: 16 $\mu g.g^{-1}$ Seawater: 0.0006 $\mu g.l^{-1}$ Deep sea clay: 20 $\mu g.g^{-1}$ Occurs mainly in the minerals thortveitile, wiikite) and tin and tungsten ores. It is produced from uranium mill tailings. World production is around 0.05 tons annually. Used in leak detectors, space industry materials, seed germinating agents. Also used in mercury vapour lamps.	50×10^2 Non toxic
V	50.94	Earth's Crust: 160 $\mu g.g^{-1}$ Seawater: 2.5 $\mu g.l^{-1}$ Deep sea clay: 150 $\mu g.g^{-1}$ Found in the minerals patronite (VS4), vanadinite [$Pb_5(VO_4)_3Cl$], and carnotite [$K_2(UO_2)_2(VO_4)_2.3H_2O$]. Vanadium is usually produced as a by-product of refining other ores and from Venezuelan oils. Annual world wide production is around 7,000 tons. It is mixed with other metals to make very strong and durable alloys which are used in construction materials, tools, springs and jet engines. Vanadium pentoxide ($V2O_5$) is used as a catalyst, dye and color fixer.	4.5×10^4 High exposure affects skin, respiratory system
Cr	51.99	Earth's Crust.: 100 $\mu g.g^{-1}$ Seawater: 0.3 $\mu g.l^{-1}$ Deep sea clay: 100$\mu g.g^{-1}$ Does not occur free in nature. Chromite [Fe, Mg (CrO_4)] is its most important mineral. Annual world production around 20,000 tons. Used to make stainless steel. Also used in plating for car parts, tools, knives, camouflage paint, stereos, video tapes and lasers.	8.2×10^3 High exposure affects eyes, skin, respiratory system
Mn	54.94	Earth's Crust: 950 $\mu g.g^{-1}$ Seawater: 0.2 $\mu g.l^{-1}$ Deep sea clay: 6000 $\mu g.g^{-1}$ Most abundant ores are pyrolusite (MnO_2), psilomelane [$(BaH_2O)_2Mn_5O_{10}$] and rhodochrosite ($MnCO_3$). Annual world production is around 6,220,000 tons. Used in steel, batteries, axles, rail switches, safes, plows and ceramics.	1.3×10^3 High exposure affects respiratory system, central nervous system, blood, kidneys
Fe	55.85	Earth's Crust: 41000 $\mu g.g^{-1}$ Seawater: 2 $\mu g.l^{-1}$ Deep sea clay: 60000 $\mu g.g^{-1}$ Obtained from hematite, magnetite, goethite, lepidocrocite and siderite. Annual world production is around 716,000,000 tons. Used in steel and other alloys which are used in countless products. It is essential for animals as it is the chief constituent of hemoglobin which carries oxygen in blood vessels. Iron is the most important element of all the metals.	5.4×10^1 Deficiency of iron leads to anaemia, but excess iron in the body causes liver and kidney damage
Co	58.93	Earth's Crust.: 20 $\mu g.g^{-1}$ Seawater: 0.05 $\mu g.l^{-1}$ Deep sea clay: 55 $\mu g.g^{-1}$ Occurs in compounds with arsenic, oxygen and sulfur as in cobaltine (CoAsS) and linneite (Co_3S_4). Annual world production is around 17,000 tons. Used to make hard alloys; for magnets, ceramics and special glasses. Also used in permanent magnets, razor blades and catalitic converters. Cobalt-60 is used in cancer therapy.	3.4×10^2 High exposure affects eyes, skin, respiratory system
Ni	58.69	Earth's Crust: 80 $\mu g.g^{-1}$ Seawater: 0.2 $\mu g.l^{-1}$ Deep sea clay: 200 $\mu g.g^{-1}$ Chiefly found in pentlandite [$(Ni,Fe)_9S_8$] and garnierite ores. Annual world production is over 1,300,000 tons. Used in electroplating and metal alloys because of its resistance to corrosion. Also in nickel-cadmium batteries; as a catalyst and for coins.	8.2×10^3 Nasal cavities, lungs, skin

Cu	63.55	Earth's Crust: 50 μg.g^{-1} Seawater: 0.1 μg.l^{-1} Deep sea clay: 200 μg.g^{-1} Pure copper occurs rarely in nature. Usually copper found in minerals such as azurite, malachite and bornite and in sulfides as in chalcopyrite ($CuFeS_2$), coveline (CuS), chalcosine (Cu_2S) or oxides like cuprite (Cu_2O). Copper is obtained by smelting, leaching and electrolysis. Annual world production is around 6,540,000 tons. Most often used as an electrical conductor. Its alloys are used in jewelry, bronze sculptures and for coins. The skin of the Statue of Liberty is made of copper.	9.7 x 10^2 Eyes, skin, respiratory system, liver, kidneys (increase(d) risk with Wilson's disease)
Zn	65.39	Earth's Crust : 75 μg.g^{-1} Seawater: 0.1 μg.l^{-1} Deep sea clay: 120 μg.g^{-1} Found in the minerals zinc blende (sphalerite) (ZnS), calamine, franklinite, smithsonite ($ZnCO_3$), willemite, and zincite (ZnO). Annual world wide production is around 5,020,000 tons. Used to coat other metals (galvanizing) to protect them from rusting. Used in alloys such as brass, bronze, nickel. Also in solder, cosmetics and pigments.	5.1 x 10^2 Toxic
Y	88.91	Earth's Crust : 30 μg.g^{-1} Seawater: 0.0013 μg.l^{-1} Deep sea clay: 32 μg.g^{-1} Found in xenotime, bastnasite, fergusonite and samarskite ores. Annual world production is around 400 tons. Combined with europium to make red phosphors for color TV's. Yttrium oxide and iron oxide combine to form a crystal garnet used in radars. Also used in lasers, camera lenses and fireproof bricks.	7.4x 10^2 Inhalation; ingestion; skin and/or eye contact
Zr	91.22	Earth's Crust : 190 μg.g^{-1} Seawater: 0.03 μg.l^{-1} Deep sea clay: 20 μg.g^{-1} Found in minerals such as zircon and baddeleyite. Annual world production is around 7000 tons. Used in alloys such as zircaloy, which is used in nuclear applications since it does not readily absorb neutrons. Also used in catalytic converters, percussion caps and furnace bricks. Baddeleyite is used in lab crucibles.	Inhalation; skin and/or eye contact
Nb	92.91	Earth's Crust: 20 μg.g^{-1} Seawater: 50 pmol kg^{-1} Deep sea clay: 20 μg.g^{-1} Found in columbite, samarskite and betafite ores. Also obtained as a by-product of tin-extraction. Annual world production is around 15,000 tons. It is used in stainless steel alloys for nuclear reactors, jets, missiles, cutting tools, pipelines, super magnets and welding rods	Non-toxic
Mo	95.94	Earth's Crust : 1.5 μg.g^{-1} Seawater: 10 μg.l^{-1} Deep sea clay: 8 μg.g^{-1} Found in the minerals molybdenite (MoS_2) and wulfenite (MoO_4Pb) also produced as a by-product of copper production. Annual world production is around 80,000 tons. Used in steel, aircraft, missiles, filaments in electric heaters, lubricants and protective coatings in boiler plates.	8.2 x 10^5 High exposure affects eyes, respiratory system, liver, kidneys
Hf	178.49	Earth's Crust : 5.3 μg.g^{-1} Seawater: 0.0007 μg.l^{-1} Deep sea clay: 4.5 μg.g^{-1} Obtained as a by-product zirconium refining. Around 50 tons are produced world wide annually. Used in reactor control rods because of its ability to absorb neutrons as a gas scavenger in vacuum tubes.	Eyes, skin, mucous membrane , liver
Ta	180.95	Earth's Crust : 2 μg.g^{-1} Seawater: 0.002 μg.l^{-1} Deep sea clay: 1 μg.g^{-1} Chiefly occurs in the mineral tantalite. Always found with niobium. Annual world production is around 840 tons. Used in metal alloys. Tantalum pentoxide is used in capacitors, condensers, cutting tools, vacuum tube filaments and in camera lenses to increase refracting power.	Eyes, skin, respiratory system

Annexure-III

Sources, abundance and residential time of selected rare-earth elements.

Element	Atomic weight	Abundance/Sources in environment	Residence time (years)
La	138.91	Earth's Crust: 32 $\mu g.g^{-1}$ Seawater: 0.003 $\mu g.g^{-1}$ Deep sea clay: 45 $\mu g.g^{-1}$ Found with rare earths in monazite and bastnasite. ~12,500 tons.yr^{-1} is the world wide production. Because of the refractive properties, it is used in camera lenses. Also used in lighter flints, battery electrodes and catalytic converters.	3.2×10^3
Ce	140.12	Earth's Crust: 68 $\mu g.g^{-1}$ Seawater: 0.001 $\mu g.g^{-1}$ Deep sea clay: 100 $\mu g.g^{-1}$ Most abundant rare earth metal. Found in many minerals like monazite [$Ce(PO_4)$]. World production is around 24,000 tons per year. Used in alloys to make them heat-resistant. Also used in glass, flints and ceramics.	1.4×10^3
Pr	140.91	Earth's Crust: 9.5 $\mu g.g^{-1}$ Seawater: 0.0006 $\mu g.g^{-1}$ Deep sea clay: 9 $\mu g.g^{-1}$ Obtained from monazite and bastnasite ores. Annual world production is around 2400 tons. Used for coloring glass and ceramic glazes. Also used with neodymium to make lenses for glass maker's goggles because they filter out the yellow light present in glass blowing.	3.1×10^3
Nd	144.24	Earth's Crust: 38 $\mu g.g^{-1}$ Seawater: 0.003 $\mu g.g^{-1}$ Deep sea clay: 40 $\mu g.g^{-1}$ Chief ores are monazite and bastnasite. Annual world wide production is around 7300 tons. Used in ceramics to color glazes, in alloys for permanent magnets, for special lens with praseodymium. Also to produce bright purple glass and special glass that filters infrared radiation.	2.8×10^3
Sm	150.36	Earth's Crust: 7.9 $\mu g.g^{-1}$ Seawater: 0.0005 $\mu g.g^{-1}$ Deep sea clay: 7 $\mu g.g^{-1}$ Found with other rare earths. The chief ore it is found in is monazite. Around 700 tons are produced world wide on an annual basis. Used in carbon-arc lighting, permanent magnets, organic reagents, lasers, alloys, headphones and as an absorber in nuclear reactors.	2.9×10^3
Eu	151.97	Earth's Crust: 2.1 $\mu g.g^{-1}$ Seawater: 0.0001 $\mu g.g^{-1}$ Deep sea clay: 1.5 $\mu g.g^{-1}$ Chief ores are monazite and bastnasite. Around 400 tons are produced world wide each year. Used with yttrium oxide to make red phosphors for color televisions. Also used in making thin-film superconductor alloys.	5.3×10^3
Gd	157.25	Earth's Crust: 7.7 $\mu g.g^{-1}$ Seawater: 0.0007 $\mu g.g^{-1}$ Deep sea clay: 7.8 $\mu g.g^{-1}$ Chief ores are monazite and bastnasite. World production is around 400 tons annually. Used in magnets, refractories, magnets, neutron radiography and is alloyed with iron for magneto-optic recording devices.	4.6×10^3
Tb	158.93	Earth's Crust: 1.1 $\mu g.g^{-1}$ Seawater: 0.0001 $\mu g.g^{-1}$ Deep sea clay: 1 $\mu g.g^{-1}$ Found with other rare earth metals (chiefly in monazite ore). Annual world wide production is around 10 tons. Used in alloys, fuel cell stablizer. Also used in the production of electronic devices	5.6×10^3

Dy	162.50	Earth's Crust.: 6 $\mu g.g^{-1}$ Seawater: 6 $pmolg^{-1}$ Deep sea clay: 45 $\mu g.g^{-1}$ Usually found with erbium, holmium and other rare earths in some minerals. Around 100 tons are produced annually. As control-rods for nuclear reactors because it readily absorbs neutrons. Also used in alloys for making magnets.	7.8 x 10^2
Ho	164.93	Earth's Crust: 1.4 $\mu g.g^{-1}$ Seawater: 0.0002 $\mu g.g^{-1}$ Deep sea clay: 1 $\mu g.g^{-1}$ Chief ores are monazite and bastnasite. Annual world production is around 10 tons. As control-rods for nuclear reactors because it readily absorbs neutrons. Also used as a flux concentrator for high magnetic fields.	1.3 x 10^4
Er	167.26	Earth's Crust: 3.8 $\mu g.g^{-1}$ Seawater: 0.0008 $\mu g.g^{-1}$ Deep sea clay: 2.7 $\mu g.g^{-1}$ Found with other heavier rare earths. Around 500 tons are produced world wide annually. Erbium oxide is used in ceramics to obtain a pink glaze. Also used to make infrared-absorbing glass and in alloys with titanium.	8.1 x 10^3
Tm	168.934	Earth's Crust: 0.48 $\mu g.g^{-1}$ Seawater: 0.0002 $\mu g.g^{-1}$ Deep sea clay: 0.4 $\mu g.g^{-1}$ Chief ores are monazite and bastnasite. Annual world production is around 50 tons. Radioactive thulium is used to power portable x-ray machines, eliminating the need for electrical equipment.	5.2 x 10^3
Yb	173.04	Earth's Crust: 3.3 $\mu g.g^{-1}$ Seawater: 0.0008 $\mu g.g^{-1}$ Deep sea clay: 3 $\mu g.g^{-1}$ Found in minerals such as yttria, monazite, gadolinite, and xenotime. Annual world wide production is around 50 tons. Used in metallurgical and chemical experiments and sometimes used in stress gauges.	8.5 x 10^3
Lu	174.98	Earth's Crust: 0.51 $\mu g.g^{-1}$ Seawater: 0.0002 $\mu g.g^{-1}$ Deep sea clay: 0.5 $\mu g.g^{-1}$ Found with ytterbium in gadolinite and xenotime. Its chief ores are monazite and bastnasite. Around 10 tons are produced globally on a yearly basis. Used in alloys and can be used as a catalyst in cracking, hydrogenation, polymerization and alkylation. It's primary use is in chemical research.	6.2 x 10^3
Th	232.04	Earth's Crust: 12 $\mu g.g^{-1}$ Seawater: 0.01$\mu g.g^{-1}$ Deep sea clay: 10 $\mu g.g^{-1}$ Found in various minerals like monazite and thorite and dispersed on pegmatite rocks. Annual world wide production is around 31.000 tons. Used in making strong alloys. Also in ultraviolet photoelectric cells. Bombarded with neutrons make uranium-233, a nuclear fuel.	3.7x 10^3
U	238.03	Seawater: 0.3.2 $\mu g.g^{-1}$ Deep sea clay: 2$\mu g.g^{-1}$ Primary uranium bearing ores are uraninite, autunite, carnotite, samarskite (some varieties of samarskite contain up to 23% uranium) and torbernite. Annual world wide production is around 35,000 tons. For many centuries it was used as a pigment for glass. Now it is used as a fuel in nuclear reactors and in nuclear bombs. Depleted Uranium is used in casings of armor piercing arterial shells, armor plating on tanks and as ballast in the wings of some large aircraft.	5.0x 10^5

Annexure-IV

Hydrogeographical parameters along the study region

Shelf

Stations		Premonsoon				Mansoon			
Transects	Depth (m)	DO (ml/l)	Temp (°C)	Org.C %	$CaCO_3$ %	DO (ml/l)	W.T.B (°C)	Org.C %	$CaCO_3$ %
Manglore	20	3.71	29.21	0.79	1.11	1.76	24.30	1.01	1.36
	50	3.43	29.31	0.41	5.17	2.35	21.50	0.20	3.61
	100	0.56	19.82	2.36	9.61	0.30	18.10	2.87	8.08
	200	0.23	14.47	2.61	2.82	0.28	13.80	2.72	7.57
Kannoore	20	3.87	29.85	0.67	0.84	1.37	23.90	1.11	0.64
	50	2.12	26.80	0.09	1.41	0.52	21.50	0.05	1.09
	100	0.75	21.29	2.36	8.49	0.26	17.90	3.52	7.98
	200	0.27	15.46	2.30	8.94	0.29	13.70	3.32	8.81
Baypore	20	3.28	29.20	0.42	1.21	2.54	24.78	1.15	0.46
	50	3.19	28.29	0.19	4.50	0.42	21.24	0.14	2.93
	75	1.52	24.10	0.15	3.29	0.40	19.73	0.22	2.86
	100	0.66	20.20	0.66	5.84	0.39	18.40	0.36	4.70
	150	0.28	16.12	2.46	9.72	0.28	14.50	4.50	12.00
	200	0.32	13.93	2.15	8.25	0.23	17.12	3.40	8.13
Ponnani	20	2.93	29.02	0.81	0.34	1.38	24.39	1.32	4.12
	50	3.52	28.03	0.55	6.35	0.56	21.10	0.67	5.90
	100	0.71	20.88	3.22	11.31	0.31	18.60	4.99	11.86
	200	0.34	14.35	2.75	8.12	0.30	13.63	2.68	11.88
Cochin	20	3.25	29.42	0.01	0.27	0.25	22.80	0.00	0.48
	50	2.70	27.05	0.06	2.15	0.73	21.70	0.15	2.37
	75	1.61	24.70	0.16	3.59	0.40	19.13	0.25	3.88
	100	0.40	19.40	0.41	4.93	0.46	18.50	0.74	4.65
	150	0.48	15.96	0.88	7.61	0.31	15.80	1.23	6.85
	200	0.40	13.82	0.97	6.83	0.27	13.50	1.22	6.08
Alleppy	20	2.43	27.80	0.19	0.67	1.29	24.13	0.25	0.75
	50	2.13	25.53	0.13	2.32	0.52	21.56	0.11	2.01
	75	0.97	21.57	0.38	6.04	0.59	20.59	0.99	6.73
	100	0.72	20.16	0.26	8.19	0.38	18.71	2.06	12.30
	150	0.51	16.65	3.10	10.36	0.27	15.46	2.69	9.98
	200	0.41	14.08	3.06	7.43	0.26	18.07	3.33	10.11
Kollam	20	2.28	27.63	0.43	1.27	0.54	22.73	1.63	1.22
	50	2.18	25.17	2.34	8.96	0.42	22.03	0.02	1.26
	100	0.61	19.40	0.09	0.00	0.38	18.46	1.24	9.57
	200	0.39	14.19	6.18	8.87	0.30	14.67	6.56	11.07
Trivandrum	20	2.45	27.12	0.03	2.78	0.82	22.84	0.50	1.95
	50	2.16	25.99	0.02	1.27	0.68	22.26	0.02	1.12
	100	1.10	21.79	2.13	11.76	0.71	20.86	2.53	8.28
	200	0.47	13.79	2.33	10.76	0.29	14.10	2.93	9.52

Estuary

St.No	Depth (m)	D.O (ml/l)	Sal	Org.C (%)	CaCO3 (%)	D.O (ml/l)	Sal	Org.C (%)	$CaCO_3$ (%)
1	3.0	3.10	21.37	2.04	4.50	4.49	4.40	0.41	4.20
2	4.5	3.20	5.63	1.54	3.20	5.03	0.00	5.05	3.10
3	2.5	5.06	5.70	2.68	4.50	4.38	0.00	2.65	4.50
4	ND	3.31	13.44	2.48	3.80	5.05	0.00	4.18	3.10
5	1.5	2.95	22.12	0.62	8.40	4.81	0.12	0.50	6.30
6	ND	6.03	15.79	2.62	12.30	5.23	0.06	3.29	11.30
7	5.5	4.60	11.75	0.30	10.20	4.72	0.00	0.37	9.40
8	4.0	5.89	10.48	1.33	13.20	4.56	0.00	0.91	12.40
9	8.5	5.08	8.92	0.40	20.40	5.16	0.00	4.93	18.30

Annexure-V

Non-transition elements during monsoon (values in ppm).

Shelf

Transects	Depth (m)	Be	Ga	Rb	Sr	Cs	Ba	Pb	Al (%)
Manglore	20	0.95	11.82	42.78	231.80	2.58	112.25	9.28	10.76
	50	0.34	2.40	12.87	396.87	0.40	77.57	6.35	2.13
	100	0.74	3.60	15.11	1110.32	0.91	56.91	8.40	3.11
	200	1.13	3.83	8.95	949.70	0.57	37.56	7.28	2.80
Kannoore	20	1.24	14.09	42.06	59.22	2.71	119.63	24.59	12.72
	50	0.25	2.29	8.13	135.11	0.41	55.13	8.80	1.95
	100	1.03	5.35	21.63	1090.64	1.27	89.03	9.36	4.83
	200	1.16	4.13	14.26	1035.63	0.85	56.23	8.44	3.55
Baypore	20	1.57	13.73	40.88	143.76	2.60	119.24	13.00	13.56
	50	0.32	2.89	7.86	386.88	0.30	105.83	9.79	2.86
	75	0.23	2.22	6.87	388.36	0.33	69.26	5.28	2.03
	100	0.41	2.41	7.99	650.24	0.40	65.78	7.43	2.12
	150	0.45	1.46	4.81	1802.43	0.31	37.57	20.62	1.30
	200	1.05	4.76	15.32	812.69	0.98	53.19	6.34	3.81
Ponnani	20	1.26	14.66	43.03	133.66	2.79	126.82	10.69	14.34
	50	0.77	4.36	14.43	643.66	0.67	162.93	6.05	4.29
	100	0.51	1.99	6.99	1871.53	0.43	41.03	5.49	1.81
	200	0.68	1.78	3.74	1544.28	0.24	30.99	8.26	1.52
Cochin	20	0.45	1.90	10.07	145.19	0.06	225.23	17.66	1.85
	50	0.55	4.03	18.07	372.97	0.32	341.26	8.30	3.99
	75	0.54	4.13	14.13	467.39	0.34	212.89	9.11	2.95
	100	1.04	5.57	23.39	662.21	0.49	394.79	9.20	5.25
	150	2.08	5.86	9.30	786.06	0.46	64.94	6.12	4.73
	200	2.22	6.09	10.45	672.72	0.55	73.42	6.50	4.80
Alleppy	20	0.83	7.03	24.92	208.69	0.79	250.65	12.23	6.14
	50	0.55	3.01	11.06	301.86	0.34	159.27	8.53	2.73
	75	0.65	3.10	11.61	841.67	0.41	124.36	8.29	2.84
	100	0.25	1.50	4.54	2526.60	0.20	66.52	6.79	1.27
	150	0.93	3.07	6.98	1207.73	0.30	69.72	7.26	2.58
	200	1.01	3.45	9.13	1375.79	0.40	88.04	9.06	3.05
Kollam	20	1.77	13.03	46.98	400.06	2.08	311.10	29.46	12.93
	50	0.45	1.78	8.00	234.91	0.13	153.55	10.74	1.67
	100	0.49	2.86	12.88	1843.09	0.27	207.44	10.30	2.65
	200	0.40	2.28	8.69	1835.51	0.41	81.46	27.42	2.10
Trivandrum	20	0.57	1.82	2.91	373.82	0.10	90.36	30.33	1.07
	50	0.39	2.68	8.98	224.18	0.14	161.53	7.02	1.81
	100	0.78	3.10	9.79	1010.11	0.17	177.67	14.28	2.71
	200	0.78	3.01	9.48	1022.86	0.14	180.53	14.45	2.63

Estuary

St.No	Depth (m)	Be	Ga	Rb	Sr	Cs	Ba	Pb	Al (%)
1	3.0	1.05	8.43	34.51	479.10	0.08	1309.25	8.89	9.308
2	4.5	2.28	26.32	78.69	219.69	2.46	1034.35	69.55	21.733
3	2.5	1.87	20.60	76.39	263.06	1.16	999.83	24.18	14.653
4	ND	2.43	23.08	82.51	239.64	2.40	864.19	25.36	20.245
5	1.5	1.10	10.92	38.27	427.10	0.50	1193.94	11.32	11.386
6	ND	0.49	4.86	10.55	48.88	0.27	173.61	11.96	2.156
7	5.5	1.11	9.48	31.79	152.29	0.87	441.23	11.27	8.145
8	4.0	1.07	9.44	33.50	131.59	1.24	393.52	8.97	8.256
9	8.5	2.06	19.36	67.19	160.61	3.57	295.01	12.74	18.368

Annexure-VI

Non-transition elements during premonsoon (values in ppm).

Shelf

Transects	Depth (m)	Be	Rb	Sr	Cs	Ba	Pb	Ga	Al (%)
Manglore	20	1.46	44.82	192.49	2.81	115.66	8.07	13.27	12.83
	50	0.35	9.26	647.38	0.48	43.20	8.50	2.12	2.02
	100	0.75	15.11	1,123.96	0.91	60.00	6.05	3.69	3.17
	200	1.61	12.82	1,058.26	0.84	50.97	8.45	4.79	3.97
Kannoore	20	1.48	41.44	172.28	2.52	122.19	8.32	13.63	13.43
	50	0.45	8.81	187.93	0.51	52.53	12.24	2.74	2.46
	100	0.81	16.66	902.82	0.96	76.58	8.96	4.36	4.07
	200	0.90	16.92	939.24	0.98	65.07	10.06	4.47	3.88
Baypore	20	1.33	32.51	246.21	1.77	225.41	7.86	10.76	10.91
	50	0.83	11.79	587.15	0.56	135.92	7.91	4.34	4.43
	75	0.50	7.58	474.86	0.37	77.25	8.01	2.68	2.48
	100	0.98	10.46	764.11	0.57	69.62	10.22	3.46	3.24
	150	1.02	10.45	1,213.94	0.66	61.75	14.74	3.78	3.11
	200	0.49	9.68	542.62	0.62	38.71	3.85	2.92	2.16
Ponnani	20	1.19	43.79	135.67	2.92	146.81	8.88	14.69	13.55
	50	0.49	13.42	675.16	0.62	186.68	6.03	3.69	3.39
	100	0.71	8.58	2,212.68	0.51	82.96	18.31	2.59	2.16
	200	1.02	21.21	1,074.14	1.34	129.50	25.21	5.71	4.66
Cochin	20	0.31	8.54	102.41	0.16	203.22	4.86	2.09	1.78
	50	0.38	14.10	404.06	0.28	359.82	16.14	3.13	3.12
	75	0.53	26.39	573.30	0.36	562.37	12.41	5.48	4.03
	100	0.78	24.75	692.69	0.51	495.14	7.71	5.71	5.23
	150	1.37	7.98	911.16	0.41	63.33	5.93	5.27	3.60
	200	1.71	9.35	748.83	0.50	75.30	6.97	5.63	4.07
Alleppy	20	0.51	25.15	170.61	0.91	284.30	7.38	5.98	5.35
	50	0.45	12.61	352.68	0.39	212.81	8.32	3.24	2.63
	75	0.46	16.16	876.89	0.42	203.26	7.31	3.30	2.74
	100	0.30	10.20	1,399.70	0.18	186.06	9.48	2.27	1.71
	150	0.90	11.42	1,472.21	0.47	138.52	11.43	3.30	2.82
	200	0.68	11.59	1,520.66	0.46	143.71	17.90	3.32	2.76
Kollam	20	1.19	41.73	385.13	1.34	578.27	17.70	11.27	10.18
	50	1.22	14.97	1,220.00	0.92	81.20	8.68	4.66	3.77
	100	0.33	15.67	984.40	0.19	324.13	17.82	5.45	2.70
	200	0.41	10.00	1,739.81	0.51	102.07	10.22	2.38	2.04
Trivandrum	20	0.35	4.39	442.31	0.12	105.21	12.56	2.29	1.17
	50	0.33	10.55	253.81	0.14	240.08	12.67	3.12	1.69
	100	0.38	8.34	1,976.51	0.26	136.62	6.08	1.87	1.70
	200	1.11	6.01	1,331.41	0.30	70.21	9.77	2.66	2.25

Estuary

St.No	Depth (m)	Be	Ga	Rb	Sr	Cs	Ba	Pb	Al (%)
1	3.0	0.92	7.96	33.93	488.08	0.10	1358.79	9.47	8.72
2	4.5	2.41	26.08	79.41	169.91	2.55	1026.91	36.87	20.50
3	2.5	2.29	21.26	75.52	285.60	1.68	1051.46	33.03	16.95
4	ND	2.29	23.17	82.90	328.87	2.41	896.05	558.08	20.12
5	1.5	1.26	10.99	37.81	525.70	0.47	1288.14	201.02	11.76
6	ND	0.49	4.43	10.65	45.97	0.30	180.80	9.69	2.18
7	5.5	1.18	9.62	33.29	139.58	0.93	456.16	9.53	7.29
8	4.0	0.55	1.67	6.76	115.76	0.13	189.47	77.69	1.46
9	8.5	1.70	16.72	58.47	174.34	3.01	309.58	13.72	15.91

Annexure-VII

Transition elements during monsoon (values in ppm).

Shelf

Transects	Depth (m)	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	Fe (%)
Manglore	20	11.70	67.47	147.34	324.48	9.69	62.99	27.15	86.60	19.35	77.91	6.21	1.43	2.33	0.59	5.80
	50	3.80	23.87	54.14	523.26	3.62	19.56	10.29	38.32	11.92	62.97	2.00	0.62	1.78	0.17	1.90
	100	6.85	78.67	87.25	447.32	6.67	41.37	17.16	51.01	18.52	31.26	2.45	1.52	0.89	0.19	5.78
	200	5.32	44.35	84.99	213.59	7.17	39.75	13.03	40.30	12.06	12.58	1.15	0.87	0.43	0.11	7.33
Kannoore	20	12.73	72.61	182.22	275.86	10.36	73.67	30.83	86.21	21.00	71.85	6.69	1.67	2.19	0.62	6.54
	50	3.18	17.43	47.89	127.70	2.22	16.87	11.15	48.01	5.55	31.69	2.87	0.96	0.95	0.21	1.24
	100	7.48	40.13	99.51	301.56	6.83	53.96	20.99	56.86	18.32	42.24	3.32	0.94	1.28	0.32	3.51
	200	5.78	52.24	85.62	277.23	6.94	45.09	17.05	52.46	13.54	22.83	2.03	1.06	0.69	0.18	5.53
Baypore	20	13.37	78.13	180.04	266.80	10.77	74.73	29.44	86.19	21.68	57.10	6.54	1.42	1.79	0.60	6.92
	50	3.12	25.83	50.81	258.19	2.97	20.68	13.17	50.99	5.70	14.97	2.22	0.59	0.45	0.16	1.65
	75	3.44	21.46	58.49	159.74	3.03	21.24	11.79	44.62	5.99	32.29	2.22	0.76	0.97	0.17	1.62
	100	3.84	28.46	53.04	257.53	3.66	24.82	12.19	53.65	11.75	26.79	2.85	0.65	0.80	0.23	2.16
	150	3.64	38.36	49.49	191.28	3.09	31.46	11.36	24.25	12.49	6.87	0.86	0.97	0.23	0.07	3.01
	200	5.81	49.35	93.44	188.64	7.43	44.07	16.70	47.49	12.15	19.28	1.88	1.29	0.66	0.18	6.88
Ponnani	20	14.41	77.80	181.16	255.96	11.59	78.00	31.85	90.16	22.73	57.44	6.77	1.56	1.75	0.64	7.16
	50	5.08	36.14	78.28	573.04	6.40	31.53	12.67	50.01	12.67	27.37	2.89	0.73	0.84	0.23	3.51
	100	3.97	39.77	52.10	225.49	3.85	35.45	11.82	33.53	12.34	10.25	1.12	0.86	0.34	0.10	2.93
	200	4.59	44.85	57.62	225.18	4.84	32.06	10.75	25.61	14.26	8.17	0.75	1.00	0.28	0.07	4.98
Cochin	20	2.26	12.74	29.25	89.86	1.05	9.47	9.89	49.02	2.53	21.53	3.82	0.62	0.63	0.25	0.77
	50	3.62	28.13	51.52	237.62	2.81	21.93	11.52	72.10	7.47	29.67	7.48	0.82	0.91	0.49	2.01
	75	5.23	47.00	57.67	594.66	4.38	22.93	18.31	181.07	10.85	97.90	20.78	1.16	2.93	1.35	3.39
	100	4.98	27.38	65.42	243.14	4.67	28.94	12.81	69.57	12.26	92.02	5.81	0.83	2.59	0.38	2.93
	150	7.53	64.94	102.83	243.72	10.84	38.05	11.03	59.80	13.85	20.61	1.94	1.08	0.70	0.25	11.12
	200	8.06	47.70	106.31	208.00	10.58	36.64	11.19	75.79	12.46	19.01	1.95	1.03	0.66	0.24	11.62
Alleppy	20	6.91	49.91	84.83	214.09	4.85	28.72	17.55	117.59	13.68	82.06	13.01	1.20	2.59	0.92	3.54
	50	3.58	25.71	53.82	144.29	2.45	18.97	11.32	62.47	6.31	28.35	7.04	0.70	0.88	0.49	2.20
	75	4.14	28.20	72.08	119.83	3.05	37.10	12.93	63.28	10.22	19.93	5.11	1.53	0.68	0.39	2.26
	100	3.69	32.63	48.74	156.28	2.46	32.36	10.90	56.35	10.85	87.67	6.14	0.76	2.53	0.44	1.88
	150	3.94	33.59	72.36	89.20	3.70	37.00	10.77	41.83	11.75	15.10	1.30	0.91	0.47	0.12	4.91
	200	4.43	41.99	95.39	98.89	4.23	50.98	13.70	50.79	12.66	14.26	1.71	1.95	0.47	0.14	4.92
Kollam	20	12.36	77.00	157.33	316.02	9.77	64.12	25.23	146.13	26.14	68.01	12.60	1.50	2.07	0.83	7.12
	50	2.49	23.29	54.23	89.64	1.53	20.18	10.29	51.27	3.21	21.38	5.82	1.54	0.64	0.40	1.05
	100	3.66	31.22	68.61	129.74	2.98	39.94	13.98	56.12	10.05	36.79	4.72	1.70	1.13	0.35	1.93
	200	3.49	20.03	82.72	59.19	2.82	49.34	13.93	31.96	11.92	13.12	1.30	2.79	0.44	0.11	2.11
Trivandrum	20	3.11	36.75	51.41	157.73	1.82	16.52	13.27	87.41	5.52	27.93	8.75	0.86	0.86	0.66	2.15
	50	3.35	31.96	46.19	158.57	2.36	12.60	12.23	109.74	5.78	35.78	15.41	0.72	1.12	1.05	1.53
	100	3.87	19.61	40.00	68.71	1.87	28.38	26.91	32.69	9.15	12.03	1.95	0.59	0.40	0.27	1.36
	200	4.09	56.40	95.32	78.35	3.47	40.18	11.36	33.60	14.67	9.29	1.07	1.01	0.31	0.10	5.48

Estuary

St.No	Depth (m)	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	Fe (%)
1	3.0	5.12	27.47	47.84	197.16	3.03	12.08	8.23	34.49	6.46	10.31	2.74	0.23	0.32	0.21	1.30
2	4.5	25.24	166.64	250.92	728.83	22.08	83.25	69.90	707.63	43.99	76.12	16.41	1.72	2.21	1.09	11.05
3	2.5	18.55	147.38	209.41	429.57	15.15	57.19	55.35	1024.27	32.33	69.38	14.81	1.10	1.97	0.97	10.64
4	ND	22.01	135.45	208.13	398.96	18.78	78.15	63.60	1129.23	51.71	66.75	14.01	1.15	1.99	0.91	10.30
5	1.5	7.58	44.50	64.71	287.07	6.49	23.76	13.41	63.92	10.35	28.79	5.02	0.31	0.82	0.52	2.68
6	ND	5.74	54.12	60.90	248.61	4.19	9.90	16.55	159.17	8.66	81.98	27.28	0.59	2.15	1.46	1.76
7	5.5	8.71	56.25	76.57	421.07	12.80	26.77	20.15	111.46	12.59	74.94	13.23	0.70	1.97	0.90	4.01
8	4.0	8.82	49.49	75.97	508.27	14.22	31.28	22.84	80.44	16.56	46.21	8.69	1.49	1.24	1.11	4.62
9	8.5	20.35	116.41	226.63	508.58	15.62	98.09	37.70	146.23	33.13	71.73	10.69	1.45	2.10	1.41	9.08

Annexure-VIII

Transition elements during premonsoon (values in ppm).

Shelf

Transects	Depth (m)	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	Fe (%)
Manglore	20	13.10	72.61	162.60	344.28	10.80	68.81	30.04	106.77	20.86	86.34	6.82	1.28	2.61	0.70	6.70
	50	3.64	27.34	50.31	307.85	3.10	24.78	10.92	42.03	8.87	36.21	1.84	0.50	1.28	0.17	1.89
	100	6.10	61.67	88.64	473.84	6.33	42.14	16.32	55.83	17.21	34.46	2.54	1.26	1.04	0.24	5.58
	200	6.09	55.14	118.05	225.05	8.22	50.07	17.19	53.17	14.44	18.37	1.66	1.01	0.62	0.16	8.66
Kannoore	20	12.99	77.80	178.30	320.26	10.57	72.26	28.96	101.17	21.74	85.95	6.96	1.38	2.67	0.72	6.76
	50	3.34	22.66	62.23	158.67	2.93	19.47	11.29	54.59	5.62	36.30	3.30	0.86	1.15	0.31	1.85
	100	5.22	34.83	82.67	254.90	5.63	43.56	17.71	61.05	15.45	39.11	2.53	0.68	1.23	0.22	3.16
	200	5.64	57.67	89.23	245.00	6.29	43.26	17.99	54.60	14.44	32.91	2.55	0.99	0.99	0.24	5.05
Baypore	20	9.97	55.91	131.17	333.01	8.30	49.35	21.41	99.16	15.99	75.88	5.53	1.81	2.31	0.50	5.23
	50	4.96	33.63	70.87	398.25	5.04	29.21	12.68	55.01	10.60	25.12	2.91	0.64	0.78	0.25	3.16
	75	3.46	26.55	73.05	214.93	3.55	31.39	13.52	50.85	8.78	30.20	2.57	1.48	0.97	0.21	2.07
	100	5.17	43.26	92.36	469.25	7.39	43.40	16.87	75.41	12.96	38.10	3.72	1.52	1.14	0.28	4.16
	150	6.67	52.73	88.52	276.79	9.30	47.38	16.19	48.63	15.96	17.90	1.63	0.94	0.52	0.15	8.29
	200	4.25	32.41	60.74	109.74	4.48	29.52	10.13	32.55	7.40	14.53	1.13	0.52	0.46	0.13	5.18
Ponnani	20	15.68	77.41	178.48	238.85	11.49	78.32	34.31	95.65	23.29	65.28	7.32	1.05	1.87	0.60	6.94
	50	4.84	31.67	64.27	492.13	4.62	28.50	12.25	46.54	11.90	26.38	2.79	0.49	0.73	0.20	2.88
	100	5.46	39.67	60.17	367.65	6.56	43.21	13.39	42.41	16.43	13.92	1.42	0.68	0.48	0.12	4.12
	200	7.71	58.17	109.66	257.43	9.51	55.35	20.72	79.57	15.44	26.20	2.72	0.91	0.81	0.23	8.00
Cochin	20	2.73	14.76	28.69	128.74	1.48	8.64	6.79	50.41	3.94	26.06	7.20	0.41	0.71	0.48	1.05
	50	3.05	16.62	41.98	139.72	1.98	17.36	9.94	42.43	5.39	21.56	2.46	0.42	0.58	0.15	1.29
	75	6.15	48.24	66.75	456.35	4.61	24.44	18.55	143.26	13.33	79.02	19.22	0.80	2.29	1.10	3.37
	100	5.76	25.46	63.15	267.59	5.23	27.72	12.29	73.82	13.08	104.77	6.38	0.49	2.87	0.41	3.17
	150	6.57	42.29	79.01	219.78	8.58	33.04	10.66	52.01	13.33	15.40	1.71	0.68	0.52	0.13	10.10
	200	6.64	46.67	96.21	207.43	9.96	35.92	13.67	65.19	13.38	21.69	1.72	0.66	0.69	0.13	11.05
Alleppy	20	6.31	36.36	73.22	168.25	4.25	26.43	14.84	82.40	11.27	52.80	8.76	1.34	1.44	0.60	2.93
	50	3.96	25.94	57.46	119.00	2.51	20.48	13.25	59.25	7.41	53.58	8.21	0.56	1.52	0.48	2.13
	75	4.65	25.76	61.06	128.10	2.96	29.52	13.51	67.24	10.95	46.19	7.93	0.60	1.22	0.52	2.13
	100	4.68	30.90	43.85	177.76	2.75	23.89	11.50	75.38	10.72	78.70	11.93	0.50	2.25	0.76	1.81
	150	4.77	22.17	87.44	88.76	3.87	49.43	13.08	40.34	13.10	20.95	2.10	1.34	0.59	0.20	3.62
	200	4.30	22.23	85.69	88.18	3.63	43.01	13.49	43.78	13.13	21.34	2.25	0.83	0.64	0.17	3.47
Kollam	20	10.49	65.83	133.02	356.37	8.20	50.67	21.67	108.15	23.00	115.03	13.96	1.37	3.20	0.85	5.18
	50	6.52	50.23	115.77	298.27	7.81	58.46	17.62	50.83	15.98	26.56	2.13	1.18	0.77	0.18	7.03
	100	8.52	81.39	87.61	542.19	5.42	29.63	21.90	239.79	15.61	181.42	39.47	1.68	4.95	2.31	3.62
	200	3.91	20.98	79.38	59.42	2.84	48.69	15.25	27.69	13.04	13.93	1.66	1.42	0.43	0.12	1.95
Trivandrum	20	3.26	37.59	68.15	108.55	2.08	21.52	12.07	87.64	8.14	40.32	15.31	0.98	1.11	1.13	1.94
	50	3.74	33.19	55.44	186.53	2.45	18.04	13.28	118.88	7.04	82.49	20.50	0.92	2.30	1.45	1.56
	100	3.49	20.32	48.91	89.30	2.40	34.80	10.92	35.19	12.52	29.35	2.68	0.46	0.94	0.18	1.57
	200	6.84	105.93	231.24	87.58	4.33	56.18	16.80	42.67	33.10	15.66	2.45	1.72	0.48	0.15	7.77

Estuary

St.No	Depth (m)	Sc	V	Cr	Mn	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Hf	Ta	Fe (%)
1	3.0	3.84	24.66	31.96	148.28	2.81	11.17	7.61	29.43	4.47	24.71	2.09	0.43	0.37	0.13	1.10
2	4.5	23.98	179.34	247.63	727.09	21.87	82.89	69.10	730.68	43.65	69.27	16.41	1.68	2.11	1.09	10.75
3	2.5	22.54	153.83	219.96	449.75	15.68	57.92	58.11	1070.64	37.55	115.22	15.04	1.12	3.35	1.03	11.34
4	ND	22.14	128.79	208.74	409.18	18.68	81.52	65.64	1150.07	52.66	68.43	14.18	1.26	2.10	1.00	10.31
5	1.5	6.95	35.44	61.71	264.65	5.99	24.67	13.32	75.31	10.11	39.56	4.35	0.38	1.16	0.32	2.43
6	ND	5.44	50.92	56.09	235.57	4.19	9.99	16.01	149.39	6.01	88.99	27.02	0.63	2.41	1.54	1.76
7	5.5	8.12	59.99	80.59	416.17	13.29	27.71	19.35	110.05	13.03	57.31	15.65	0.76	1.51	0.98	4.03
8	4.0	2.64	25.61	34.69	119.55	2.67	15.27	10.52	47.20	1.96	10.44	4.40	0.79	0.29	0.20	0.70
9	8.5	17.13	97.45	193.33	607.45	14.24	83.58	35.18	144.49	29.01	69.25	9.08	1.24	2.00	0.66	7.99

Annexure-IX

Rare-earth elements during monsoon (values in ppm).

Shelf																	
Transects	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Manglore	20	20.65	44.89	4.35	17.85	3.68	0.89	3.16	0.55	3.27	0.69	1.97	0.28	1.66	0.25	6.39	2.46
	50	11.21	22.97	2.50	11.02	2.45	0.52	2.12	0.38	2.04	0.40	1.13	0.14	0.84	0.12	2.56	1.11
	100	14.35	30.42	3.30	14.31	3.20	0.75	2.80	0.52	2.99	0.63	1.79	0.24	1.43	0.20	3.93	1.96
	200	9.01	20.24	2.22	9.83	2.20	0.53	1.91	0.35	2.03	0.41	1.13	0.16	0.92	0.13	2.77	1.49
Kannoore	20	23.45	52.06	4.89	20.60	4.13	1.01	3.66	0.63	3.70	0.77	2.25	0.32	1.90	0.29	6.76	2.21
	50	7.84	16.43	1.75	7.53	1.55	0.28	1.30	0.21	1.09	0.20	0.55	0.07	0.43	0.06	2.44	0.89
	100	17.81	36.46	3.93	16.62	3.44	0.82	3.00	0.52	2.94	0.61	1.71	0.23	1.40	0.21	4.56	2.18
	200	12.48	27.30	2.93	12.62	2.67	0.65	2.32	0.42	2.30	0.48	1.31	0.18	1.06	0.15	3.49	1.69
Baypore	20	24.56	54.15	5.15	21.28	4.26	1.08	3.73	0.64	3.69	0.76	2.24	0.32	1.85	0.28	6.65	2.07
	50	6.89	13.77	1.39	5.77	1.20	0.36	0.98	0.17	0.95	0.19	0.53	0.07	0.42	0.06	1.65	0.76
	75	6.58	13.09	1.38	5.54	1.17	0.30	1.04	0.18	0.99	0.23	0.61	0.08	0.47	0.07	1.44	0.95
	100	13.73	26.76	2.97	12.52	2.60	0.59	2.25	0.38	2.05	0.42	1.14	0.15	0.86	0.12	2.78	1.12
	150	10.31	22.85	2.49	10.94	2.40	0.59	2.18	0.37	2.11	0.43	1.21	0.17	0.90	0.13	1.91	1.51
	200	12.14	26.96	2.85	12.03	2.48	0.58	2.17	0.39	2.11	0.44	1.21	0.17	0.97	0.14	3.44	1.95
Ponnani	20	26.23	58.04	5.51	23.20	4.59	1.11	3.93	0.69	3.86	0.81	2.38	0.33	1.97	0.29	6.81	2.15
	50	18.09	38.42	3.77	15.56	2.96	0.70	2.50	0.40	2.13	0.42	1.22	0.17	0.92	0.14	5.22	1.34
	100	11.66	26.32	2.76	12.33	2.50	0.63	2.30	0.40	2.18	0.44	1.22	0.17	0.95	0.13	2.20	1.81
	200	10.83	25.27	2.71	11.85	2.66	0.68	2.49	0.44	2.48	0.51	1.40	0.18	1.07	0.16	2.27	1.75
Cochin	20	18.71	30.04	2.51	8.90	1.31	0.34	1.09	0.13	0.49	0.09	0.29	0.03	0.21	0.03	6.58	0.55
	50	37.47	66.04	6.15	23.39	3.79	0.76	3.09	0.38	1.62	0.27	0.80	0.09	0.50	0.08	15.43	1.30
	75	161.03	256.67	21.63	73.13	7.73	0.74	7.86	0.76	2.61	0.38	1.43	0.12	0.79	0.12	99.10	2.11
	100	58.45	101.03	8.98	32.60	4.79	0.95	4.16	0.52	2.37	0.43	1.32	0.16	0.96	0.14	22.54	2.19
	150	18.02	45.06	4.31	18.47	3.67	0.81	3.13	0.51	2.62	0.51	1.44	0.18	1.06	0.15	6.00	1.62
	200	16.31	40.07	3.88	16.33	3.19	0.75	2.73	0.45	2.41	0.47	1.25	0.17	0.99	0.15	5.78	1.47
Alleppy	20	75.99	143.55	13.90	53.47	7.89	0.81	6.33	0.74	2.89	0.50	1.60	0.17	1.03	0.16	38.33	2.80
	50	38.26	64.44	5.62	19.70	2.50	0.42	2.27	0.28	1.17	0.21	0.66	0.08	0.47	0.07	18.06	1.13
	75	27.33	48.96	4.61	16.98	2.73	0.47	2.39	0.34	1.68	0.33	1.02	0.13	0.73	0.11	9.77	2.02
	100	34.68	61.63	5.85	22.31	3.58	0.44	3.15	0.41	1.83	0.34	1.05	0.13	0.82	0.12	13.53	3.31
	150	13.13	25.96	2.72	11.10	2.16	0.49	1.92	0.33	1.81	0.37	1.09	0.15	0.84	0.12	4.34	2.53
	200	11.63	23.12	2.57	10.87	2.27	0.55	1.98	0.34	1.87	0.40	1.12	0.15	0.90	0.14	3.50	2.51
Kollam	20	39.28	80.08	7.95	31.93	5.99	1.40	5.02	0.78	4.42	0.90	2.62	0.37	2.11	0.30	11.08	2.74
	50	10.11	18.82	1.84	6.89	1.20	0.28	0.89	0.12	0.62	0.11	0.35	0.04	0.26	0.04	4.53	0.76
	100	24.30	43.62	4.20	15.91	2.63	0.56	2.27	0.33	1.59	0.33	0.98	0.13	0.72	0.12	10.41	2.33
	200	10.29	17.98	2.10	8.98	1.80	0.44	1.62	0.28	1.69	0.35	1.03	0.14	0.86	0.13	2.72	3.06
Trivandrum	20	19.25	41.87	4.52	18.26	3.40	0.27	2.63	0.35	1.36	0.21	0.61	0.07	0.42	0.06	11.52	1.74
	50	63.57	125.85	12.71	49.43	7.64	0.38	5.63	0.57	1.76	0.22	0.81	0.06	0.44	0.06	36.60	3.29
	100	10.91	22.11	2.20	9.16	1.71	0.33	1.52	0.23	1.33	0.28	0.82	0.11	0.63	0.10	4.57	1.77
	200	10.97	21.13	2.41	10.11	2.07	0.46	1.96	0.35	2.08	0.43	1.31	0.19	1.03	0.16	4.89	2.97

Estuary																	
St.No	Depth (m	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
1	3.0	9.80	16.14	1.63	7.12	2.17	1.22	1.19	0.18	1.07	0.21	0.56	0.09	0.46	0.07	0.57	0.42
2	4.5	105.71	204.76	19.13	75.42	12.53	2.39	10.62	1.46	7.33	1.38	4.26	0.56	3.18	0.51	35.66	10.19
3	2.5	73.62	140.88	13.27	52.57	9.19	1.85	7.45	1.02	5.16	0.98	2.97	0.42	2.38	0.37	23.97	8.04
4	ND	95.40	179.71	17.52	70.98	11.84	2.31	10.05	1.42	7.65	1.45	4.39	0.61	3.40	0.53	26.41	9.69
5	1.5	18.32	31.46	3.14	12.91	3.11	1.37	2.06	0.31	1.75	0.33	1.01	0.14	0.78	0.13	2.49	0.81
6	ND	89.37	180.09	18.11	71.48	10.53	0.50	8.03	0.82	2.54	0.32	1.19	0.10	0.59	0.09	50.08	3.93
7	5.5	40.37	80.20	7.46	29.42	4.90	1.00	3.96	0.51	2.50	0.43	1.32	0.17	0.96	0.15	17.02	3.81
8	4.0	39.42	80.84	7.59	31.24	5.51	1.04	4.56	0.63	3.06	0.55	1.58	0.22	1.22	0.18	12.99	4.58
9	8.5	48.02	98.90	9.31	38.31	7.04	1.68	6.21	0.99	5.57	1.13	3.14	0.45	2.54	0.39	11.65	3.33

Annexure-X

Rare-earth elements during premonsoon (values in ppm).

Shelf

Transects	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
Manglore	20	22.43	48.98	4.73	19.60	3.97	0.97	3.59	0.62	3.57	0.75	2.20	0.32	1.92	0.29	7.50	2.75
	50	7.39	15.06	1.66	7.39	1.59	0.38	1.39	0.25	1.46	0.31	0.84	0.12	0.71	0.11	1.67	1.13
	100	13.88	29.17	3.19	14.15	3.02	0.74	2.74	0.49	2.95	0.61	1.72	0.24	1.43	0.21	3.33	1.98
	200	11.08	24.45	2.73	11.88	2.57	0.64	2.25	0.42	2.36	0.51	1.44	0.18	1.12	0.17	3.36	2.27
Kannoore	20	23.99	52.23	5.03	21.08	4.23	1.02	3.70	0.64	3.60	0.78	2.22	0.32	1.99	0.30	6.85	2.63
	50	7.04	15.01	1.42	5.81	1.11	0.27	1.00	0.17	0.96	0.20	0.62	0.08	0.53	0.08	1.99	1.04
	100	14.76	30.46	3.23	13.73	2.81	0.69	2.49	0.44	2.54	0.52	1.47	0.20	1.23	0.18	3.44	1.77
	200	14.94	30.92	3.30	13.70	2.81	0.67	2.52	0.44	2.45	0.50	1.43	0.20	1.21	0.17	3.86	1.73
Baypore	20	22.44	45.42	4.43	18.23	3.57	0.99	3.12	0.51	2.81	0.56	1.72	0.23	1.43	0.21	6.36	2.33
	50	12.92	26.32	2.62	10.73	2.24	0.61	1.95	0.32	1.79	0.36	1.08	0.14	0.80	0.13	2.82	1.26
	75	21.27	40.70	4.02	15.80	2.62	0.44	2.29	0.34	1.62	0.30	0.87	0.11	0.62	0.10	4.41	1.01
	100	17.25	36.62	3.74	16.07	3.08	0.71	2.73	0.45	2.41	0.47	1.29	0.17	0.99	0.15	3.85	1.65
	150	15.34	34.90	3.49	15.57	3.23	0.78	2.77	0.50	2.88	0.55	1.56	0.21	1.21	0.19	4.06	1.85
	200	7.09	15.45	1.62	7.05	1.43	0.33	1.24	0.22	1.30	0.25	0.73	0.10	0.59	0.09	2.07	1.01
Ponnani	20	27.08	59.97	5.46	23.37	4.49	1.10	3.93	0.67	4.07	0.80	2.30	0.34	1.98	0.30	7.53	2.38
	50	17.11	35.71	3.45	14.62	2.76	0.61	2.31	0.36	2.06	0.38	1.12	0.15	0.85	0.13	5.99	1.59
	100	17.42	39.47	4.04	17.97	3.57	0.88	3.08	0.55	3.05	0.57	1.62	0.22	1.22	0.18	3.18	2.34
	200	16.55	36.29	3.62	15.91	3.21	0.77	2.75	0.47	2.73	0.52	1.46	0.22	1.15	0.18	4.91	2.39
Cochin	20	38.79	65.48	5.45	19.05	2.27	0.31	2.01	0.22	0.89	0.14	0.46	0.05	0.28	0.04	13.08	0.72
	50	12.82	22.77	2.08	8.14	1.47	0.50	1.12	0.17	0.90	0.17	0.52	0.07	0.39	0.06	3.78	0.83
	75	213.45	341.00	29.24	106.73	10.94	1.12	10.16	0.99	3.45	0.46	1.75	0.15	0.87	0.13	80.09	1.76
	100	62.78	109.43	9.85	36.64	5.47	0.99	4.57	0.58	2.64	0.44	1.33	0.17	0.97	0.15	32.76	2.27
	150	20.89	47.96	4.43	18.98	3.57	0.75	3.05	0.49	2.57	0.49	1.32	0.18	1.01	0.14	7.20	1.79
	200	19.52	46.51	4.30	18.05	3.39	0.77	2.92	0.47	2.52	0.48	1.39	0.18	1.01	0.15	6.81	1.47
Alleppy	20	31.57	60.83	5.71	21.95	3.73	0.68	2.97	0.41	2.02	0.38	1.15	0.15	0.88	0.14	12.96	2.54
	50	27.45	46.83	4.07	15.02	2.20	0.44	1.90	0.26	1.31	0.24	0.73	0.10	0.54	0.09	13.57	1.89
	75	22.36	42.01	4.10	16.85	3.11	0.56	2.60	0.38	1.86	0.36	0.97	0.13	0.71	0.12	9.12	2.08
	100	43.77	74.34	6.52	24.23	3.12	0.49	2.81	0.36	1.77	0.32	1.00	0.13	0.77	0.11	16.37	2.29
	150	22.14	40.03	3.97	16.36	2.77	0.55	2.38	0.37	2.01	0.39	1.11	0.16	0.88	0.14	9.00	2.74
	200	14.54	26.67	2.78	11.75	2.27	0.55	2.02	0.34	1.97	0.41	1.14	0.16	0.92	0.15	4.53	2.86
Kollam	20	71.00	137.82	13.46	54.57	8.88	1.39	6.96	0.90	4.27	0.77	2.32	0.30	1.77	0.27	31.97	3.60
	50	15.03	33.01	3.42	14.66	3.08	0.74	2.74	0.47	2.77	0.54	1.50	0.21	1.28	0.18	4.39	2.07
	100	258.15	431.61	37.20	133.05	14.01	0.90	13.43	1.26	4.33	0.56	2.06	0.16	0.95	0.15	139.45	2.74
	200	11.43	19.57	2.23	9.44	1.86	0.45	1.67	0.30	1.82	0.37	1.03	0.15	0.88	0.14	3.26	2.70
Trivandrum	20	35.12	72.48	7.38	30.06	5.03	0.34	3.80	0.45	1.82	0.29	0.85	0.10	0.59	0.08	23.11	2.29
	50	88.68	184.14	18.86	76.14	10.46	0.43	7.60	0.75	2.26	0.26	1.03	0.07	0.51	0.08	68.28	3.14
	100	20.86	37.77	3.71	14.61	2.49	0.45	2.19	0.33	1.82	0.36	1.09	0.15	0.82	0.12	9.14	2.44
	200	18.02	32.77	3.74	17.14	3.54	0.84	3.49	0.65	4.16	0.88	2.52	0.36	2.15	0.33	6.41	8.75

Estuary

St.No	Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
1	3.0	8.66	13.41	1.32	5.60	1.83	1.23	0.83	0.13	0.77	0.14	0.43	0.06	0.35	0.06	0.79	0.28
2	4.5	105.50	204.31	19.00	75.56	12.62	2.35	10.48	1.48	7.48	1.38	4.16	0.57	3.20	0.49	43.08	10.48
3	2.5	84.47	156.33	15.61	62.73	10.65	2.12	8.55	1.19	6.23	1.15	3.46	0.48	2.76	0.43	23.80	9.04
4	ND	98.93	184.43	17.90	72.47	12.35	2.37	10.37	1.48	7.78	1.52	4.47	0.62	3.54	0.55	27.77	9.99
5	1.5	29.29	49.26	4.48	17.41	3.38	1.46	2.37	0.33	1.76	0.34	1.03	0.14	0.80	0.12	4.53	0.98
6	ND	59.72	112.19	10.53	40.64	5.41	0.41	4.35	0.45	1.63	0.22	0.78	0.08	0.44	0.07	32.23	2.50
7	5.5	33.78	64.01	5.80	22.81	4.03	1.05	3.25	0.47	2.37	0.43	1.32	0.17	1.01	0.15	10.52	3.82
8	4.0	4.79	9.33	0.84	3.36	0.69	0.24	0.46	0.07	0.35	0.07	0.19	0.03	0.16	0.03	1.21	0.48
9	8.5	44.07	89.59	8.40	34.90	6.39	1.54	5.56	0.88	4.94	0.95	2.80	0.40	2.27	0.35	10.43	2.76

List of Publications

[1] **Laluraj.C.M.**, Padma.P, Sujatha.C.H, N.C.Kumar, J.Chacko and S.M.Nair. (2002). Base-Line Studies on the Chemical Constituents of Kayamkulam Estuary Near to the Newly Commissioned NTPC Power Station. **Indian Journal of Environmental Protection,** 22, 721-731.

[2] **Laluraj.C.M.**, Girish Gopinath and Dinesh Kumar. P.K. (2005). Groundwater chemistry of shallow Aquifers in the coastal zones of Cochin, India. **Applied Ecology and Environmental Research,** 3(1), 133-139.

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Base - line Studies on the Chemical Constituents of Kayamkulam Estuary Near to the Newly Commissioned NTPC Power Station

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The objective of this study was to evaluate the back - ground levels of various hydrochemical parameters along with some major ions in the Kayamkulam estuary, one among the largest backwater system in the south west coast of India, nearer to the newly commissioning National Thermal Power Plant, in view of assessing the future pollutional load, if any. The ratio of Na, Mg, Ca, K and SO_4^{2-} with chlorinity are quite comparable with those in marine water and indicated considerable conservative character. Nitrites values were low. But nitrates, urea and phosphate concentrations were typically esturine. Silicates concentration remained moderately high.

INTRODUCTION

The circumstances of the natural environment are facing significant deterioration owing to the speedy advancement in science and technology coupled with the terrifying growth in population. An important ecological characteristics of estuaries and their associated-marshes is the biological and chemical variability seen at a wide range of temporal and spatial scales (Wolfe, 1986). The basic influences on esturine chemical processes are essentially related to the compositional gradients associated with fresh water dilution.

Kayamkulam lake, one among the largest backwater systems in the south west coast of India provides the nursery grounds for several marine prawns. The sandy bar of the Kayamkulam estuary is situated almost midway between northern and southern ends. The Kayamkulam estuary differs from a typical estuary since the barmouth, witch opens to the Arabians sea, remains closed by a sand bar for a period of almost 3 month in the summer. Domestic sewage, agricultural runoff and the effluents from the retting grounds are the main source of pollutants in this area.

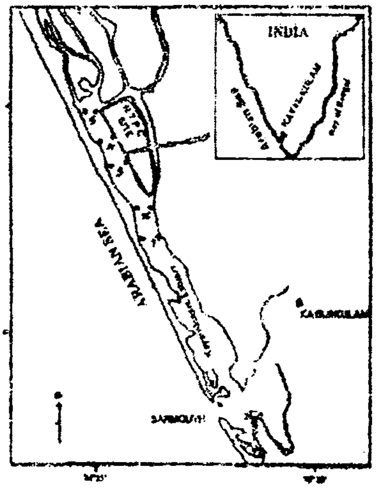

Figure 1. *Location of the study area and sampling stations*

The present study is worthy of attraction in the view of the newly establishing gas based thermal power project, stationed at Kayamkulam estuary. Very few studies have been carried out on the biogeochemical aspect of Kayamkulam estuary. In 1997, Sivankutty Nair (1997) made a study on the hydrography of the estuary. Biological studies on the distribution of prawn larvae in Kayamkulam estuary were reported by Kuttiyamma (1980) and Gopakumar (1991). Padmalal *et al.* (1997) recently published some of the sedimentological features, like texture, carbon and heavy metals. The cardinal theme of this study is not

Table 1. *Distribution of hydrographical parameters along the Kayamkulam estuary*

Parameter	Station	January		February		March	
		Surface	Bottom	Surface	Bottom	Surface	Bottom
Temp., °C	1	29.0	29.0	34.0	33.0	33.0	33.0
	2	30.8	31.0	33.0	34.0	33.0	33.0
	3	31.3	31.0	34.0	34.0	33.0	32.0
	4	32.0	31.0	33.0	33.0	32.5	32.0
	5	32.0	31.0	33.0	34.0	33.0	33.0
pH	1	8.05	8.00	7.64	7.72	7.60	7.52
	2	7.80	7.80	7.45	7.55	7.35	7.45
	3	8.15	7.95	7.48	7.40	7.57	7.34
	4	8.00	7.85	7.85	7.46	7.57	7.53
	5	7.70	7.65	7.44	7.44	7.40	7.42
Salinity, ppt	1	21.61	22.25	32.41	31.25	28.85	28.85
	2	20.56	21.46	29.46	32.16	26.34	28.22
	3	21.13	20.80	31.22	31.05	28.85	28.85
	4	21.36	20.86	32.28	30.37	27.60	27.91
	5	20.75	19.40	30.75	31.74	27.60	27.60
DO, mg/L	1	3.87	4.28	4.46	4.80	4.04	3.20
	2	3.75	3.95	4.35	4.38	3.67	3.95
	3	4.86	4.46	4.30	4.07	3.38	3.20
	4	4.32	4.20	4.40	4.34	4.30	3.34
	5	3.99	3.81	4.54	4.68	3.99	3.64

Table 2 *Correlation equation and 'r' values between the major ions and salinity* (30)

Major Ions, mg/L	Correlation equation	r
Calcium	$[Ca] = 4 S\%^0 + 189$	0.466
Magnesium	$[Mg] = 37 S\%^0 + 19$	0.850
Potasium	$[K] = 5 S\%^0 + 118$	0.606
Sodium	$[NA] = 76 S\%^0 + 7086$	0.581
Sulphate	$[SO_4] = 56 S\%^0 + 546$	0.606

Table 3 *Major ion - chlorinity ratio during the time of collection at different stations*

Major ion	Station	January	February	March
Calcium	1	0.0228	0.0178	0.0210
	2	0.0220	0.0169	0.0218
	3	0.0215	0.0169	0.0202
	4	0.0203	0.0172	0.0211
	5	0.0261	0.0165	0.0216
Magnesium	1	0.0665	0.0632	0.0747
	2	0.0657	0.0620	0.0811
	3	0.0642	0.0659	0.0762
	4	0.0662	0.0645	0.0770
	5	0.0639	0.0645	0.0774
Potasium	1	0.0189	0.0155	0.0185
	2	0.0174	0.0124	0.0189
	3	0.0174	0.0164	0.0185
	4	0.0182	0.0146	0.0192
	5	0.0200	0.0146	0.0193
Sodium	1	0.7265	0.5577	0.6136
	2	0.7325	0.4930	0.6557
	3	0.7252	0.5466	0.6200
	4	0.7292	0.5318	0.6446
	5	0.7759	0.5271	0.6349
Sulphate	1	0.1382	0.1179	0.1479
	2	0.1439	0.1226	0.1520
	3	0.1379	0.1245	0.1432
	4	0.1421	0.1233	0.1512
	5	0.1467	0.1233	0.1543

seasonal variations but an investigation of the background concentration of various major ions and nutrients along with other hydrographical parameters, like temperature, salinity, dissolved oxygen, pH, etc., the base line data obtained in this work would be useful to appraise the pollutional loads, if any in future, due to the NTPC power plant.

MATERIAL AND METHOD

Study area

Kerala is famous for its long stretches of backwa-

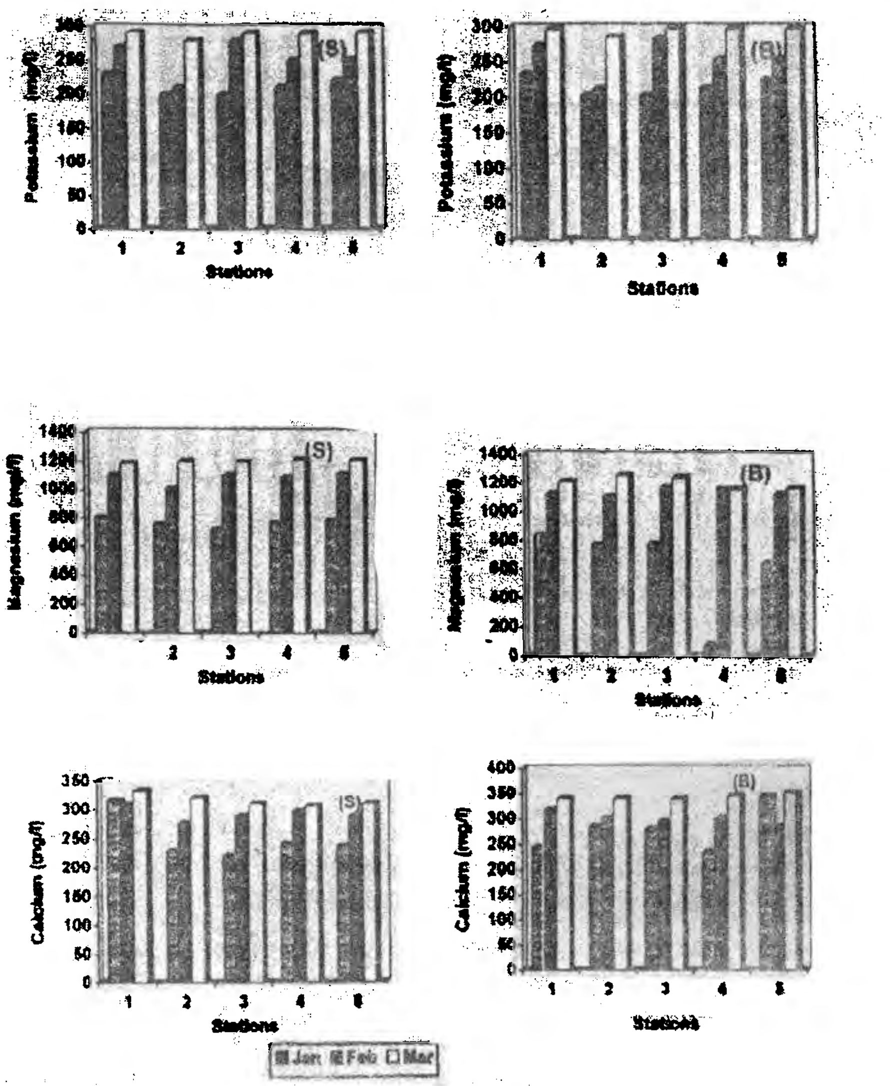

Figure 2. *Distribution of calcium, potassium and magnesium on surface (S) and bottom (B) waters of Kayamkulam estuary*

ters spread along the coastal line. The total brackish water area is estimated to be around 2, 42,000 ha (Anon, 1890). The Kayamkulam estuary extended parallel to the west coast line of Kerala. This narrow stretch of backwaters lies between (9° 2° - 9° 16' N; 76° 20' - 76° 32' E) (Figure 1). The depth is almost uniform (1.8 - 2.0 m). The estuary is supplied from the north by 3 canals which are the source of discharge of part of the flood water accumulating from the Pamba and Achankovil rivers in the estuary during the monsoon (Sivankutty Nair, 1991). In the south, the estuary merges with Vattakkayal which forms a sort of reservoir for the flood waters brought down from the adjoining land and canals during the monsoon. The barmouth closes

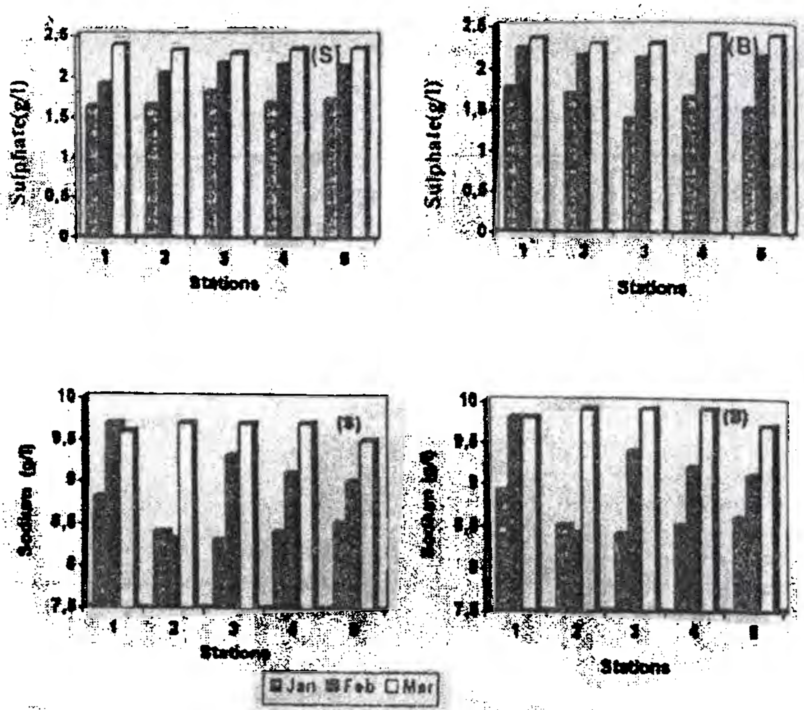

Figure 3. *Distribution of sodium and sulphate on surface (S) and bottom (B) waters of Kayamkulam estuary*

Table 4. *Correlation 'r' values between the hydrographical parameters and various nutrients studied* ($n = 30$)

Parameter	Salinity	Temp.	pH	DO	Nitrite	Nitrate	Urea	Phosphate	Silicate
Salinity	1.00								
Temp.	0.78	1.00							
pH	-0.63	-0.69	1.00						
DO	0.09	-0.04	0.39	1.00					
Nitrite	-0.43	-0.36	0.32	-0.06	1.00				
Nitrate	-0.27	-0.19	0.24	0.13	-0.22	1.00			
Urea	0.29	0.27	-0.29	-0.31	0.14	-0.30	1.00		
Phosphate	0.56	0.53	-0.58	-0.29	-0.07	-0.41	0.60	1.00	
Silicate	0.13	0.09	-0.11	-0.04	0.03	0.04	0.29	0.13	1.00

some time between March and April and then onwards the water in the estuary is almost stagnant till the middle of June when the flood water accumulates and the bar is cut open to allow the progress of flood water into the sea (Gopakumar, 1991). The sandy bar of the Kayamkulam estuary is situated almost midway between the northern and southern ends. In front of the barmouth, the estuary is about 2.5 km wide. From the barmouth, the width decreases towards the north and south. The southern half of the estuary is very narrow, the average width not exceeding 0.4 km. From the region opposite to the barmouth, an arm of the estuary extends to the Kayamkulam town in the north estuary direction (Gopakumar, 1991).

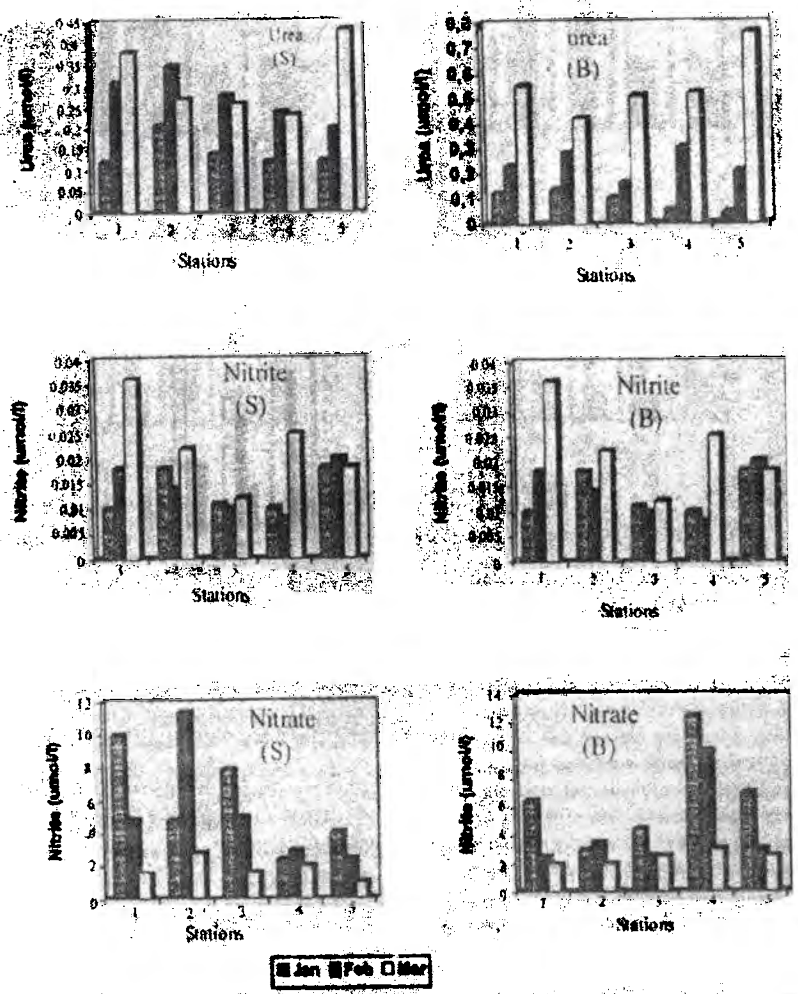

Figure 4. *Distribution of nitrate, nitrite and urea on surface (S) and bottom (B) waters of kayamkulam estuary*

Sampling

The selection of stations was based on the hydrographical feature and the expected future influence of the commissioned power station. Five stations were selected as shown in the figure 1 and from each station 2 samples were taken transversely. The distance each one is 1 km. The stations are considered to be representative, being closer to the site. Period of collection was before monsoon (January to March, 1995). Surface and bottom water samples were collected using a well - cleaned plastic bucket and precleaned PVC hytech water sampler, respectively.

Analysis

The temperature was determined using a sensitive thermometer. The pH of the estuarine samples was obtained from a digital pH meter. The estimation of salinity was based on Mohr - Knudsen's method (Grasshoff *et al.*, 1983) and the dissolved oxygen was estimated using Winkler's mehod (Gr-

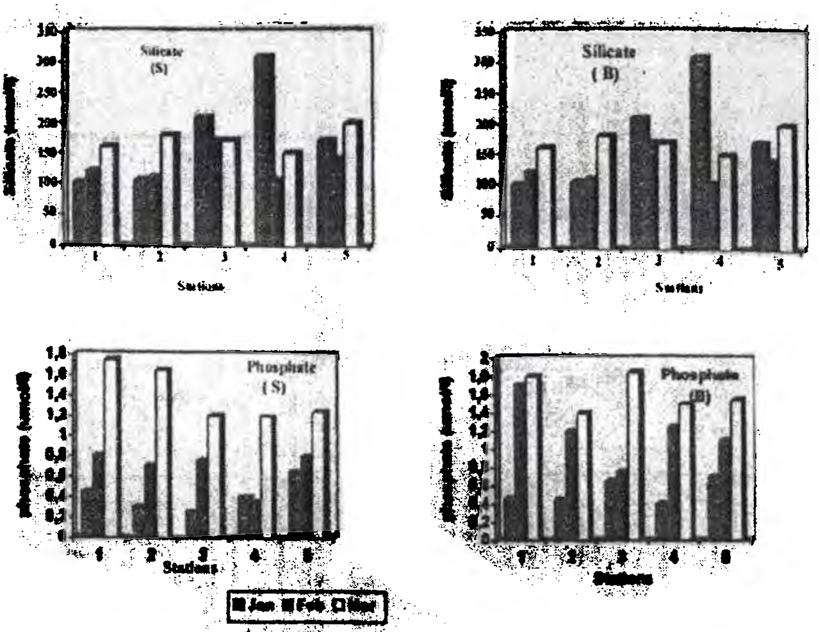

Figure 5. *Distribution of phosphate and silicate on surface (S) and bottom (B) waters of kayamkulam estuary*

asshoff *et al.*, 1983). Sodium and potassium were determined by using flame photometers with the respective filters. Calcium and magnesium were determined by complexometric titrations using EDTA at the respective pH conditions and incorporating necessary corrections. Gravimetric and iodometric methods were used for the estimation of sulphate and bromide, respectively. Anlyses of dissolved nutrients, like nitrite, nitrate, urea, phosphate and silicate were carried out using the methods introduced by Grasshoff *et al.* (1983). The principle was specific colourimetric analysis using a 150 - 2 - Hitachi UV - visible spectrophotometer.

RESULT AND DISCUSSION

Temperature

The surface temperature varies between 29 °C and 36 °C and the temperature of bottom water shows the range of 29 °C to 34 °C (Table 1). Generally, the differences between surface and bottom water temperatures are low which can be attributed to the shallowness of the water column. The dominant factors controlling the temperature in an estuary are the influx of fresh water and the cold saline water from the sea. Thus, the cold water might be the factor for the lowering of the bottom water temperature. Consequently, the surface water showed generally a higher value. Not only the tidally influenced sea water and inflowing river water, but also processes, like exchange of heat with the atmosphere and other localized phenomena also influence the distribution of temperature.

Salinity

Salinity is the well recognized parameter for studying the mixing processes and intrusion of saline waters into estuaries by tidal action. The salinity values exhibited much greater fluctuations (Table 1). The fluctuation may be due to the large intrusion of sea water during premonsoon and the mild influx of river water. The salinity values for surface warer samples ranged from 20.66 to 32.41 % and for the bottom water samples it varied from 19.39 to 32.42 %. The January collection showed lower values. During February, the values for salinity increased much. This may be due to the reduced flow from river. Again the tend decreased in March. The salinity of surface and bottom waters of all stations remained closer, which may be due to the shallowness of the estuarine system. The premonsoon periods are predominantly characterized by saline water intrusion and monsoon period by river water influx.

pH

Life processes depend on and are sensitive to the hydrogen ion concentration in the medium which depends on factors, like photosynthetic activity, rainfall, nature of materials involved, discharge of effluents, sewage, etc. The pH values ranged from 7.2 to 8.1 in the surface waters and from 7.4 to 8.1 in bottom waters. (Table 1). Values of surface and bottom samples were nearly the same. From the present data, higher values were obtained during January. Fluctuations occur because the nearby backwaters are retting areas. This can have a reasonably high influence on the pH values at various stations. A unique feature encountered in the Kayamkulam estuary is the coconut husk retting yards due to the plentiful availability of the raw material used in the production of coir (Maqbool, 1993). Large temporal variations in pH can also be lined to variations in the contribution of acidic soil water and less acidic ground water into the estuary.

Dissolved oxygen

Dissolved oxygen is an important water quality parameter in assessing water pollution. Oxygen is fixed in water either due to the direct dissolution from the atmosphere or a result of primary production. Organic decomposition depletes the level of dissolved oxygen. Actually, surface waters in the estuary showed higher oxygen contents. The oxygen contents in the estuary at Kayamkulam, are found to be comparatively low. The distribution pattern can observed in figure 3. The low values can be due to high temperature or decomposition or organic matter. In surface waters, the dissolved oxygen values varied from 2.78 to 5.08 mL/L, and in bottom waters the range was 3.17 to 4.69 mL/L (Table 1). The backwaters of Kayamkulam are highly prone to the toxic affects due to retting. The remarkable feature associated with retting is the depletion of oxygen leading to anoxic condition juxtapositioned with increase in hydrogen sulphide in the surface waters. This situation often depletes the fauna of the retting zone when compared to non - retting zones (Maqbool, 1993). The depletion of oxygen content leads to undesirable obnoxious odours under anaerobic conditions (Nelson, 1978). The energy metabolism due to enzymatic activity in certain marine organisms in found to be markedly influenced by depletion or increase in dissolved oxygen (Esparcia *et al.*, 1992).

Major ions

The major ions in ocean water are usually conservative or almost or but considerable variations in their concentrations are occur in a typical conditions, like estuaries. This variations in the conservative behaviour, that is the dependence of concentration of the physical processes of dilution and mixing and independent of biogeochemical processes, are due to various factors, such as inflow of fresh water from rivers, oxidative decomposition of organic matter, precipitation and dissolution of carbonate minerals, the tidal characteristics and dynamicity of the estuarine processes, etc.

Calcium

The concentrations of calcium in Kayamkulam estuary during the period of sample collection were given in the figure 2. The distribution pattern of calcium showed that bottom waters have higher concentrations of calcium than that of surface waters. This fact shows that dissolution of detritus material takes place during the premonsoonal season. The minimum value of 220 mg/L in January and maximum value of 338 mg/L in March observed was in agreement with the general trend of increase in concentration of calcium ion from January to March in premonsoonal season.

The calcium concentration in Kayamkulam estuary shows significant correlation with salinity (r= 0.466, n=30) indicating the conservative behaviour of calcium in this estuary (Table 2). The Ca/Cl ratio (Table 3) for the month of January was almost constant and the average value of 0.022 was slightly higher than that of other 2 month. This increase in ratio may result from dilution effect by river water, since the calcium to chlorinity ratio for river water was higher than that of sea water. In February, this ratio was much lower then that of many other water bodies and an average of 0.017 was obtained. This could be attributed to the utilization of calcium by biota and the mixing with more saline water, since the salinity was much higher than that of the month January. In March, the calcium to chlorinity value was almost same as that of most water bodies, and was 0.021 (Culkin and Cox, 1966; Narvekar *et al*., 1981; Noronha *et al*., 1981; Sengupta and Naik, 1981).

Magnesium

The distribution of magnesium in Kayamkulam estuary was given in the figure 2 and it varies from F37 to 1158 mg/L The results show that magnesium content increases in this estuary during premonsoon season similar to that of calcium. Since magnesium is biologically less active this may be due to higher evaporation than precipitation and stagnant nature of estuary water during the premonsoon season. A significant correlation (r = 0,850. n=30) was obtained between salinity and magnesium content and it shows conservative character of magnesium in this (Table 2). The magnesium - chlorinity ratio (Table 3) was almost constant in this estuary and the slight variation of magnesium to chlorinity ratio during the month of March is probably due to the influence of land run off.

Potassium

Potassium values vary from 210 to 280 mg/L (Figure 2). The potassium to chlorinity ratio of all the 5 stations during the premonsoon period were given in the table 3. A general conservative character has been shown by potassium also (Table 3). The low value of potassium chlorinity ratio may be attributed to the adsorption of potassium in the detritus material and subsequent deposit on sediment.

Sodium

The distribution of sodium in the study area was given in figure 2. The average sodium chlorinity ratio for each station was given in table 3 Sodium also shows generally a conservative behaviour and given a linear relation with chlorinity (r = 0.581, n = 30). In this estuary it was found that the value of sodium to chlorinity ratio slightly decreases as the salinity increases. The dilution of estuarine water with fresh water from land may contribute to this variation.

Sulphate

The maximum and minimum concentrations of sulphate content in Kayamkualm estuary, during the period of January to March 1996 were given in the figure 3. The sulphate conteut is significantly co - related (r = 0.606, n = 30) to salinity (Table 2).

In the premonsoon season the sulphate concentration increases from January to March. The average sulphate chlorinity ratio during the period, January, February and March were 0.140, 0.122 and 0.150, respectively. The low value of 0.122 is attributed to stagnant nature of the water body by being cut of from sea water and also due to coir retting activities. In some stations sulphate contents were low for bottom waters which indicated the influence of sulphate decaying bacteria (the presence of hydrogen sulphide was noted for some of the sediment samples). In March, though the salinity value was low for this estuarine waters, sulphate content increases. The inflow of river and agricultural land drainage enriched in sulphate content also influences this change.

Nutrients

Information concerning the nature and causes of dissolved inorganic nutrient variability in estuaries on seasonal and inter - annual time scales is important to a variety of research efforts including studies of the effects of man and climate on estuarine bio-chemistry (Officer *et al*., 1984; Seliger *et al*., 1985), global nutrient cycles and estuarine ecology. The distributions of nutrients, in particular, conservative or near - conservative distributions are associated with periods of high river flow whereas, non - conservative distributions are associated with phytoplankton assimilation. What follows is a brief overview about the behaviour of the nutrients, namely nitrite, nitrate, urea, phosphate and silicate in the estuary at Kayamkulam, for a high restricted period of 3 month, which limits our knowledge to go deep into the seasonal or inter - annual variations.

Depending upon the degree of mixing of the fresh water and saline water, the estuary may vary from a well mixed type to a stratified type. The concentrations of nutrients in the riverine and coastal waters and their proportions and the extent of primary production determine the nutrient content of the estuarine water. Fresh water zone can be the richest in nutrients and the marine zone the least. Again, nutrients cycling mechanisms can play a key role. The factors affecting variation of nutrients in estuaries and inshore regions are the rate of plankton production, seasonal factors, such as light, temperature, length of the day and the influx of new water masses by upwelling, river influx and changes in currents. Generally very low concentrations of nutrients were observed during the premonsoon. There can be due to the utilization by primary producers. Low concentrations in the inflowing rivers also play a significant role.

Nitrite

Taking into consideration, the importance of nitrogen in regulating primary production, many investigators have followed the seasonal changes in the concentrations of nitrogen species in relations to phytoplankton production (Konnonen, 1992; Childers *et al.*, 1993). Manipulative studies have shown nitrogen to be a key element in the eutrophication processes in certain marine environment (Kivi *et al.*, 1992). The nitrite values varied from 0.008 mm/L to 0.069 mmol/L in surface waters and 0.006 to 0.046 mmol/L in bottom waters. No significant monthly variations were observed (Figure 4). Very low values were obtained which can be attributed to excessive dilution by low nitrite river waters and to biological conversion of nitrite to nitrate, that is bacterial nitrification processes.

Nitrate

Comparatively high values of nitrate were obtained during the month of January, this decreased in February and a further decrease was observed in March. This may be associated with primary production or nitrification processes. The values varied from 0.393 to 12.006 mmol/L for the surface waters and 1.058 to 29.336 mmol/L for bottom waters. The rather high concentrations can be attributed to the biological processes rather than hydrodynamical mechanisms.

River sources of nitrate are quantitatively importent, but are highly variable. For example in temperate rivers nitrate concentrations are typically high in winter and low in summer. Ocean sources are also variable. When the continental shelf is narrow, ocean upwelling is an important source for nitrates in estuaries (Helder *et al.*, 1983). Municipal waste has a considerable source of nitrate in highly populated river basins and estuaries (Wollast, 1983). These factors are applicable to rivers which make a contribution to Kayamkulam estuary. Also the benthos has been implicated both as a source and sink for nitrate. Biotic transformation including plants and animals is the principal sink for nitrate in estuaries.

Urea

The surface waters showed variation in urea from 0.033 to 0 517 mmol/L and the concentrations in bottom samples ranged from 0.023 to 0.752 mmol/L (Figure 4). The values were typically estuarine. No significant monthly variations were noticed. Riverine sources of urea are generally less than for nitrate except in polluted waters. Waste and anthropogenic sources form a major contributor to urea in estuarine waters. In coastal waters, urea is used in preference to some inorganic nitrogen forms (NO_2^-, NO_3^-, etc.), even when inorganic nitrogen concentrations are in excess (Kristiansen, 1983). Abundence of urea in tropical waters are functioned by both hydrographical as well as biological production and regulated well by hydrochemical changes (Nair *et al.*, 1994).

Phosphate

The values ranged from 0.26 to 1.76 mmol/L in surface waters and 0.24 to 1.94 mmol/L bottom waters. The figure 5 shows moderately wide variations. Slight increase was observed from January to March which may be associated with the rate of uptake by phytoplankton. The values showed trend as to the phosphorus concentrations of Cochin estuery (Anirudhan, 1988).

During the plant growing season, phosphate concentrations may be depleted relatively clear water estuaries due to phytoplankton uptake or appear in excess due to massive waste source. In estuaries, the riverine influx of phosphorus may be substantially modified by deposition and dissolution changing the quantity of phosphorus (Fox *et al.*, 1985). Waste is a rich source of phosphate. Coastal upwelling is also potential source of phosphate for estuaries. Only a quantification of fluxes can give an indication of events in the biochemistry of phosphate (Lebo, 1990). These include photosynthesis, remineralization of organic phosphorus, or the precipitation - adsorption and desorption - redissolution of phosphate. Biota are an important sink for dissolved inorganic phosphate in estuaries (Vaithiyananthan *et al.*, 1993), but probably less so than for nitrate. Abiotic adsorptian - desorption phenomena are also considered to control phosphate concentrations in estuaries. Domestic sewage, loading of rock phosphate and riverine discharges may be contributing to the phosphate concentration in this region.

Silicate

The concentrations of dissolved silicate were found to be moderately high in the waters of Kayamkulam estuary. Also significant variation was observed. In esturine chemistry, wide change in dissolved silica concentration during esturine mixing has been of considerable interest. The range of concentration was found to be 87.6 to 493.0 mmol/L in the surface waters (Figure 5). Bottom waters also showed a similar trend in concentration which may be due to the shallowness of lake. The range was 54.9 to 290.6 mmol/L.

The concentration of silicate within water bodies exhibits marked-variation in seasonal and spatial distribution. River transport is a major factor influencing the variation of silicate concentration in marine environment. Temperature and solubility of certain minerals also have a significant influence on the silicon concentration. Weathering of rocks and soil in the principal sores of silica in rivers and estuaries (Wollast and Mac Kenzie, 1983). In estuaries with large areas and relatively small river inflow, the benthic flux to overlying waters is quantitatively important even exceeding the riverine source. Waste can be a relatively significant local source relative to other sources of dissolved silica.

Correlation between nutrient and other hydrographical parameters

The relationship between the distribution pattern of various parameters studied has been determined from the Pearson coefficient 'r'. The correlation matrices are displayed in table 4. Significant positive correlation was obtained for salinity/temperature and negative correlation for pH/salinity and pH/temperature. This agree well with the analysis of Rohling *et al.* (1992), who analyzed the warming trend in the waters as a response to the increase in salinity in Medeterranean deep waters. The concentration of nitrate was found to decrease with increase in salinity. The influence of biologically important phosphate on various hydrochemical parameters is firmly established. The phosphate showed significant positive correlation with salinity and temperature and negative correlation with pH. Similar salinity/phosphorus correlation has been obtained by Anirudhan (1988) during the analyses of these parameters in Cochin estuary. Phosphate - salinity distributions in estuaries are commonly linear or near linear (Smith and Longmore, 1980). Concentration of urea is found to decrease with increase in phosphate concentration. The non - conservative behaviour of silicate is also established.

SUMMARY

An outline result of a survey of the hydrochemical constituents at different station of Kayamkulam backwaters, near the newly constructed power plant, during the premonsoon months (January, February and March) is produced. The study has incorporated hydrographical parameters, like distribution of temperature, salinity, pH and dissolved oxygen. Temperature remained nearly the same though surface values were marginally high. The pH values showed condition similar to those of open ocean. The oxidation of organic compounds generally reduced the oxygen content. Salinity values showed highly prominent variations which are considered as of typical esturine nature. Significant correlations were obtained among salinity, temperature and pH. The estuary being shallow, no significant variation were observed between bottom and surface waters for hydrochemical parameters as well as for nutrients.

Though the major ions are conservative in its biochemical reactivity in sea water systems, considerable modifications to the ratio between the ions and deviations from the constancy of composition are regular phenomenon in estuarine waters. The Kayamkulam estuarine system is a tropical positive estuary with the tidal influx of sea water and fresh water discharge from Pamba and Achankovil river waters. It is also subjected to considerable modifications due to heavy agricultural activity on the bank of rivers. Based on the result obtained, the major ions generally exhibit a conservative behaviour. The ratio of Na, Mg, Ca, K and SO_4 with chlorinity are comparable with those in oceanic water and indicated considerable conservative character. A slightly low value for calcium to salinity ratio observed in this system may be due to the extensive agriculture activity on the bank of the river and also adsorption to clay minerals. Estuaries are not yet fully understood as complete systems and many factors influence the dissolved inorganic nutrient distribution in estuaries. They include hydrochemical parameters, influence of sewage, fertilizer runoff and much more biochemical process which sustain life in the marine environment.

Nitrite values were very low. But nitrate, urea and phosphate concentrations were typically estuarine. The phosphate showed significant positive correlation with salinity and temperature and negative correlation with pH. Silicate concentrations remained moderately high. Since no considerable work has been done on the hydrography, distribution of nutrients and extent of pollution of the estuary at Kayamkulam, the present analysis may be of great help as an analytical tool in marine pollution studies, especially after the advent of the thermal power plant.

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GROUNDWATER CHEMISTRY OF SHALLOW AQUIFERS IN THE COASTAL ZONES OF COCHIN, INDIA

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Abstract. The coastal aquifers of Kerala, India experience severe degradation of water quality due to various anthropogenic activities. An attempt is made here to study the groundwater chemistry of aquifers, which lie along the coastal zone of central Kerala. Results in general indicated that the groundwaters in the shallow aquifers were found to be deteriorated. Based on Hill-Piper trilinear diagram it is confirmed that some of the dug wells were characterised by high amount of sodium and chloride (>200 mg/l) indicating the influence of saline water incursion. The presence of *E. coli* in all dug wells indicated potentially dangerous fecal contaminations, which require immediate attention. The study further raises points for the need of action for a sustainable utilization of precious resources.

Keywords. *coastal aquifer, groundwater, trilinear diagram, saline water incursion*

Introduction

Kerala, the southernmost state of India has unique hydrogeological characteristics with wide variation in the rainfall pattern (average 3107 mm). Both qualitatively and quantitatively, the coastal zones of Kerala in recent years witnessed serious groundwater problems [8, 9, 11, 24, 25]. Several studies invariably showed that water quality in the shallow aquifers situated in the coastal zone of Kerala is deteriorating alarmingly amidst plenty of water all around [1, 6, 7, 10, 12, 21, 33]. Owing to the high demand of groundwater to cater a large population in the coastal zones of Cochin, mitigation of the deterioration in the quality of groundwater in shallow coastal aquifers was initiated through groundwater recharge [30]. High population pressure, intense human activities, inappropriate resource use and absence of proper management practices leads into the deterioration. The coastal sedimentary formation serves as an excellent condition for aquifer and the average groundwater potential of this region is estimated to be more than 0.3 MCM/km [b]. In the shallow coastal aquifer, open wells are the dominant groundwater abstraction structures and the density of the open wells in the coastal area is high in the range of 400 wells/km^2 [30]. During rainy seasons, the sea becomes rough and encroaches towards land and during summer seasons the saline water finds its way through tidal channels and it admixes with shallow coast aquifers. So the qualities of water in the shallow and deeper zones become brackish [9, 20, 30].

Added up problems such as urbanisation, industrialization, unscientific landuse, lack of awareness of the people and saline intrusion all makes the quality of groundwater in Cochin coastal zone worsen. All these contribute to less recharge into the coastal aquifers thereby accentuating groundwater quality and the problem of salt water intrusion. The present investigation attempts to illustrate the scenario of groundwater quality and saline water intrusion during post monsoon (November 2003) in the coastal zones of Cochin.

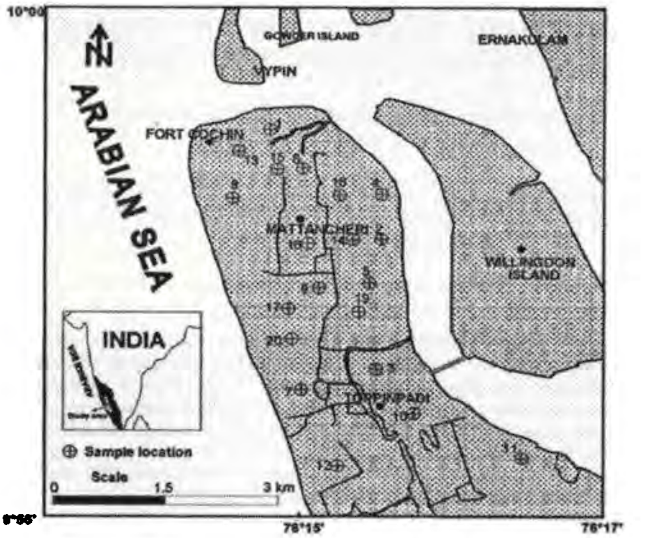

***Figure 1.** Base map and sample locations of the study area*

Study area

The study area extends from north of Fort Cochin to the south of Thoppumpadi which lies between 9°55'–10°00'N and 76°13'–77°17'E (*Fig. 1*).

The area is bordered by Arabian Sea on west and a part of Cochin estuary in the eastern side. The area is characterised by a number of tidal channels, results into seawater encroachment, which deteriorate the water quality.

Exploratory borehole study conducted by Central Groundwater Board indicates the recent coastal alluvium followed by Tertiary sediments consists of two distinct formations. The upper most formation is Warkalais with thickness of nearly 80 m underlined by thick sequences of sediments called Vaikom beds. The Tertiary sedimentary formation of Kerala basin unconformably overlays Precambrians. In the present study most of the dug wells are tapping groundwater at depth ranging 2 to 8 m fall in recent coastal alluvium [29].

Data and methodology

Groundwater samples have been collected from 20 dug wells during post monsoon (November 2003) at stations as shown in *Fig. 1*. The pH was measured at the spot, whereas the concentration of major cations, anions and *E. coli* were analysed at the laboratory as per the standard analytical procedures [2, 14].

Sodium and potassium in groundwater samples were analysed using Flamephotometer (Systronics FPM digital model). Calcium and magnesium were estimated by EDTA titri metric method, whereas chloride was determined by argentometric titration using standard silver nitrate as reagent. Carbonate and bicarbonate concentrations of the groundwater were determined titrimetrically [2, 14]. Sulphate concentration was carried out following turbidity method using double beam UV-Visible spectrophotometer

(Hitachi Model 2000) [2]. The microbiological quality of samples were analysed in terms of most probable number (MPN) of faecal coliforms using lactose broth and incubation at 44.5 °C. Tubes showing positive results after 24 to 48 hours of incubation were streaked on to Mac Conkey Agar and esoine methyl blue (EMB) agar and incubated at 37 °C for 24 to 48 hours. Typical *E. coli*-like colonies were isolated and confirmed biochemically as *E. coli* using IMViC test. The number was expressed as MPN index / 100 ml.

Results and discussion

Table 1 presents the results of groundwater analysis.

pH

The pH values of groundwater were varied from 7.01 to 8.2 indicating slightly alkaline nature. Groundwaters with pH value above 10 are exceptional and may reflect contamination by strong base such as NaOH and $Ca(OH)_2$ [22]. The range of desirable limit of pH of water prescribed for drinking purpose by ISI [27] and WHO [35] is 6.5–8.5 while that of EEC [23] is 6.5–9.0.

The analysed groundwater samples are within the limit prescribed by ISI [17], WHO [35] and EEC [23]. There is no much distinct variation of pH in the different wells selected for the present study, indicating that the groundwater is tapping from aquifers of a single formation. The slight alkaline nature of groundwater may be due to the presence of fine aquifer sediments mixed with clay and mud, which are unable to flush off the salts during the monsoon rain and hence retained longer on other seasons.

***Table 1.**: Chemical and E. coli analysis data of groundwater*

well no.	pH	Na^+ (mg/l)	K^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	CO_3^{2-} and HCO_3^- (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	MPN index FC / 100 ml
1	8.08	380.7	23.5	57.9	20.2	200.2	470.4	1.8	150
2	7.61	145.7	90.6	102.1	12.0	317.8	145.2	2.1	290
3	8.01	480.4	110.0	190.4	22.7	334.1	749.4	5.6	95
4	7.67	457.1	75.2	117.7	10.3	321.9	640.3	2.4	95
5	7.10	120.0	18.2	72.9	22.5	352.4	36.1	1.8	460
6	7.14	110.9	19.8	74.1	26.5	310.1	63.5	2.2	290
7	8.20	546.0	72.2	122.0	11.2	276.9	757.4	3.8	93
8	7.26	90.7	30.2	52.8	5.0	179.7	96.7	2.2	460
9	7.30	70.6	38.4	48.8	4.8	187.0	49.8	1.1	460
10	7.36	445.9	45.9	70.2	11.0	160.1	612.0	3.4	120
11	7.53	110.6	38.3	50.8	15.3	203.6	128.2	2.5	240
12	7.60	339.0	95.1	87.0	22.8	187.4	541.6	3.5	150
13	7.57	111.5	65.2	54.4	3.6	185.7	126.0	1.9	210
14	7.20	65.0	23.7	82.6	3.5	238.5	23.7	0.9	240
15	7.67	85.3	42.5	97.1	2.5	234.0	70.6	2.1	210
16	7.54	64.5	15.2	61.4	1.2	167.4	37.5	0.8	460
17	7.50	34.0	8.9	24.6	2.3	77.0	23.1	0.6	290
18	7.07	20.1	10.2	25.6	1.7	62.5	26.0	1.2	460
19	7.50	48.5	27.6	83.2	10.1	202.2	55.4	1.3	240
20	7.01	11.7	5.2	34.0	8.9	74.1	25.2	0.9	460

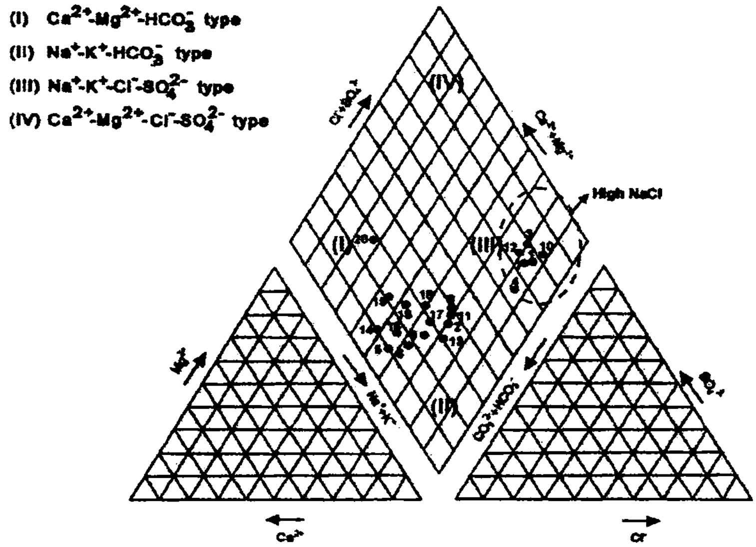

Figure 2.: Trilinear diagram of dugwell samples

Major cations and anions

Major cations and anions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, CO_3^{2-}, SO_4^{2-} and Cl^- (*Table 1*) were plotted in hydrochemical trilinear diagram. In general high concentrations of chloride in groundwater is attributed to rainwater, seawater, natural brines, evaporate deposits and pollution [18, 19]. In dug wells (Nos. 1, 3, 4, 7, 10 and 12) high concentrations of chloride and sodium were measured. This high concentration can be due to the proximity of the wells to the tidal channel and the poor muddy sediments present in the aquifer system which further infers saline incursion. The high chloride content is generally taken as an index of impurity of groundwater. The clogging nature of sediments permit only intermittent flushing and hence the impurity (sodium and chloride) was sustained longer as compared to other wells. The dug wells (Nos. 1, 3, 4, 7, 10 and 12) had higher values, which were above the permissible limit of 250 mg/l [17, 23, 35]. Sulphate concentration in groundwater of coastal zone were within the permissible values recommended by WHO [35], EEC [23] and ISI [17]. The major cations and anions were further analysed based on Hill-Piper trilinear diagram.

Hill-Piper diagram

Pattern diagram was initially conceived by Hill [16] and later improved by Piper [27] and the detailed analysis of Hill-Piper trilinear diagram for post monsoon season (*Fig. 2*) is explained below using facies diagram.

The hydrochemical pattern diagram helps in hydrogeochemical facies classification [5]. The trilinear diagram of this study is classified into four hydrochemical facies based on the dominance of different cations and anions: facies 1: Ca^{2+}-Mg^{2+}-HCO_3^- type I; facies 2: Na^+-K^+-Ca^{2+}-HCO_3^- type II; facies 3: Na^+-K^+-Cl^--SO_4^{2-} type III and facies 4: Ca^{2+}-Mg^{2+}-Cl^--SO_4^{2-} type IV.

Fig. 2 shows that the majority of samples were in type II (Na^+-K^+-Ca^{2+}-HCO_3^-) followed by type III (Na^+-K^+-Cl^--SO_4^{2-}) and type I (Ca^{2+}-Mg^{2+}-HCO_3^-). This indicates that post monsoon samples are enriched with sodium, bicarbonate and chloride types and, from this it is evident that sea water and tidal channel/canals plays a major role in controlling the groundwater chemical composition in the coastal shallow aquifer, which consists of recent alluvium. Nageswara [26] conducted study on groundwater salinity of the shallow aquifers in the central Kerala and inferred that salt-water encroachment into shallow aquifers can be minimised by construction of tidal barriers. The removal of sodium ions from seawater which has infiltered into fresh water aquifer has been described by a number of workers by the method of ion exchange [28, 31]. Sodium ion present in seawater will exchange to Ca^{2+} ions. The conversion of calcium bicarbonated water to sodium bicarbonate water in many aquifers is also undoubtedly due to ion exchange [4, 13]. The freshwater will change into $NaHCO_3$ type water [3]. Further, the trilinear diagram (*Fig. 2*) revealed that dug wells (Nos. 1, 3, 4, 7, 10 and 12) falling in facies 3 showed the saline water intrusion of coastal aquifers with high percentage of sodium and chloride.

Escherichia coli

The bacteriological content is one of the most important aspects in drinking water quality. The most common and widespread health risk associated with drinking water is the bacterial contamination caused either directly or indirectly by human or animal excreta. *E. coli*, a typical fecal coliform is selected as an indicator of fecal contamination. The present study revealed a high incidence of fecal coliform, which ranged 93 to 460 MPN index FC / 100 ml (*Table 1*), indicating poor sanitary condition and improper waste disposal. The seepage of *E. coli* is easier in the sedimentary formation compared to hard rock terrains [15], which supported the present study. The fecal contamination is mainly due to improper solid waste disposal from farmyard into the soak pits located very near to drinking water wells, which do not have any protecting wall [34]. According to Woods [34], effluents from point-like sources such as septic tanks and general farmyard wastes are considered as the main sources of contamination of groundwater. The lack of protecting walls will lead to the entry of contaminated runoff water into the well from the upstream. Rojas *et al.* [32] have studied the contamination of the waters of River Rimac, Peru, and the adjoining groundwater and found that the cause of pollution is due to mining and agricultural activities as well as domestic fecal pollution upstream. The presence of *E. coli* in groundwater indicates potentially dangerous situation, and requires immediate attention.

Conclusion

Analysis of groundwater samples from the study area indicated signs of deterioration, which highlights the need for a sustainable utilization of precious resources. Groundwaters present in the shallow aquifers of some of the stations were poor in quality and beyond potable limit as per the standard set by WHO and ISI. Samples from rest of these zones indicated that the groundwater quality is satisfactory (geochemically) but requires attention, with a thrust on proper sanitation and waste disposal of the adjacent coastal region. The groundwater collected from the six dug wells indicated that there is a mixing of fresh and saline water during post monsoon. The study revealed that these wells need more controlled withdrawal of water with more recharging in order to maintain fresh-saline water equilibrium. Further, it stressed that the coastal zone of the study area need more attention in order to maintain the ground water quality. The study also recommends the necessity of proper sanitation and waste disposal to sustain the groundwater quality.

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Heavy metal accumulation in a flow restricted, tropical estuary

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Abstract

Levels of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn), organic carbon content and textural characteristics in the surficial sediments of Cochin estuary (SW coast of India) and adjacent coast are presented. Anthropogenic inputs from industries have given rise to a gradient in concentration of metals in estuarine sediments. Metal accumulation initiated by precipitation of iron complexes is probably responsible for the enrichment of Cd, Cu, Pb and Zn in the estuary, whereas the coastal sediments did not accumulate them to the same degree. Statistical analyses of the coastal and estuarine geochemical data indicated a different association of elements in the two provinces. The present enrichment factors for Zn (×25) and Cd (×10) place the region among the impacted estuaries in the world. Accumulation of metals in this estuarine system is aggravated by the weak flushing. These pressures are deemed inevitable with growth initiated in the harbour and associated with mega city development in the offing.

Keywords: heavy metals; accumulation; enrichment factor; correlation; Cochin estuary

1. Introduction

In its pristine condition, the Cochin backwaters and estuary sustained rich bio-resources (Gopalan et al., 1983). Over the past five decades, the estuary and feeders have been subjected to damaging changes following increased anthropogenic loadings, which are currently 0.104 $Mm^3 d^{-1}$ industrial and 260 $t d^{-1}$ domestic wastes (Central Pollution Control Board, 1996). A recent study has reported an annual transformation in the behavior of elements from an inorganic deposition to organic association followed by sedimentary modifications and normalization along the coastal environment of Cochin (Balachandran et al., 2003). In the present study, we report data on organic carbon and heavy metals in sediments of estuarine and coastal region of Cochin collected during a winter monsoon period. The study area comprising Cochin backwaters and the adjoining shelf annually experiences two distinct regimes of alluvial loading: high during monsoon and silting during lean flow. The ox-bow shape of the lake (Soman, 1997) has a strong bearing on the tidal modulations and flushing characteristics, which eventually govern the estuarine water balance and the biological dynamics.

2. Methods

Surficial sediments were collected by Van Veen grab from the inner shelf of Cochin and from the lower reaches of the backwaters (Fig. 1). Sampling was carried out in November 2000 covering 23 km of the shelf as well as 9 km of estuarine region. Samples were frozen until analysis. Textural characteristics were determined

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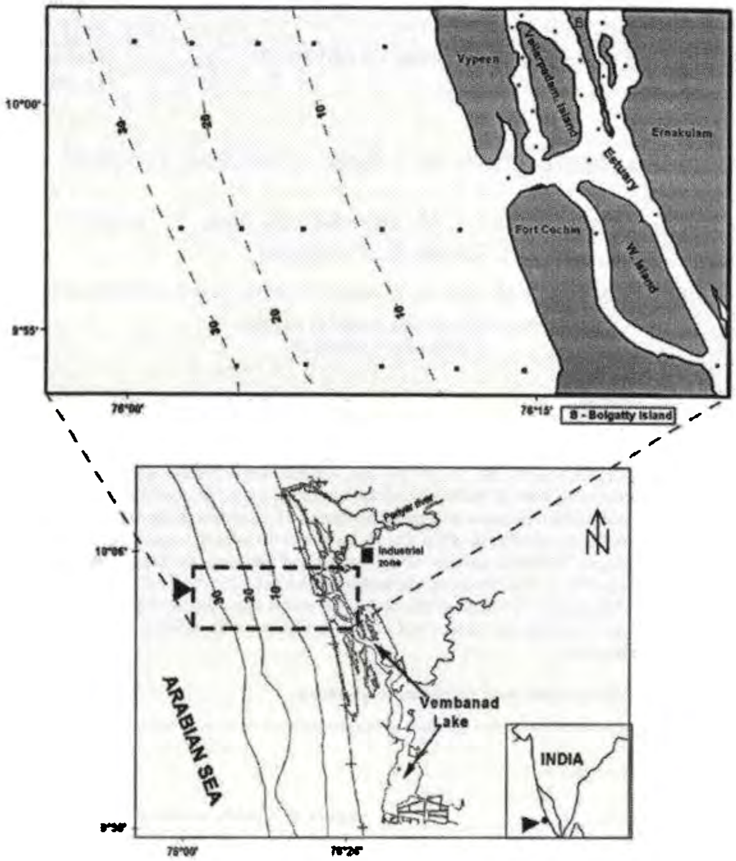

Fig. 1. Study area showing station locations in the Cochin estuary (Vembanad Lake) and its adjoining marine area. Bathymetric depths are given in meters.

by pipette analysis (Krumbein and Pettijohn, 1938) and sediment organic content by wet digestion (El Wakeel and Riley, 1957). Finely-powdered and dried (at 70 °C) sediments were digested in a mixture of $HF–HClO_4–HNO_3$ (Loring and Rantala, 1992) and brought into solution in 0.5 M HCl (25 ml) using Milli Q water. Samples were analyzed on a flame AAS (PE AAnalyst 100) after calibration with suitable E-Merck elemental standards. For cadmium analysis, a GF-AAS (ZL 4110 PE) was used. The accuracy of the analytical procedure was checked using a triplicate analysis of a certified reference material (BCSS-1) from the National Research Council of Canada. The Standard Deviations (SDs) were typically ±5% for Cu and Pb, ±12% for Cr, Ni, Mn and Zn and ±21% for Cd and Co (Table 1).

3. Results

3.1. Texture and organic composition

The coastal sediments were dominated by silty-clay fractions (>70%) extending from the C-west basin to N–NE coast (Fig. 2) whereas the estuarine region contained silty-clay (>50%) to clayey-silt (>30%) of grayish black colour. The bar mouth and surrounding regions were sandy and low in clay and silt, possibly due to stronger flushing. Sand was generally sparse and localized along the NW offshore (>80%) and entrance channel (>40%) where the organic carbon was also low (0.1–2%). The high organic carbon (4.2%) in the SE coastal region was rich in clay fraction. It is reported that the dominance of along-shelf transport of sediments

Table 1
Metal extracted from the standard reference material BCSS-1 ($n = 3$)

Concentration (mg kg^{-1})	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn	Cd
Metals extracted[a]	22.70	55.3	11.4	123	–	18.5	119	229	0.300
Metals extracted[b]	23.98	60.9	13.86	108	29000	17.99	105.5	204	0.362
Accuracy (±%)	5	11	21	12	–	3.7	11	11	21

[a] Certified values corresponding to the total extraction of metals from the standard reference material BCSS-1.

[b] Values of the metals extracted from the standard reference material BCSS-1 in this study.

over cross-shelf transport on the western continental shelf restricts coastal inputs to the inner shelf (Ramaswamy and Nair, 1989). The estuarine sediments generally contained a higher organic content (3–4%), but impoverished near the entrance channel (< 1–3%). The upstream northern channels showing high organic carbon (4–5%) at places are anomalous (Fig. 2).

3.2. Sediment geochemistry

The sediment texture, clay and organic carbon of the coastal region displayed similar trends in the distribution of elements (Fig. 3). In contrast, estuarine sediments showing a sharp gradient in textural and organic

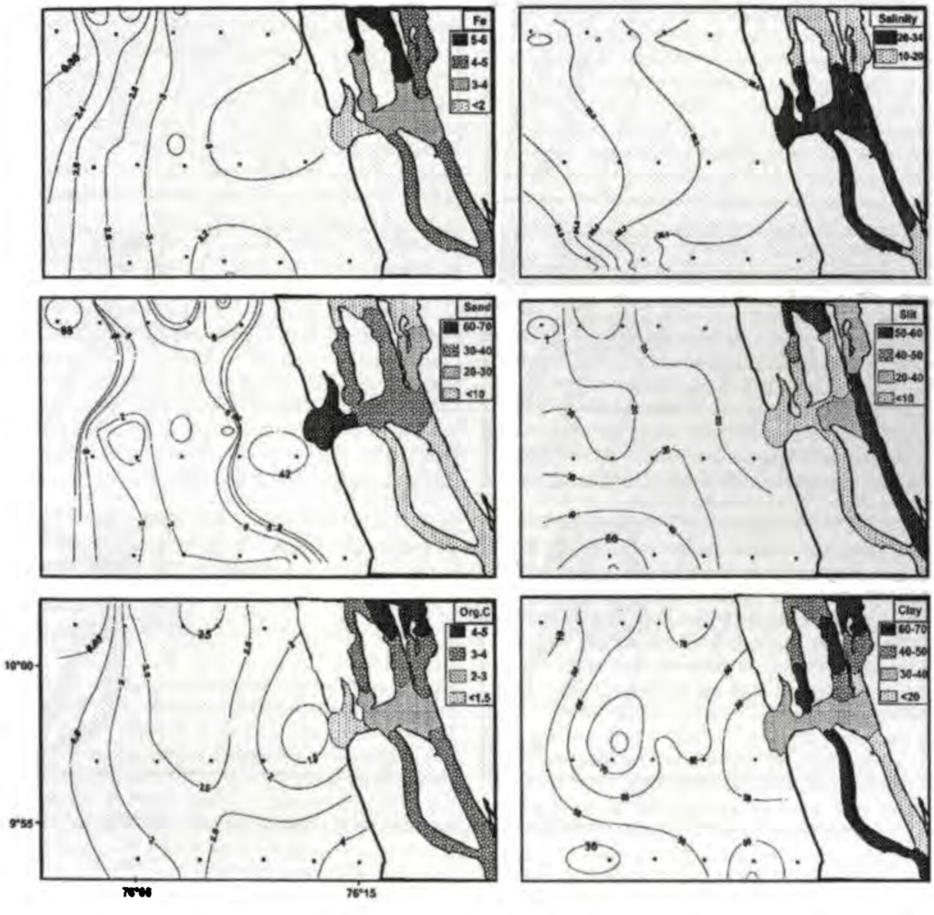

Fig. 2. Distribution of iron, bottom salinity, texture (sand, silt, clay) and organic carbon in the study region (%dry wt., except for salinity).

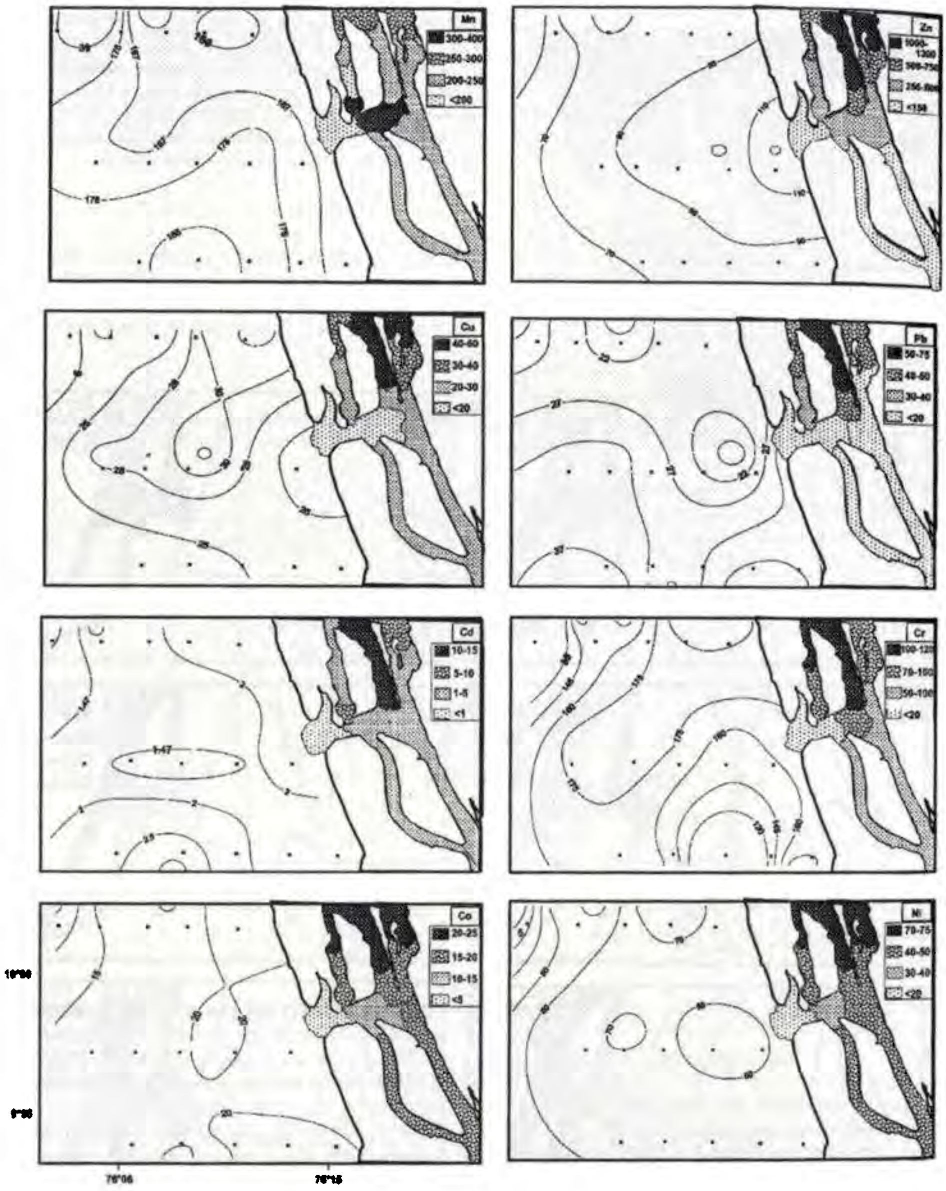

Fig. 3. Distribution of manganese, zinc, copper, lead, cadmium, chromium, cobalt and nickel (mg/kg dry wt.) in the study region.

characteristics were not matched by their corresponding geochemistry. Elemental levels in the coastal sediments generally increased towards the inshore. Concentrations of Fe, Mn, Zn and Cu were consistent with patterns of clay and organic carbon contents. Distribution of elements such as Cr, Co and Ni showed no clear pattern. On the other hand, Pb and Cd showed the opposite behavior, as a result of their affinity for silt,

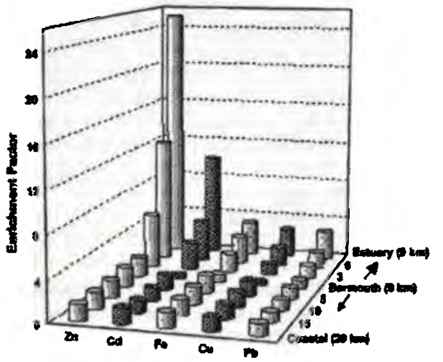

Fig. 4. Cross-sectional gradient in enrichment factors of potentially toxic elements in the study region.

the case of Co, Cr, Mn and Ni; (2) moderate contamination (EF ≥ 2–4), which is the case of Cu, Fe and Pb and (3) high to severe contamination (EF > 4), which is the case for Cd and Zn. Fig. 4 shows the impact of metal enrichment from the Cochin backwaters into the receiving coast. Cd, Cu, Zn and to a lesser extent Fe and Pb, are the metals contaminating the estuarine sediments. The highest EFs obtained for sediments in the northeast (NE) and northwest (NW) part of the backwaters are × 25 for Zn, × 10 for Cd and × 3 for the other elements (Cu, Fe and Pb). These values declined steadily towards the harbour and coastal regions, indicating a progressive diffusion of metal contaminants. The significant correlation among these metals indicates a common source of contamination, typical of any impacted coastal marine areas (Ruiz, 2001). Specific contamination due to harbour activities, a common feature of other estuaries (Rubio et al., 2000), seems to be less in Cochin backwaters. Periodic dredging and moderate flushing in the harbour region may be preventing long-term accumulation.

4. Discussion

The contrasting textural and organic characteristics of coastal and estuarine sediments were also reflected in their geochemical properties. The distribution of elements in the estuary indicates a point-source. The metal enrichments (Cd, Cu, Fe, Pb and Zn) observed along the northern limb of the estuary were not consistent with the uniformly-high organic content in the estuary. The poor correlation between organic carbon and the metals in the estuary, unlike the case in the coastal sediments (see Section 3.3), indicates that metal enrichment in the estuary may possibly be initiated by inorganic processes, such as precipitation and scavenging by hydroxides of Fe and Mn. Contrary to expectations, accumulations of Fe and Mn in the estuary were spatially segregated, perhaps as a consequence of their different flocculation properties. Sholkovitz (1978) and Richard et al. (1981) have observed that Cu, Fe and Zn are flocculated at low salinities (< 20) whereas flocculation of Mn requires high salinity. Hence, the upper estuary favors early flocculation of Fe followed by scavenging other elements, whereas Mn is transported further downstream where salinity is higher (Fig. 2 showing overlying salinity). The possible enrichment mechanism appears to be estuarine coagulation–flocculation of elements as colloids in association with hydrous iron oxides under fluctuating salinity. Inadequate flushing of pollutants released to flow restricted water bodies can promote coagulation or co-precipitation of metals under the prevailing ionic (salinity) condition (Cobelo-Garcia and Prego, 2004). These processes could be critical in estuaries such as the Cochin backwaters, which are characterized by frequent development of null zones of relatively long residence time. A seasonally-oscillating zone has been noted earlier here (Ramamirtham and Muthusamy, 1986). We quote: "*Because of the position of these two mouths, which are exposed to the same tidal cycles, the high tides and low tides each producing two opposite flows respectively converge and diverge leaving a null zone, almost free of the tidal effect, around Kadakkara, situated midway between Cochin and Azhikode*". The geomorphology (ox-bow shape) of the estuary and meandering flow can induce the formation of perennially-undulating water bodies or null zones. The weak flushing could result in entrapment of fine particles in this region, thereby increasing the metal contamination. Identifying and estimating the carrying capacity of such zones is of great significance in regulating the estuarine pollution.

Given the moderate enrichment of certain elements found in the estuarine sediments, it will be worth to assess their potential toxicity towards benthic organisms. The contamination level of metals (mg kg^{-1}) in marine sediments has been classified into 'target', 'standard' and 'limit' values (Table 4, Van Veen and Stroetelder, 1988). Our data suggest that 67% of coastal sites and 69% of the estuarine sites exceeded the 'target' value for Cu whereas in the case of Zn, 88% of the estuarine sites exceeded the 'target' value (> 180) and 31% exceeded the 'standard' value (> 750), which is significant and indicates potential harm for benthic organisms.

Long et al. (1995) proposed guideline concentration for a range of heavy metals to assess their possible adverse effects on a wide variety of aquatic biota. They suggested two guideline values namely the ER-L (Effective Range-Limit) and ER-M (Effective Range-Medium) delineating three concentration ranges of a particular chemical (Table 4). If a metal occurs in concentrations below ER-L value, effects on the biota

Table 4
Comparison of potential toxicity of heavy metals in Cochin backwaters (mg kg^{-1})

EF < 2 (e.g. Co, Cr, Ni, Mn) Negligible/low		EF ≥ 2–4 (e.g. Cu, Fe, Pb) Moderate		EF > 4 (e.g. Cd, Zn) High/severe		Hakanson, 1980
Sediment quality guidelines						
Element	Zinc	Cadmium		Copper		Long et al., 1995
ER-L	150	1.2		34		
ER-M	410	9.6		270		
Target value		Standard value		Limit value		Van Veen and Stroetelder, 1988
Copper	Zinc	Copper	Zinc	Copper	Zinc	
25	180	70	750	400	2500	

would rarely be observed. At concentrations $\geq$ER-L but <ER-M, the biota could "occasionally" be affected by the pollutant, whereas at concentrations $\geq$ER-M, effects would be expected to occur "frequently". Accordingly in the estuarine sediments, 53% of sites for Zn and 24% of sites for Cd are well above the guideline concentrations (ER-M), where adverse effects on the benthic biota can be expected frequently.

A long-term assessment of the metal pollution levels in sediments of the NW part of Cochin backwaters showed an increase in concentrations of Zn (×18) and Cd (×9) over the past 24 years (Fig. 5). During the period 1976–2000, Zn concentration in sediments increased from 70 to 1266 mg kg^{-1}. Similarly, the Cd content increased from 1.7 to 14.94 mg kg^{-1} during 1990–2000. This could be expected since an annual loading of approximately 80 t of Zn and 63 Mm^3 of effluents from 247 chemical industries situated upstream of the northern estuary could lead to such a gross pollution (Shibu et al., 1995; SCMC, 2004).

The persistent stress on the Cochin backwaters might have induced a gradual shift in benthic community (Remani et al., 1983; Saraladevi and Venugopal, 1989; Sheeba, 2000, pers. comm.). One of the adverse effects has been the marked decline in the clam fishery (*Villorita* sp.) of this estuary over the years. Here, pollution-tolerant benthic organisms (opportunistic species) like polychaetes are found to take over the vacated niche (Gopalan et al., 1983; Saraladevi et al., 1992; Sheeba, 2000, pers. comm.). The reduced biodiversity and high biomass of such tolerant species observed in this region are also indicative of pollution stress. The possible impacts from industry and agricultural run off of excessive nutrients have been noted (Balachandran, 2001, 2002). The monsoonal regimes that govern the environment and biological destinies could be an important mitigating factor minimizing the gross pollution.

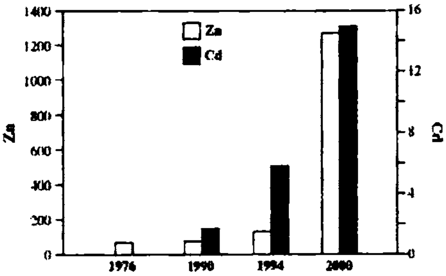

Fig. 5. Long-term changes in the concentrations of Zn and Cd (mg/kg dry wt.) in the surficial sediments of NW part of Cochin backwaters between 1976 and 2000 (1976 – Venugopal et al., 1982; 1990 – Nair, pers. comm.; 1994 – Rajamani, pers. comm.; 2000 – Present study).

5. Conclusion

The heavy metal concentrations in Cochin estuary has not yet reached levels that could be considered 'extreme'. But, the metal enrichment observed in the present study, especially in the case of Zn (×25-fold) and Cd (×10-fold) is high, placing the region among the impacted estuaries in the world. The sediment heavy metal contamination of this estuary is a cause for concern as these metals may undergo bio-accumulation and affect the benthic organisms. The complex nature and flow restrictions favoring the accumulation of pollutants have transformed this estuary into a delicately poised ecosystem. It is important to determine the source of these heavy metals and to manage their input into the estuary so that their concentrations in the sediment do not reach toxic levels. The pressures are deemed inevitable with growth initiated in the harbour and associated mega city development in the offing. In view of the projected population stress (0.6 Million in 1975 to 3 Million in 2002 and an expected 5 Million population by 2025), adequate conservation plans should be made to minimize the inevitable pollution, consequent to developmental activities.

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which was the dominant component in the offshore sediments. The gradient in geochemical and textural properties of the coastal sediments infers this coastal environment was geochemically stable.

Iron was the major element in all the sediments, ranging from 0.34 to 3.42% in the coast and 1.41–6.18% in the estuary (Fig. 2). Manganese was the second in abundance, displaying enrichment towards the inshore (278.7 mg kg^{-1}) and central estuary (141–337 mg kg^{-1}). Some of the metals tend to accumulate towards the northern estuary where Cd, Cu, Pb and Zn showed a clear anthropogenic influence along NW and NE parts of Bolghatty Island, situated just downstream from the industrial area in the river Periyar (Fig. 1). In this region, zinc concentration was high (1266 mg kg^{-1}) compared with that of other elements (Cd 14.94, Pb 71 and Cu 53.15 mg kg^{-1}, Fig. 3). The mean and maximum concentrations (mg kg^{-1}) of Zn (592, 1266), Cu (32.42, 53.15), Cd (6.24, 14.94), Pb (39.93, 71.28) and Fe (4.47, 6.18%) obtained in this estuary are therefore comparable to impacted estuaries elsewhere (Table 2). The remaining metals (Cr, Ni and Co) did not show any pronounced anthropogenic influence. This kind of heavy metal accumulation in Cochin estuarine sediments is reported earlier also (Nair, 1992, pers. comm.; Rajamani Amma, V., 1994, pers. comm., Shibu et al., 1995; Shajan, 2001).

3.3. Correlation with texture, organic carbon and elements

The significant correlation between organic carbon and clay ($r = 0.65$) in the coastal sediments compared with a low correlation for the estuarine sediments ($r = 0.07$) suggests their different origins (Table 3). There is a close similarity of Fe distribution to that of clay and organic carbon in the coastal region. The significant correlation of Fe with organic carbon and clay ($r = 0.70$ and 0.65, respectively) in the coastal sediments was not found in the estuarine sediments ($r = 0.40$ and 0.27, respectively). The "dual character" exhibited by iron in these two environments was reflected in the depositional patterns of other elements. It would appear from the correlation analysis that in the coastal region, the sediment geochemistry is characterized by strong associations of metals (Me) with three matrices (Me–Me, Me–organic carbon and Me–clay), whereas in estuarine region, it is confined to Me–Me associations alone. The poor correlation for Mn with clay, organic carbon or other elements in the estuarine sediments is noteworthy indicating the absence of a common source for the element. The correlation of Zn and Cd with clay ($r = 0.29$ and 0.34, respectively) and organic carbon ($r = 0.25$ and 0.24, respectively) indicates their reduced affinity towards these fractions inside the estuary. The correlation of chromium with iron, copper and zinc was less significant ($r < 0.70$).

3.4. Factored elemental enrichment across the study region

To assess the extent of metal enrichment in the study region, the metal content in the total sediment was compared with the background values of the region. The enrichment factors (EFs) were estimated as EF = C_{Me}/BG_{Me}, where C_{Me} is the concentration of a given metal, Me, in a particular location and BG_{Me} is the background value for that metal in the region. The background value (BG_{Me}) for this study was obtained from Balachandran et al. (2003) and the enrichment factors of each metal (Zn, Cd, Fe, Cu and Pb) computed for coastal and estuarine regions are furnished in Fig. 4 against their position on a transect across the study region (as distance in kilometers from bar mouth). It is observed that Zn, Cd, Pb, Fe and Cu are enriched in estuarine region whereas; Cr, Ni and Mn are impoverished. Co and Mn did not show any trend across the region (hence Mn, Co, Ni and Cr are not included in Fig. 4).

Modifying the analysis given by Hakanson (1980), metals in this region can be classified into the following groups depending on the pollution potential: (1) negligible to low contamination (EFs < 2), which is in

Table 2
Comparison of heavy metal levels in the Cochin backwaters to that of other Indian and globally impacted coastal systems (mg kg^{-1}, except for Fe%)

Location	Fe	Zn	Cd	Pb	Cu	References
1. Cochin estuary	6.18	1266	14.94	71.28	53.15	Present study
2. Mumbai harbour, India	–	155	–	48	105	Zingde et al., 1987
3. Thana creek, India	–	206	–	28	132	Zingde et al., 1987
4. Ganges estuary, India	4.6	611	–	115	53	Subramanian et al., 1988
5. Jurujuba sound, Brazil	1.3	158	–	61	51	Baptista Neto et al., 2000
6. Tolo harbour, Hong Kong	–	270	–	144	84	Owen and Sandhu, 2000
7. Gulf of Venice, Italy	6.7	870	–	84	44	Donazzolo et al., 1981
8. Belfast Inner Lough, UK	–	798	–	207	54	Smith and Oxford, 1989
9. Bilbao Estuary, N. Spain	5.5	1092	–	314	263	Cearreta et al., 2000
10. Port Phillip Bay, Victoria	1.22	–	2.37	43.5	25	Talbot et al., 1976
11. NSW, Australia	0.9	–	1.60	21	6	de Forest et al., 1978

Table 3
Pearson correlation coefficient matrix for heavy metals, texture and organic carbon in sediments (a) Coastal region and (b) Estuarine region

	Pb	Ni	Co	Cr	Cu	Zn	Mn	Cd	Fe	Sa	Cl	Si	OC
(a) Coastal region													
Pb	1.000												
Ni	0.503	1.000											
Co	0.603	0.951	1.000										
Cr	0.183	0.712	0.632	1.000									
Cu	0.286	0.946	0.878	0.733	1.000								
Zn	0.478	0.725	0.677	0.549	0.648	1.000							
Mn	0.477	0.797	0.850	0.561	0.703	0.685	1.000						
Cd	0.509	0.675	0.777	0.466	0.506	0.469	0.820	1.000					
Fe	0.555	0.943	0.948	0.602	0.869	0.744	0.878	0.756	1.000				
Sa	−0.269	−0.820	−0.781	−0.588	−0.784	−0.441	−0.828	−0.643	−0.817	1.000			
Cl	0.122	0.766	0.630	0.689	0.846	0.469	0.511	0.243	0.647	−0.741	1.000		
Si	0.240	0.234	0.348	−0.011	0.076	0.052	0.567	0.635	0.379	−0.528	−0.179	1.000	
OC	0.102	0.665	0.646	0.419	0.689	0.259	0.535	0.449	0.697	−0.727	0.647	0.247	1.000
(b) Estuarine region													
Pb	1.000												
Ni	0.546	1.000											
Co	0.778	0.834	1.000										
Cr	0.756	0.547	0.783	1.000									
Cu	0.797	0.787	0.806	0.585	1.000								
Zn	0.866	0.565	0.752	0.569	0.870	1.000							
Mn	0.118	0.297	0.320	0.487	0.296	0.222	1.000						
Cd	0.835	0.396	0.616	0.678	0.659	0.827	0.235	1.000					
Fe	0.724	0.937	0.895	0.666	0.919	0.770	0.342	0.585	1.000				
Sa	−0.176	−0.816	−0.499	−0.205	−0.552	−0.187	−0.286	0.045	−0.692	1.000			
Cl	0.346	0.279	0.311	0.389	0.331	0.286	0.153	0.338	0.275	−0.034	1.000		
Si	−0.118	0.396	0.142	−0.124	0.166	−0.069	0.100	−0.274	0.308	−0.704	−0.686	1.000	
OC	0.184	0.423	0.164	0.073	0.488	0.249	0.310	0.236	0.398	−0.538	0.075	0.338	1.000

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ASSESSMENT ON SEASONAL VARIATION OF GROUNDWATER QUALITY OF PHREATIC AQUIFERS – A RIVER BASIN SYSTEM

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Abstract. Spatial distribution of pH, electrical conductivity (EC), total dissolved solids (TDS), fluoride and total iron content of ground water samples collected from the muvattupuzha river basin, Kerala, India, has been studied for pre monsoon and post monsoon periods of year 2001. Results showed the groundwater of the basin is acidic for which the pH values ranged between 5.5 and 8.0. Average EC was found to be less than 100 μS/cm, for most of the study region. The pre monsoon minimum and maximum TDS were found as 25.6 and 227.84 mg/L respectively, where as post monsoon values ranged between 16 and 162.56 mg/L. The relatively low EC and TDS values found both during the seasons in the lateritic terrain of the river basin signifies the lower residence time of ground water with the country rock. This makes the groundwater quality of this river basin as good. Pre monsoon season samples showed high total iron content than that during the post monsoon period. During the study period values of the fluoride contents were found to be within the permissible limits.

Keywords: groundwater quality, phreatic aquifers, pre and post monsoon periods, river basin

1. Introduction

Increased industrialization, urbanization and agricultural activities during the last few decades have deteriorated the surface water and groundwater quality of Kerala, the southern most state of India (Nageswara Rao and Ramadurai, 1970; CGWB, 2002). Understanding the special distribution of pH, electrical conductivity (EC), total suspended solids (TDS), fluoride and total iron content will help to identify the quality of ground water. Groundwater contamination can often have serious ill effects on human health. Groundwater with low pH values can cause gastrointestinal disorders, such as hyper acidity, ulcers, stomach pain and burning sensation. pH values below 6.5 cause corrosion of metal pipes, resulting in the release of toxic metals such as Zn, Pb, Cd, Cu etc. (Trivedy and Goel, 1986). Electrical conductivity (EC) of groundwater is considered as an important parameter for irrigation and industrial purposes. Total dissolved solids help to identify the potability of groundwater. Total iron content may not have direct effects on human health but is of importance due to aesthetic reasons. The excess presence of iron in groundwater causes stains to cloths and fixtures and has a bad taste and odour. These problems arise when iron concentration approaches more than 0.3 mg/L in groundwater. High concentration of fluoride in drinking water are also linked with cancer (Smedly, 1992).

Except a preliminary report (CGWB, 1989), no detailed study in terms of water quality of the Muvattupuzha river basin, Kerala have been carried out. Hence a detailed investigation of this dimension has been taken up in the present study.

2. Study Area

Kerala is characterised with forty-four rivers, which originates from Western Ghats, follows a meandering course before debouching into the coastal waters. Muvattupuzha, the major perennial river in central Kerala, drains through zones of highly lateritised crystalline rocks before finally entering into the Vembanad estuary and the Arabian sea. The river basin is bounded by the Periyar river basin on the north and the Meenachil river basin on the south. Geographically, the river basin is lying between latitudes 9°40′ and 10°10′ N and longitudes 76°20′ and 77°00′ E (Figure 1). For further discussion the basin is sub divided into four sub basins as illustrated in (Figure 2).

The basin consists of highly varied geological formations such as Pre-Cambrian crystallines, laterites and Tertiary sedimentary rocks. Charnockites,

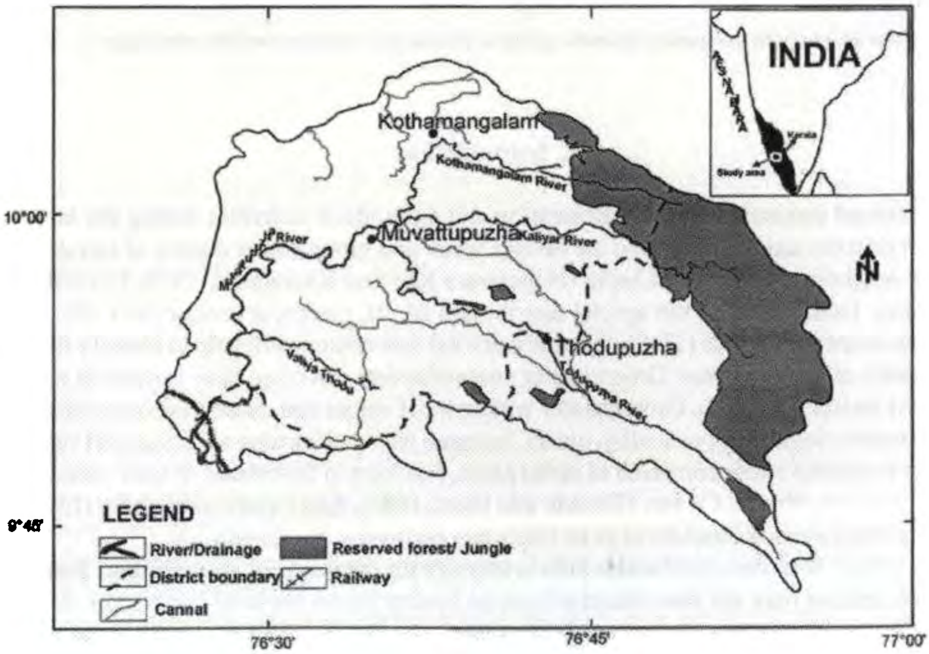

Figure 1. Base map of the Muvattupuzha river basin.

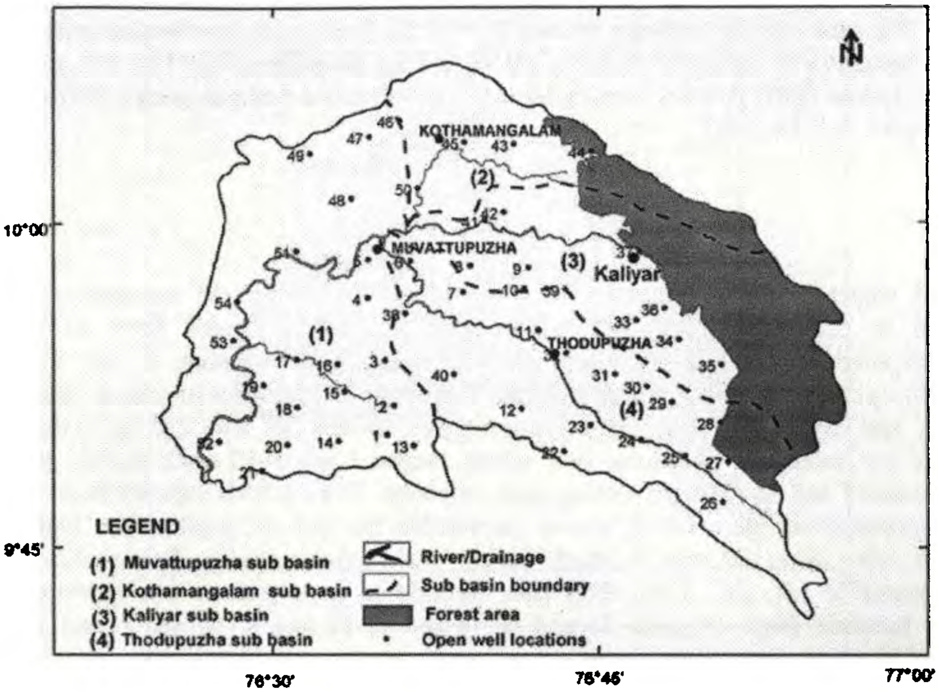

Figure 2. Sub-basins and location map of open wells in the Muvattupuzha river basin.

hornblende-biotite gneisses and other unclassified gneisses cover a major portion (~85%) of the drainage basin. These rock formations are often intruded by rocks of acidic (granite, pegmatite and quartz vein) and basic (gabbro and dolerite) types. Laterite is found almost in the entire basin as a cap rock, whereas Warkallai beds of Tertiary are found near the river mouth. The basin is also characterized by lateritic soil (over 70%) and the remaining as riverine alluvium and brown hydromorphic soil. The movement of groundwater in this basin is mostly controlled by numerous fracture systems and high gradient.

3. Materials and Methods

Groundwater samples collected from 55 dug wells from the river basin (Figure 2) during the year 2001 covering both pre monsoon and post monsoon periods were analysed for the present study. Samples were drawn with a pre cleaned plastic polyethylene bottle. Prior to sampling, all the sampling containers were washed and rinsed thoroughly with the groundwater. Water quality parameters such as, pH, EC and TDS were measured in the field itself. Samples of total iron were preserved by adding concentrated HCl, which were transported immediately to the laboratory following the standard guidelines (APHA, 1985).

The total iron and sulphate in samples were analysed using Spectrophotometer (Hitachi Model 2000, double beam UV-Visible Spectrophotometer). Fluoride concentrations in the samples were measured by colorimetric methods using SPADNS reagent (APHA, 1985).

4. Results

pH values of groundwater varied from 5.5 to 8.0 during pre monsoon and 5.6 to 8.1 during post monsoon season. EC values ranged from 40 to 356 μs/cm during pre monsoon whereas during post monsoon it was 27–254 μs/cm. Respective minimum and maximum TDS values observed were 16 and 160 mg/L during post monsoon season and 25 and 227 mg/L during pre monsoon. The total iron values ranged from 0–4.7 mg/L during pre monsoon and 0–1.2 mg/L during post monsoon. During both seasons fluoride concentrations were found within permissible limits (<0.5 mg/L). The highest value observed was 0.4 mg/L during pre monsoon season. Spatial distributions of pH, EC, TDS, total iron, fluoride in both seasons are presented in thematic maps (Figures 3a and b, 4a and b, 5a and b, 6a and b and 7a and b).

5. Discussion

5.1. pH

The pH of natural waters is often found slightly acidic (5.0–7.5). This may be due to the presence of dissolved carbon dioxide and organic acids (fulvic and humic acids), which are derived from the decay and subsequent leaching of plant materials (Langmuir, 1997). Waters with pH values above 10 are exceptional and may reflect contamination by strong base such as NaOH and $Ca(OH)_2$. The ranges for desirable limit of pH of water prescribed for drinking purpose by ISI (1983) and WHO (1984) as 6.5–8.5 while that of EEC (Lloyd and Heathcote, 1985) as 6.5–9.0.

Based on the pH distribution of the groundwater of the basin presented (Figure 3a and b), the region can be classified into five zones, viz. (i) 5.5–6.0, (ii) 6.0–6.5, (iii) 6.5–7.0, (iv) 7.0–7.5 and (v) >7.5. During the present investigation, pH value as low as 6.5 was recorded in most of the study region (almost 1/3 of the basin). In general, the distribution of pH did not show any specific trend within the basin. It's also found that at the eastern parts of sub basin, the pH distribution did not show any variation during both seasons. On the other hand, the north sub basin showed an increase in pH values during post monsoon, while the southern part of sub basin showed a decreasing trend during post monsoon. In an unconfined aquifer system (similar to the present study region) the pH was often found to be below 7

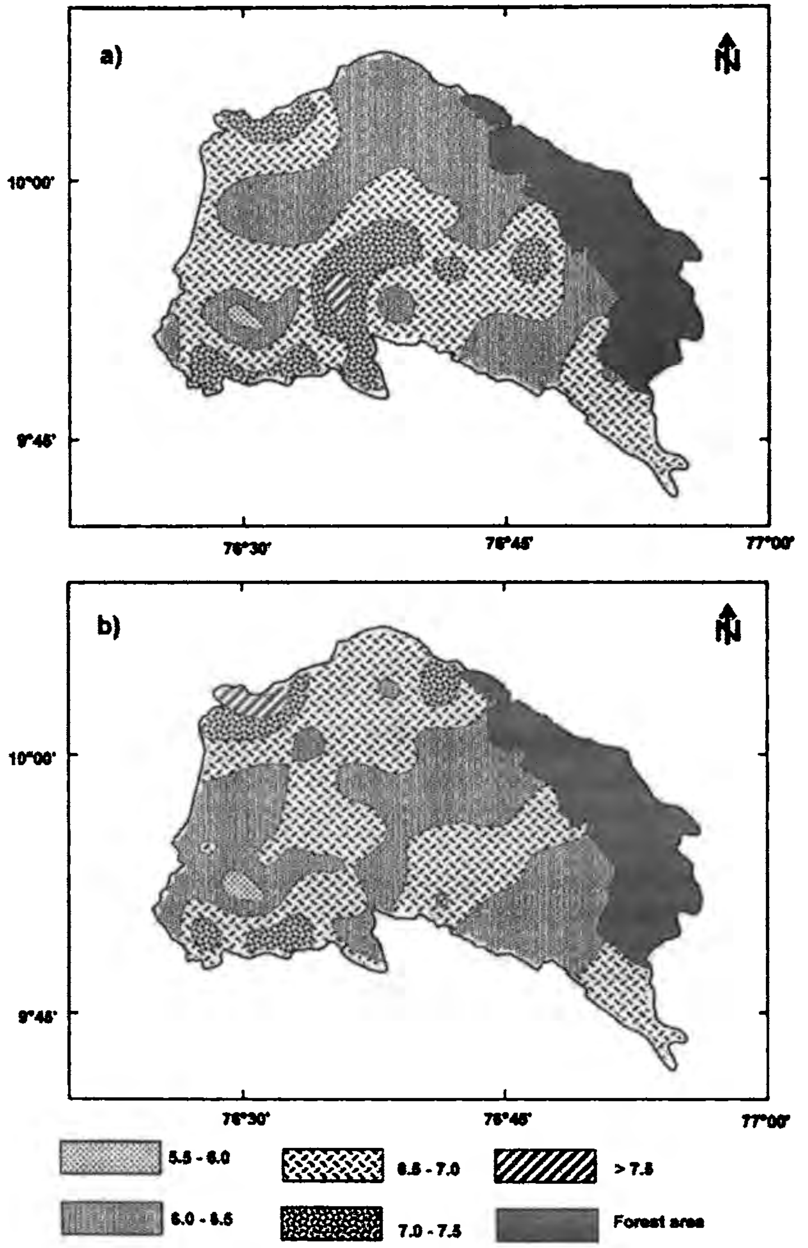

Figure 3. Distribution of pH in the Muvattupuzha river basin: (a) pre monsoon and (b) post monsoon.

(Langmuir, 1997). The low pH of the groundwater of the basin may be related to the wide distribution of lateritic soil whose pH is always acidic (CESS, 1984). Further, the study area also encompasses extensive agricultural fields. Another reason for the observed low pH values could be thus related to the use of acid producing fertilizers like ammonium sulphate and super phosphate of lime as manure for agriculture use (Rajesh *et al.*, 2001).

A low pH (below 6.5) can cause corrosion of water carrying metal pipes, thereby releasing toxic metals such as zinc, lead, cadmium, copper etc. (Trivedy and Goel, 1986). Davies (1994) while carrying out hydrochemical studies of Madhupur aquifer, Bangladesh has also found a moderately high concentration of zinc and attributed that to low pH of groundwater. Furthermore, low pH values in groundwater can cause gastrointestinal disorders like hyper acidity, ulcers, and stomach pain with burning sensation (Rajesh *et al.*, 2001).

5.2. ELECTRICAL CONDUCTIVITY (EC)

EC is measured in microsiemens/cm (μS/cm) and is a measure of salt content of water in the form of ions (Karanth, 1987). In the present study, EC values ranged from 40 to 356 μS/cm during pre monsoon period whereas it ranged from 25 to 254 μS/cm during post monsoon. The distribution of EC values is presented in Figure 4a and b. It is clear that a vast majority of the area showed EC values less than 100 μS/cm. During the pre monsoon period, low EC values were found in an east west stretch running at the centre of the basin while the northern, southern and southeastern parts of the basin showed higher EC values (>100 μS/cm). On the other hand during the post monsoon period, most of the basin (except the northern part) showed low EC values. The occurrence of high EC values (Figure 4b) on the northwestern part of the study area might also be due to addition of some salts through the prevailing agricultural activities. Comparatively zones with low EC values (<100 μS/cm) are found more during post monsoon than for pre monsoon period and are due to dilution of soluble salts by rainfall. As low EC values were recorded during the entire period, the water is found to be safe for drinking and domestic purposes. Moreover, a low EC value further signifies the anoxic condition of groundwater.

5.3. TOTAL DISSOLVED SOLIDS (TDS)

The quality of groundwater for drinking purpose can be expressed in terms of total dissolved solids (TDS). Groundwater with a TDS value less than 300 mg/L can be considered as excellent for drinking purpose (WHO, 1984). The distribution of TDS values for both seasons (Figures 5a and b) clearly showed that the entire basin falls within this range. During pre monsoon, values ranged between 25 and 227 mg/L, whereas it ranged between 16 and 162 mg/L during post monsoon period. Relatively high TDS values during pre monsoon were found on the northern and

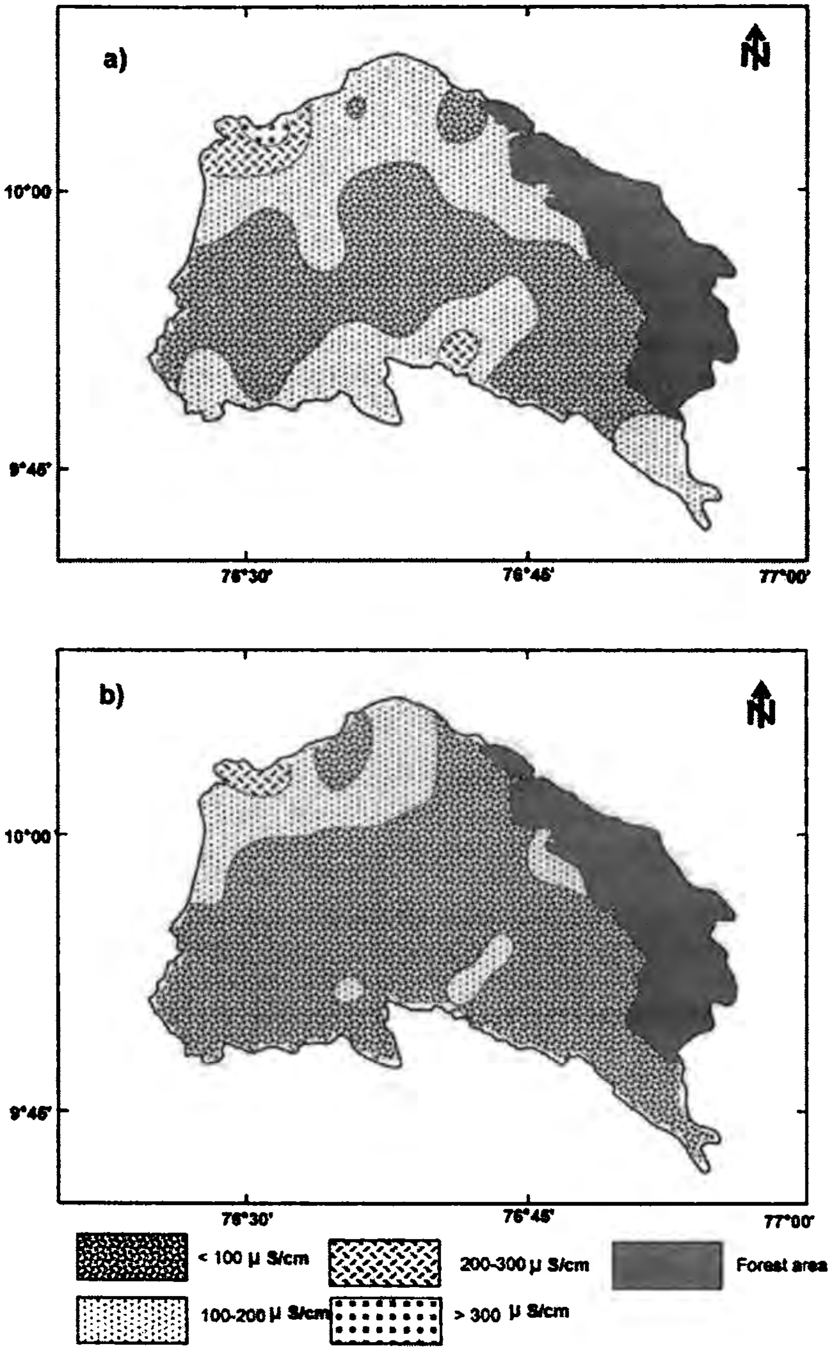

Figure 4. Distribution of electrical conductivity in the Muvattupuzha river basin: (a) pre monsoon and (b) post monsoon.

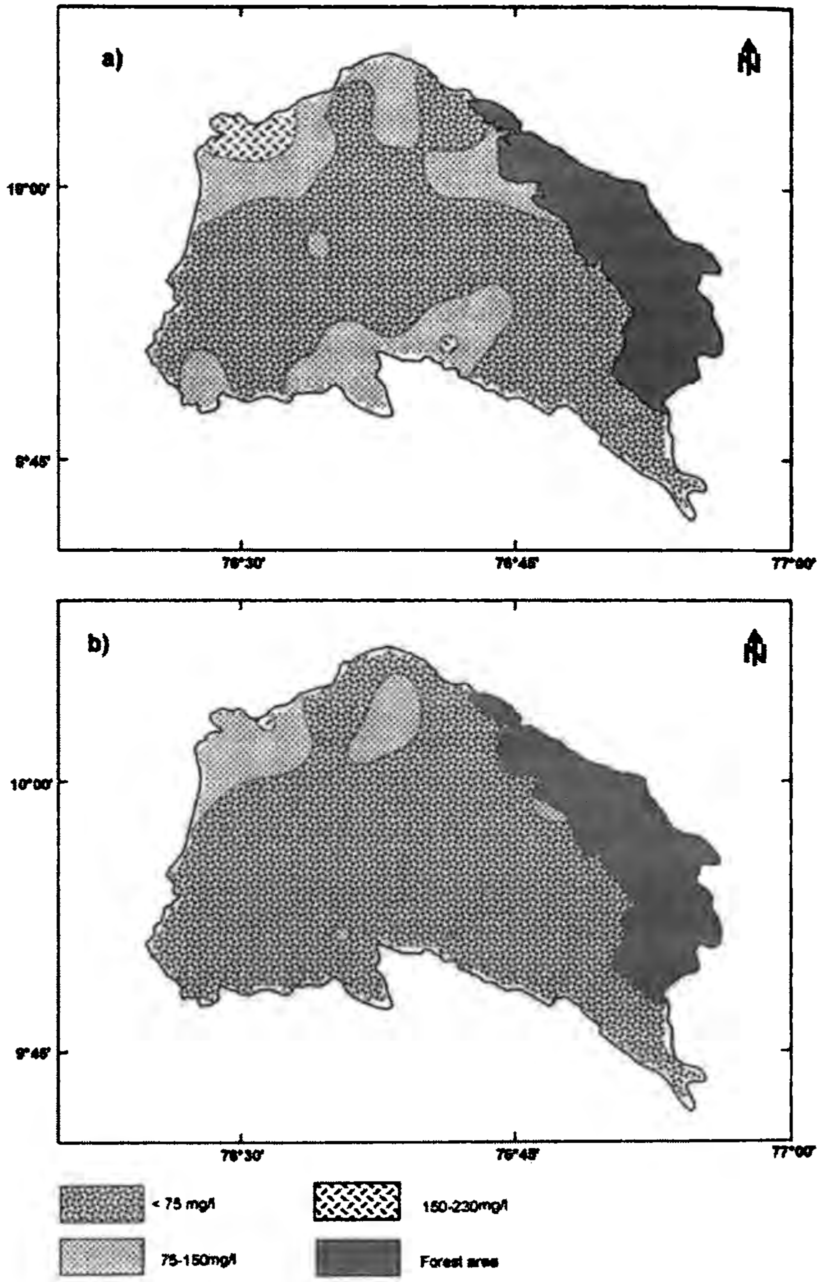

Figure 5. Distribution of total dissolved solids in the Muvattupuzha river basin: (a) pre monsoon and (b) post monsoon.

southern parts of the basin. On the other hand during post monsoon period only the northwestern parts of sub basins showed TDS values of over 75 mg/L. According to Venugopal (1998) and Aravindan (1999) the TDS values were higher during pre monsoon than during the post monsoon season. However, this basin is encountered with low TDS values which may be due to the prolonged leaching of topsoil under the existing anoxic condition.

Usually unconfined aquifer system has relatively low TDS (Langmuir, 1997). The hydrogeological properties of rocks will have a strong influence on the extent of water/rock reaction. Zones with high groundwater-flow velocities usually will have relatively low dissolved solids because of the shorter groundwater- rock contact time and high water/rock ratios, and vice-versa (Langmuir, 1997). Typical high groundwater velocities were found in highly fractured or weathered near-surface igneous and metamorphic rocks. Such conditions are usually found in shallow water table (unconfined) aquifers but not in deep, (confined) aquifers. The low TDS values found can be attributed to high rainfall prevailing, which causes significant dilution.

5.4. TOTAL IRON

Pre monsoon samples showed high total iron content than that during post monsoon period. During pre monsoon, the western part of sub basins and small patches in the southeastern part of the sub basin showed total iron values greater than 0.3 mg/L, whereas during post monsoon only the north western and south western parts of the sub basin showed more than 0.3 mg/L of total iron (Figures 6a and b). The concentration of iron in groundwater will be higher under more reducing conditions due to bacteriological degradation of organic matter which leads to the formation of various humic and fluvic compounds (Applin and Zhao, 1989; White *et al.*, 1991). Under reducing condition, the iron from biotite mica and laterites are leached into solution in ferrous state. According to Singhal and Gupta (1999) iron content in groundwater is mainly due to the dissolution of iron oxides. The common method for the removal of iron from water is by aeration followed by sedimentation. In high rainfall zones of India such as, Assam, Orissa and Kerala, it is reported that the total iron content ranges from 6.83 to 55 mg/L (Singhal and Gupta, 1999). As the study area is primarily covered with laterites (70%), leaching of iron can take place easily under the existing anoxic condition, which may be attributed to the high concentration of total iron in groundwater.

5.5. FLUORIDE

In groundwater, fluorine occurs mainly as simple fluoride ion. It is capable of forming complexes with silicon and aluminium, and is believed to exist at a $pH < 7$. Distributions of fluoride during pre monsoon and post monsoon periods of the river basin are shown in Figures 7a and b. During both seasons the fluoride contents were

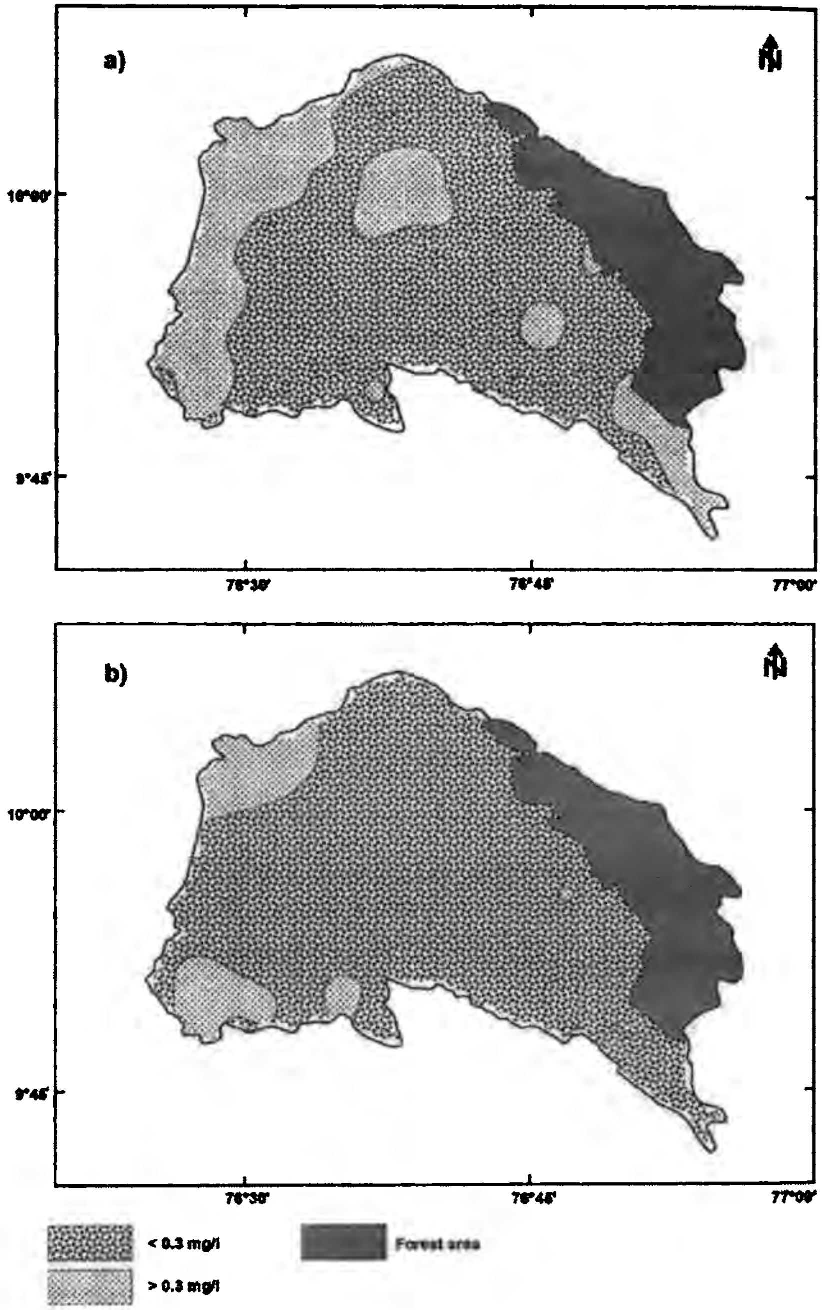

Figure 6. Distribution of total iron in the Muvattupuzha river basin: (a) pre monsoon and (b) post monsoon.

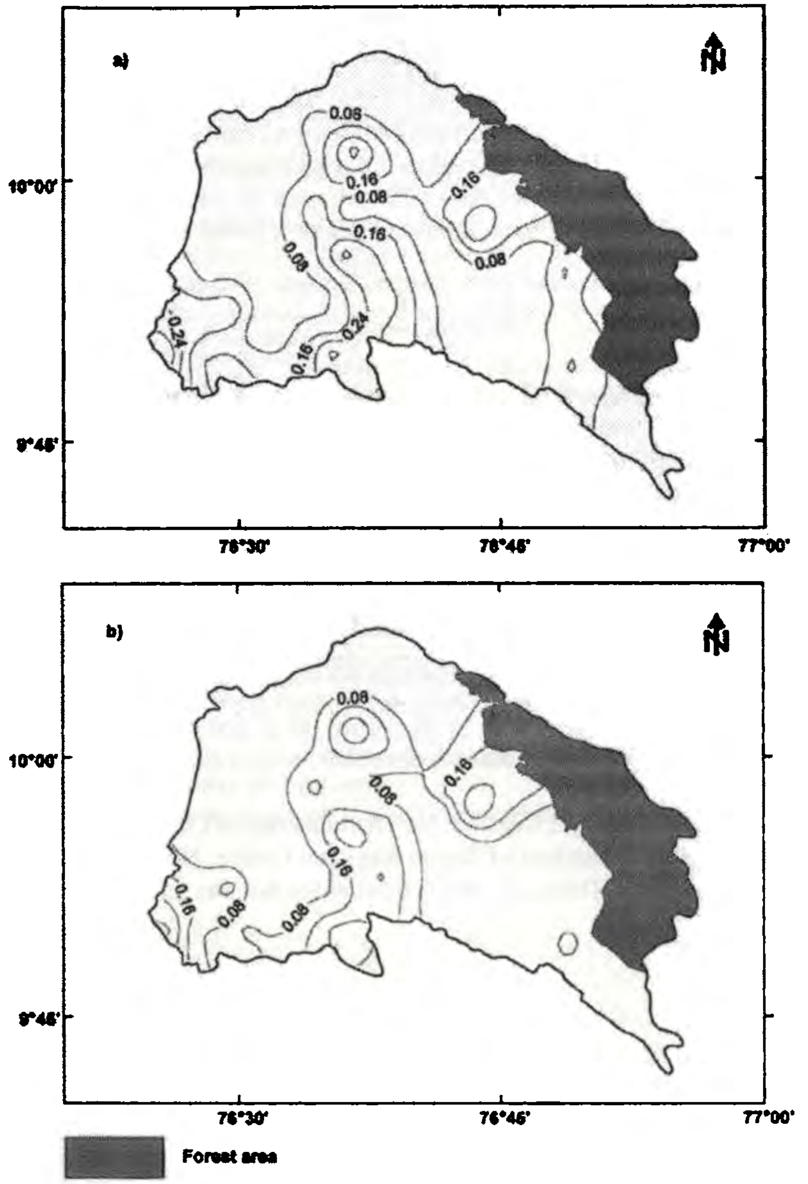

Figure 7. Isocone map of fluoride in the Muvattupuzha river basin: (a) pre monsoon and (b) post monsoon.

within permissible limits. The highest value (0.4 mg/L) is found recorded during pre monsoon season. The distribution of fluoride for both the seasons were showed more or less of an identical pattern.

Fluoride is beneficial when present in small concentrations (0.8 to 1.0 mg/L) in drinking water for calcification of dental enamel. However, it causes dental and skeletal fluorosis if high. Higher concentration of fluoride in drinking water is also linked with cancer (Smedly, 1992). A review of literature indicates that an abnormal concentration (> 1.5 mg/L) of fluoride recorded in the Rift valley of Ethiopia due to calcium fluoride derived from bedrocks (Ashley and Burley, 1995). In Kerala too high concentration of fluoride (as high as 1.5 mg/L) was recorded in some parts of the coastal zones and is possibly due to the saltwater intrusion (CGWB, 2003). However, the fluoride concentration in the study area is found to be negligible.

6. Conclusion

The groundwater of the Muvattupuzha river basin, Kerala, India in general is found to be acidic in nature with an the average EC value of less than100 μS/cm. The total iron content is found to be more than 0.3 mg/L in certain areas of the basin. During the pre monsoon period the observed maximum TDS was 227.84 mg/L and 162.56 mg/L during post monsoon. In general, the low concentration of EC and TDS in the groundwater of the phreatic zone reveals the shorter groundwater-rock-contact time. Both during pre monsoon and post monsoon seasons the fluoride contents were found to be within the permissible limits. Based on these observations the groundwater in the study region in general can be considered good.

Acknowledgments

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Geochemical index of trace metals in the surficial sediments from the western continental shelf of India, Arabian Sea

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Abstract

The present study focuses on the determination and abundance of trace metals (viz. Cu, Ni, Zn, Cr, Co, Cd, Mn and Fe) in the surficial sediments of west coast of Arabian Sea along the Indian subcontinent. Sediment samples were collected from three transects along the western continental shelf of Arabian Sea. The enrichment of Fe and Mn in coastal oxic-sediments indicates the precipitation of these redox sensitive elements as Fe- and Mn-hydroxides and oxides, whereas the low Fe and Mn concentrations in the oxygen deficient sediments of deeper stations reflects the dissolution of their hydroxides and oxides. Concentrations of fairly redox insensitive trace metals like Cu, Ni, Zn, Cr and Cd (with the exceptions of Cr) showed higher values at nearshore sediments, then it decreased towards seaward and again showed a slight increase at oxygen minimum stations in all the three transects. This geochemical variability in their distributional characteristics is mainly associated with the extent to which the precipitation or dissolution of Fe- and Mn-oxides/hydroxides occur since the scavenging or releasing effects of Fe- and Mn-oxides/hydroxides act as significant 'sinks' or 'sources' of heavy metals. The change in wind pattern, coastal upwelling and increased productivity are also the reported factors which influence the biogeochemical cycling of trace metals in the surface sediments of west coast of India. Enrichment factor generally showed a high gradient accumulation from nearshore to shelf.

Introduction

The determination of trace metals in recently deposited sediments is a useful tool in the assessment of status of environmental pollution as the surficial sediments are potentially good indicators of the quality of overlying waters (Berrow 1991). Once trace metals were discharged into coastal waters, they rapidly become associated with particulates and are incorporated in bottom sediments (Forstner & Wittmann 1983; Hansen *et al.* 1993). The trace metals associated with sediments are not essentially sheltered permanently, and under changing environmental conditions they may be released to the water column by various processes of remobilisation. Thus in aquatic system, sediments may be both a carrier and a possible source of metals.

The present study focuses on the determination and abundance of trace metals (viz. Cu, Ni, Zn, Cr, Co, Cd, Mn and Fe) in the surficial sediments of west coast of Arabian Sea along the Indian subcontinent. These trace metals all share a common trait of being authigenically enriched in sediments under reducing conditions. The mechanism of authigic enrichment of trace metals in sediments, along with their behaviour has a vital role in the surficial distribution of trace metals in western continental shelf of Arabian Sea.

Materials and methods

Study area

Arabian Sea is a semi-enclosed sea bordered on the northern, eastern and western sides by the landmasses of Asia and Africa. The width of the continental shelf along the south west coast of India is found to vary from place to place. It is narrower on southern side and gets widened towards the north. This is an area of negative water balance where evaporation exceeds precipitation and run off, the high rate of evaporation results in the formation of high salinity water masses (Venkateswaran 1956). The maximum production was reported nearer to the coasts, with in 50 m depths and gradually decrease towards the open ocean (Nair *et al.* 1973).

An outstanding feature of the Arabian Sea is the development of its oxygen minimum layer. The mid-depth oxygen defiency in the Arabian Sea is perhaps the most severally observed anywhere in the ocean, as the concentrations within 150–1000 m are < 0.2 mL L^{-1} in a large part of Arabian Sea and which narrower from north to south (Naqvi & Jayakumar 2000). The compatibly high photosynthetic activity in the Arabian Sea than that of the average of all other ocean often leads to a greater concentration of the dead cell and detritus at the thermal discontinuity layer, which consume oxygen during decomposition (Sen Gupta *et al.* 1976). The supply of oxygen to the waters below the euphotic zone gets restricted by the intense strong density gradient and poor horizontal advection due to semi-enclosed nature of Arabian Sea, results in severe depletion of oxygen below the thermo cline and at intermediate depths (Naqvi & Qasim 1983). The high organic carbon content (2–6%) in the western continental shelf of Arabian Sea (Prakash Babu *et al.* 1999) has also enhanced the oxygen minimum nature of water column.

The west coast of India is under the influence of changing wind patterns associated with almost all seasons. The coastal currents are southerly from April to September and reverse their direction to northerly from November to February. The coastal zone of western India experiences upwelling in most of the seasons and intense local wind stress (Banse 1959; Naqvi *et al.* 2000). Thus, high overlying productivity and sluggish intermediate water moments during northeast monsoon (December–February) can lead to higher consumption of oxygen and more intense suboxic and denitrifying conditions in Arabian Sea (De'Souza *et al.*, 1996; Madhupratap *et al.* 1996). So the intense suboxic condition, change in wind pattern and coastal upwellings are the major factors which influence the biogeochemical cycling of trace metals in the surface sediments of west coast of India.

Sampling

Surficial sediment samples were collected during the 192A cruise of FORV SAGAR SAMPADA of Department of Ocean Development, Government of India from 12 stations off west coast of India between Cochin and Bombay during winter monsoon (February 2000). The area lies between latitude 10°27.25′–17°29.39′ N and longitude 71°26.74′–75°51.45′ E. Sediment samples were collected from three transects along the western continental shelf of Arabian Sea. One transect is in the northern zone (17°29′39 N) with intense reducing condition, one in the central zone (13°29′52 N) and one in western zone (10°28′45 N) of the western continental shelf of India and the details are given in Figure 1. Sediment samples were collected from the sediment bed using Smith-Mc Intyre grab, which is 0.1 m^2 and is of moderate weight of 45 kg. About 250 g of the samples were transferred to polythene bag and were kept shock frozen to preserve their chemical integrity until analysis. The sampling reproducibility was checked by duplicate subsampling measurements.

Analysis

Hydrographical parameters such as water salinity and temperature were obtained from the CTD instrument. The bottom-dissolved oxygen from each station was also estimated chemically on-board using Winkler's method (Grasshoff *et al.* 1999).

The sediment samples were dried at room temperature at constant weight (0.5 g) and were heated with perchloric acid, nitric acid and

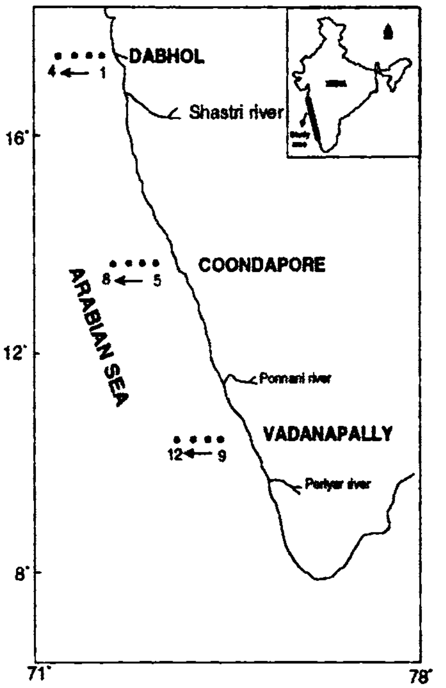

Fig. 1. Location of 12 sampling stations along the 3 transects from the western continental shelf of Arabian Sea.

hydrochloric acid (2:10:8) in closed beaker in a hot plate at 90 °C for 20 h. The acidic solutions were centrifuged in glass containers at 6000 rpm and the final solution made upto 50 mL with 1 N HNO_3. All the chemical treatments were carried out using Milli Q 18 mΩ quality deionised water. Care was taken during sample handling and analysis to prevent the samples coming into contact with dust and metals. The metal concentrations were estimated in Graphite furnace atomic absorption spectrometer (Perkin Elmer model 3110). Procedural blank and a reference material (BCSS-1) were analysed in similar way to check the accuracy of analysis, which was better than 6% for Cu, Co, Fe & Mn and better than 10% for Zn, Ni, Pb and Cr (Table 1). Analytical reproducibility was checked by performing duplicate analyses of each of the duplicated subsamples. Thus, final analytical date are presented on a weighted-average bases of quadruplet values.

Results and discussion

Salinity, temperature and dissolved oxygen

Salinity, temperature and dissolved oxygen values of the sampling stations are given in Table 2.

The coastal stations showed lowest values of salinity, and increased towards seaward in all transect. The low values at coastal stations are due to the surface dilution. The bottom temperatures were found to decrease from south to north. The high values were observed at coastal stations and decreased towards seaward. The variations of salinity and temperature in all transects were found to be a similar pattern. The farthermost seaward stations (4, 8 & 12) in all the three transect were distinguished with comparatively very low temperature (≈16.0–17.0 °C) and all the three stations were significantly above 195 m deep.

The dissolved oxygen values were found to decrease from coastal to seaward. In higher depth stations (4, 8 &12), the values were very low (≈0.1–0.2 mL L^{-1}) which are very close to almost an anoxic condition. The very low values were found in the northern transect and increased towards the south. These values were well supported by the earlier findings of Naqvi & Jayakumar (2000). The dissolved oxygen was more in the surface layer due to high primary productivity. The observed variations in the distribution of dissolved oxygen may be due to the interplay between biochemical process, and those by which

Table 1. Comparison of standard reference material (BCSS-1) with the present study (μg g^{-1} dry weight expect for Fe, which is in %).

BCSS-1	Cu	Ni	Mn	Fe	Pb	Co	Cr	Zn	Cd
Certified values	18.5 ± 2.7	55.3 ± 3.6	229 ± 15	5	22.7 ± 3.4	11.4 ± 2.1	123 ± 14	119 ± 12	0.59 ± 0.1
This study[a]	18 ± 2.0	49.8 ± 2.3	216 ± 17	4.7	20.4 + 2.9	10.8 ± 2.5	111 ± 19	107 ± 9	0.53 ± 0.2

[a] SD is for $n = 4$.

Table 2. Sample location and analysis of primary parameters.

Transect	Station No.	Depth (m)	Lat. (N)	Long. (E)	Temp. (°C)	Salinity	D.O. (mL L⁻¹)
17°29′39	1	35.0	17°29′39	72°57′22	26.70	35.68	3.87
	2	57.0	17°29′39	72°43′09	26.66	35.60	3.72
	3	96.0	17°29′39	72°16′25	25.69	35.68	2.03
	4	192.0	17°29′39	71°26′74	16.18	35.47	0.10
13°29′52	5	34.0	13°29′52	74°30′04	28.48	34.60	3.87
	6	54.0	13°29′52	74°05′81	27.71	35.75	3.11
	7	104.0	13°29′52	73°31′63	25.90	35.83	2.26
	8	193.0	13°29′52	73°26′55	16.04	35.30	0.11
10°28′45	9	38.0	10°28′45	75°42′59	28.47	34.66	3.30
	10	53.0	10°28′45	75°31′57	28.27	35.27	3.13
	11	103.0	10°28′45	75°52′53	25.42	35.62	2.46
	12	197.0	10°28′45	75°25′52	17.18	35.24	0.20

the oxygen enters and is transported in the water. But the ultimate factor causing the depletion of O_2 in deep stations were due to the oxidation of organic matter.

Trace metals

Analytical results and variation with depth of trace metals in the surface sediments of western continental shelf of India are given in Figures 2 to 4.

Fe concentration was found to be the highest among all metals at all stations studied. In all the three transects, the highest concentrations of Fe and Mn were present in the nearshore stations (1, 5 &12) and decreased with depth. Among the values, the highest values were found at the northern transect. This was due to the high anthropogenic activities from riverine input at the northern transect. It is well known that Fe and Mn are enriched in oxic sediments due to precipitation as their corresponding oxyhydroxides (Klinkhammer *et al.* 1982). The low Fe and Mn concentrations in the sediments of deeper stations (4, 8 &12) were mainly due to the fact that development of reducing conditions around the sediment-water interfaces. Under these oxygen minimum conditions these metals are released from sediments to the surrounding waters due to the subsequent reduction of their oxyhydrides (Sullivan *et al.* 1997; Manford *et al.* 2001; Nameroff *et al.* 2002). The reducing condition may be developed due to the high productivity and high organic matter in the sediment, which is very much effective in removing and adsorption of number of elements from the sediments (Calvert & Perderson 1993; Sagar 1994). Mn and its compounds such as manganese nodules are important constituents of pelagic sediments and control the transition metal concentration in marine sediments. Almost similar trend of Fe was exhibited by Mn at all the stations and shows a high correlation between them

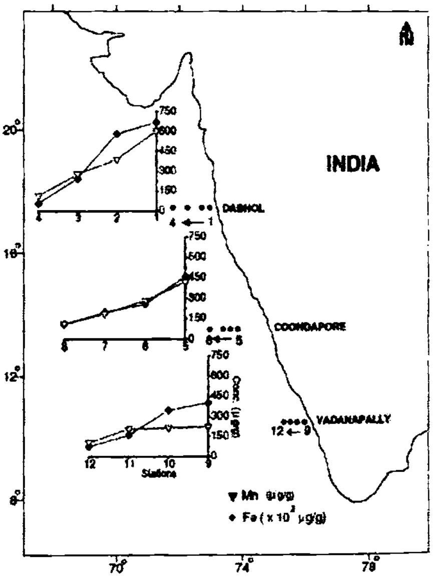

Fig. 2. Surface sediment concentrations of Fe and Mn at 12 stations along the 3 transects from the western continental shelf of Arabian Sea (each value is an average of quadruplet sample analysis).

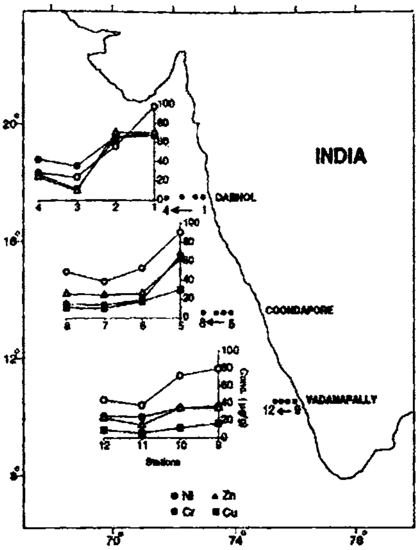

Fig. 3. Surface sediment concentrations of Ni, Cr, Zn and Cu at 12 stations along the 3 transects from the western continental shelf of Arabian Sea (each value is an average of quadruplet sample analysis).

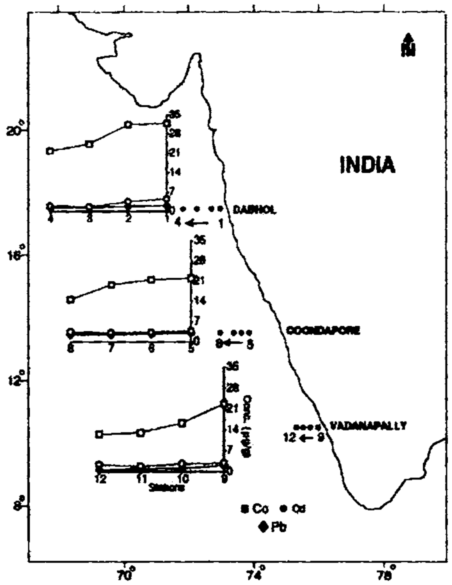

Fig. 4. Surface sediment concentrations of Co, Cd and Pb at 12 stations along the 3 transects from the western continental shelf of Arabian Sea (each value is an average of quadruplet sample analysis).

($>$0.91). So it could be viewed that Fe and Mn behaves as similar way in the marine environment.

The concentrations of Co range from 31.93 $\mu g\ g^{-1}$ at station 1-4.41 $\mu g\ g^{-1}$ at station 12. The higher concentrations of Co were seen at nearshore stations and decreased with increasing depth. Co was also highly correlated with Fe. The adsorption of the clay minerals, iron and manganese oxides may be contributing to the observed concentration of Co in this study. The trace metal studies in anoxic water revealed that the reduced species of Mn, Fe and Co are more soluble than the oxidised one. A similar association of Co with the Mn cycle has been reported in many earlier works in anoxic waters (Haraldsson & Westerlund 1988; Dyressen & Kremling 1990; Lewis & Landing 1991).

Concentrations of Cu, Ni, Zn, Cr and Cd showed higher values at nearshore sediments, then it decreased towards seaward and again showed a slight increase at oxygen minimum stations (4, 8 & 12) in all the three transects. The maximum concentrations were observed in northern transect and minimum were in the western transect. This geochemical variability in their distributional characteristics was mainly attributed to the scavenging or co-precipitating effect of Fe- and Mn-hydroxides on these trace metals. The slight increase in the concentrations of these redox sensitive metals at oxygen minimum layers was due to the development of reducing conditions at the end of continental shelf stations (4, 8 & 12). Under this reducing conditions, these elements whose valency does not change but which form highly insoluble sulphides such as Cu, Cd, Ni, Cr and Zn. They exist as a network of interconnected sulphur complexes and sulphides and are removed from seawater by diffusion into anoxic sediments (Calvert & Perderson 1993; Manford *et al.* 2001; Marcus *et al.* 2003). So an enrichment of Cu, Cd, Zn, Cr and Ni in the upper slope stations (4, 8 & 12) suggests that a reducing condition do prevail in this environment, which was impinged by the oxygen minimum zone in Arabian Sea. The values further revealed that the extend of enrichment of these metals were comparatively high in northern transect. So that the geochemical behaviour of Cd, Cu, Zn, Ni and Cr can be used as indicator of sedimentation under redox condition. Among these metals, Cr showed higher values in all stations which is possibly due to their high enrichment in earth crust, especially in marine environment.

The concentrations of lead ranged from 0.505 $\mu g\ g^{-1}$ (station 12) to 3.04 $\mu g\ g^{-1}$ (station 5). The higher concentrations were at central transect and lower were at western transect. Lead also showed coastal enrichment but the variation is not significant. These low and less fluctuated Pb concentrations indicated that anthropogenic inputs were of minor importance, this in contrast to other areas around the world. Lead is easily removed from the water column by adsorption to mineral particles and subsequent sedimentation (scavenged elements) with Fe- and Mn-hydroxide precipitate.

Anthropogenic deposition of trace metals is a significant source for these metals in sediments. In the case of nearshore sediments due to the constant turbulent nature of water by wave action, nearshore environment become more oxic which in turn increases the deposition of precipitate with adsorption of different elements in the sediments. The coastal enrichment of these elements is consistant with previous studies in other areas of the world ocean (Klomp *et al.* 1986; Sanudo-Wilhelmy & Flegal 1996). Those elevated coastal concentrations have been attributed to benthic remobilisation, including particle resuspension and diffusive fluxes, upwelling and continental weathering (Martin & Gordon 1988; Westerlund & Ohman 1991). The coastal current in the coastal zone of western India and the coastal upwelling are the other important mechanism of metal transport in coastal waters and sediments in Arabian Sea (Naqvi *et al.* 2000; Shankar 2000). The samples analysed in this study were collected in February, when coastal upwelling and primary productivity were intensified. Thus, the most of the metals enhanced sorption onto sinking particles. Several studies have provided evidence that these coastal processes can enhance trace metal concentrations in coastal waters and sediments (Bruland 1980; Jones & Murray 1984).

General features and correlations

In order to find the dependency of trace metal levels in surface sediments as a function of water column depth/dissolved oxygen/temperature/iron content, a simple correlation has been used (Figures 5 and 6). Salinity has not been considered as a function for the interpretation of the trace metal data of the present study since the values of salinities are in the range 34.64–35.83 (Table 2) and hence the variations are insignificant. The correlation coefficient (r) values which are significant at ± 1 levels are only considered here. For interpretation, we consider $r > 0.70$ as a most significant association which has very high realistic correlation and r values between 0.56 and 0.7 as moderate association. These associations are in agreement with nature of sediment and the relative enrichment or depletion of elements in the zones (such as temperature, dissolved oxygen and Fe), suggesting well-defined carriers of metals to the sediments.

The moderate positive correlation observed for Fe and Mn with temperature and dissolved oxygen (Figure 5) can be attributed to their redox-potentials (Sullivan *et al.* 1997; Russell & Manford 2001). The reducing condition may be developed due to the high productivity and high organic matter in the sediment, which is very much effective in removing and adsorption of number of elements from the sediments (Calvert & Perderson 1993; Sagar 1994). Dissolution of these elements from sediments to overlying water makes them impoverished at low temperature and oxygen depleted environment. The supply of oxygen to the waters below the euphotic zone gets restricted by the intense strong density gradient and poor horizontal advection due to semi enclosed nature of Arabian Sea, results in severe depletion of oxygen below the thermo cline and at intermediate depths (Naqvi & Qasim 1983). The high organic carbon content (2–6%) in the western continental shelf of Arabian Sea (Prakash Babu *et al.* 1999) has also enhanced the oxygen minimum nature of water column.

The oxygen deficiency in the bottom sediments may lead to the dissolution of hydrous iron and manganese oxides and to a release of co-precipitated heavy metals (Forstner & Wittmann 1983). It also follows that environment observed with increase in temperature is possibly due to its accelerated precipitation towards the coastal region, where the overlying waters were warmer and saturated. The impact of redox potential for Cd, Cu, Cr, Ni and Zn on temperature and dissolved oxygen is quite contrary, while on precipitation

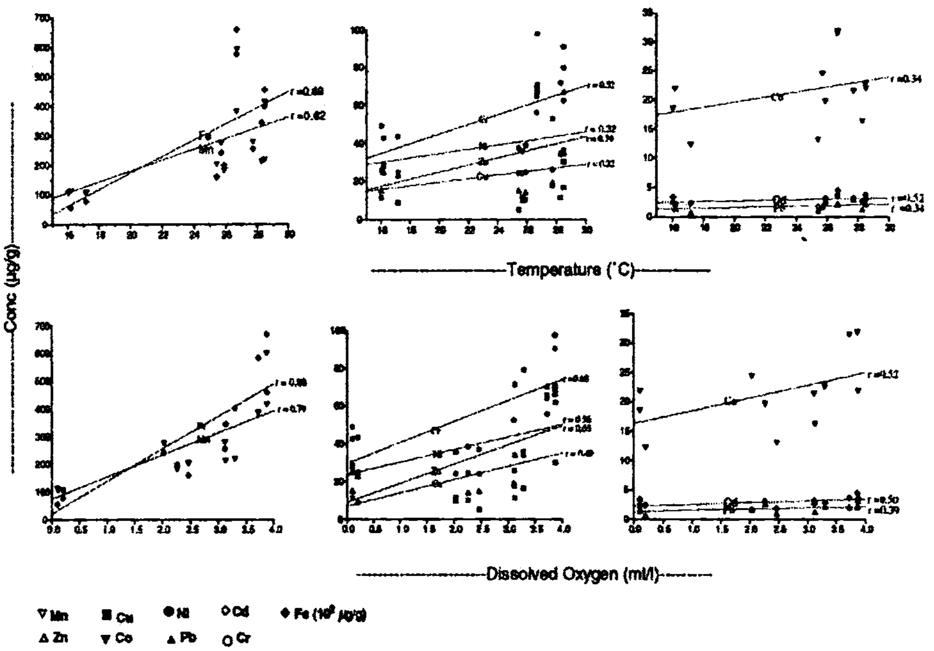

Fig. 5. Correlation of trace metals in surficial sediments with temperature and dissolved oxygen (n = 12, and each reported value is a weighted average of quadruplet sample analyses).

was the mechanism for their accumulation at low temperature and dissolved oxygen (Calvert & Perderson 1993: Marcus *et al.* 2003) for stations 4, 8 & 12. The depth wise negative correlation (Figure 6) shows that trace metals burial progressively decreased from nearshore to the shelf. The uniform moderate correlation exhibited by elements Cd, Cu, Cr, Ni and Zn probably indicates their common sources. The compatibly high photosynthetic activity in the Arabian Sea than that of the average of all other ocean often leads to a greater concentration of the dead cell and detritus at the thermal discontinuity layer, which consume oxygen during decomposition (Sen Gupta *et al.* 1976).

The bivarient analysis for different elements in the study showed their preferential burial mechanism in marine environment. Since Fe was the most abundant element in the study region, its linear correlation with other elements varied in the order Mn > Zn > Ni > Cu > Cr > Co > Cd > Pb (Figure 6). It is evident that the high significant correlation between Fe and Mn is due to their characteristics as scavenging elements (Lewis & Landing 1991). The geochemistry of sediments shows that Fe and Mn form the principle lattice for adsorption of other elements due to their scavenging property, which leads accumulation by co-precipitation. Thus, the distribution and digenetic mobility of trace metals is largely controlled by redox cycles of Mn and Fe. Many workers have pointed out similar condition in other similar areas (Sullivan *et al.* 1997; Manford *et al.* 2001; Nameroff *et al.* 2002).

So the intense suboxic condition, change in wind pattern and coastal upwellings are the major factors which influence the biogeochemical cycling of trace metals in the surface sediments of west coast of India.

Geochemical normalisation

Since the concentrations of metals from environmental sediment samples depend on large number

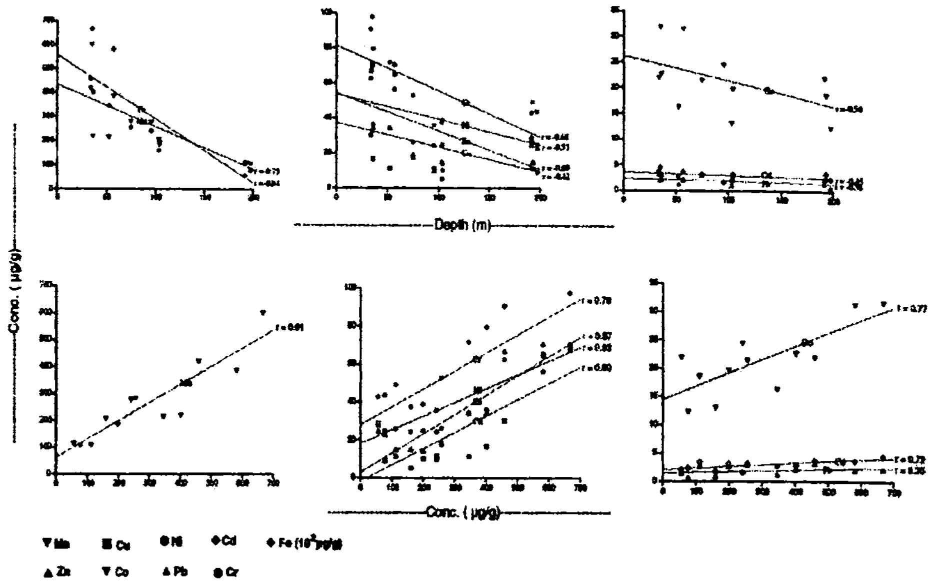

Fig. 6. Correlation of trace metals in surficial sediments with Fe content and water column depth (*n* = 12, and each reported value is a weighted average of quadruplet sample analyses).

of factors, normalisation for metal contamination in surfacial sediments is very difficult and uncertainties are inherent to any methodology employed. The simplest and most frequently used method of assessment of metal contamination is to compare the values with those of global shale of Turekian & Wedepohl (1961). The ratios however suffers from errors due to mismatching of genesis of matrix, which play as a crucial role in metal contaminations. Here, the procedure applied has some change, instead of the global shale values, the concentration of offshore values (depth ≈ 200 m) from corresponding transect (stations 4, 8 & 12) has been taken for getting a more critical evaluation of the regional anomaly. The enrichment factor's computed should be noted that many of these values exceed the corresponding Global shale levels (Table 3).

Table 3. Enrichment factor (EF) of metals analysed[a] in the sediments of western continental shelf of Arabian Sea.

Transect	Fe	Mn	Cr	Zn	Cu	Cd	Ni	Pb	Co
17'29'39	11.93	5.23	3.38	2.88	2.46	2.20	1.65	1.51	1.45
	10.41	3.36	1.94	2.87	2.34	1.78	1.53	1.46	1.43
	4.32	2.42	0.84	0.39	0.41	0.79	0.84	1.18	1.11
	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
13°29'52	4.11	3.81	1.85	4.50	2.68	1.09	2.42	1.22	1.18
	2.30	2.57	1.07	1.27	1.56	0.94	1.01	1.12	1.15
	1.78	1.69	0.79	0.94	0.90	0.92	0.96	1.00	1.06
	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
10°28'45	5.19	2.05	1.82	1.50	1.86	1.22	1.45	3.96	1.84
	4.46	1.99	1.64	1.50	1.26	1.15	1.38	2.12	1.32
	2.06	1.91	0.86	0.65	0.59	0.75	0.97	1.64	1.06
	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

[a] Factors have been derived from the average values of quadruplet sample analyses.

Enrichment factor (EF) generally showed a high gradient accumulation from nearshore to shelf. An abnormality was observed in EF of Cd, Cu, Cr, Ni and Zn, where they were unusually low (stations 3, 7 & 11) compared to the farther stations (stations 4, 8 & 12) in all transects (Figure 7). As the normal trend should give a lesser EF values at stations 4, 8 and 12, and since this was observed right through the study area, there seems to be some mechanisms associated with low dissolved oxygen. It is widely accepted that metal precipitation was favoured to elements exhibiting redoxpotential in oxygen depleted environment (Calvert & Perderson 1993; Sullivan *et al.* 1997; Russell & Manford 2001). The location of the farthest stations in each of the transects are lying in the low oxygen (even OMZ) in the Arabian Sea. It is hence possible that of its adjacent zone to the east, thus upsetting an unusual dip in the EF distribution.

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Seasonal Variations in Groundwater Chemistry of a Phreatic Coastal and Crystalline Terrain of Central Kerala, India

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This article investigates the seasonal variation in geochemical characteristics of groundwater in phreatic aquifers of the coastal plain and crystalline terrain of central Kerala, India. Within the coastal plain, the western barrier island area shows values of electrical conductivity (EC, >3 times), Na^+, K^+, Cl^- (four times), Mg^{2+} (10 times), Ca^{2+} (two times), and $HCO_3^- + CO_3^{2-}$ (approximately two times) higher than those of the eastern coastal plain during both seasons. In contrast, pH and SO_4^{2-} concentrations showed little variation. The alkaline nature and high EC of groundwater in the western barrier island–coastal plain is found to result from the intrusion of saltwater from the adjacent Vembanad estuary. In contrast, groundwater of the crystalline terrain is found to be slightly acidic with low EC. Within the crystalline terrain, the area east of Muvattupuzha River showed high EC values during both seasons while other parameters showed marginal variation. The trilinear diagram reveals that most of the groundwater samples from the crystalline terrain, which is of type IV (Ca^{2+}–Mg^{2+}–Cl^-–SO_4^{2-}) during the premonsoon period, changed character to type II (Na^+–K^+–Ca^{2+}–HCO_3^-) during the postmonsoon period. This shift is possibly caused by the addition of Na^+ and HCO_3 through the leaching of the country rock. Results for the western barrier island reveals that most of the samples are affected by the saline water incursion. Fecal contamination is found to be comparatively high in the groundwater of the coastal plain versus that of the crystalline terrain. This study indicates that the groundwater from the crystalline terrain is of higher quality than that of the coastal plain. The study further reveals the need for seasonal or multi-seasonal sampling when a geochemical characterization is performed and the recognition of physical events, such as heavy precipitation or droughts, when interpreting the geochemical characteristics of an aquifer.

Keywords: groundwater chemistry, phreatic aquifer, coastal plain, crystalline terrain, trilinear diagram, Kerala, India

Introduction

Integrity and sustainability of groundwater resources is controlled by the complex interplay of environmental forcing including urbanization. An understanding of cumulative nature of these impacts to geochemical conditions and to groundwater conditions may help in forensic studies dealing with groundwater geochemistry. Accurate estimations on the origin of chemical constituents and their seasonal geochemical variations are often needed when a forensic evaluation is undertaken. This article provides an explanation of the geochemical conditions in Kerala (India), based on the chemical constituents found in groundwater samples and how the forensic scientist may use and explain the resulting data. In particular, it is often asked to differentiate between natural and anthropogenic sources for the constituents in groundwater and to identify the provenance of these chemical constituents. Physical events (e.g., monsoons, seawater intrusion) must be considered when interpreting these geochemical results, especially when trying to identify the sources for these constituents.

Kerala, a southwestern coastal state of India, has unusual hydrogeological and climatic conditions. This narrow stretch of land, 600 km long with an average width of 50 km, is bound by the Arabian Sea on the west and the Western Ghat Mountains on the east. The groundwater resources of this densely populated 100% literate state play a crucial role in various developmental activities especially during the summer (March to May) season. Kerala enjoys a tropical monsoon climate and receives an average annual rainfall of approximately 3,100 mm. Approximately 70% of the rainfall occurs during the southwest monsoon (June to September), 15% during the northeast monsoon (October to December), and the rest as summer showers. Steady base flow from groundwater emerges as surface run off during the non-monsoon periods. The drying up of rivers and streams during the summer leads to non-availability of water from rechargeable sources of groundwater in the coastal plain and crystalline terrain. Further problems arising from rapid urbanization, industrialization, irrational land use, and overexploitation of groundwater, in addition to seawater intrusion, lead to worsening of the groundwater quality to alarming proportions in several stretches in the region. This decline in quality is further triggered by activities such as unregulated sand mining of riverbeds in the midlands and lowlands and deforestation in the upstream terrain. The shallow coastal aquifers of Kerala and open wells (density approximately 400 wells/km^2) are the dominant groundwater abstraction structures

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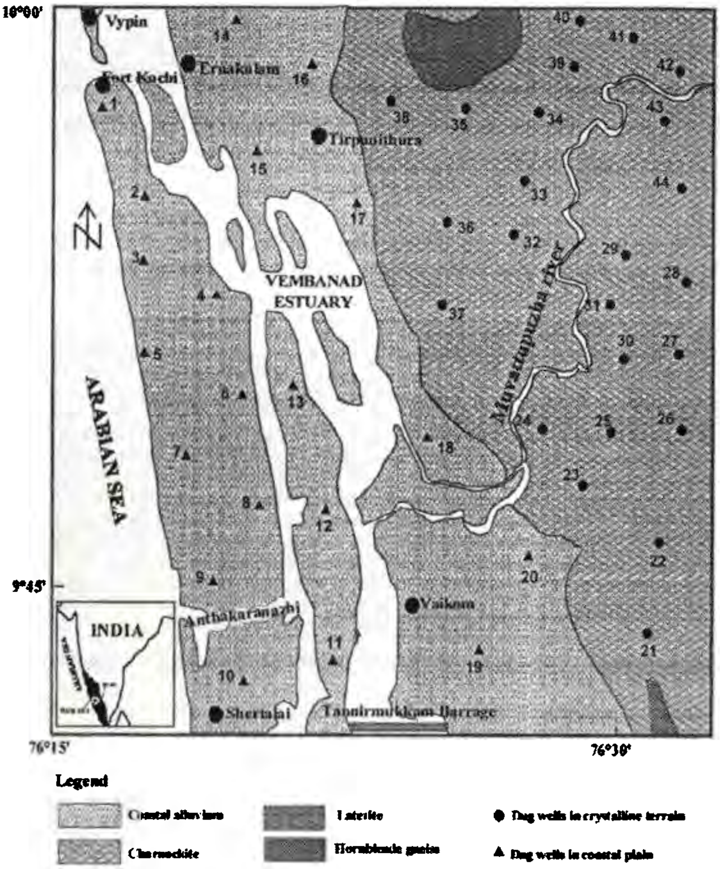

Figure 1. Base map showing station locations along the study region.

(Rajendran et al., 2002). The coastal plain has reported qualitative and quantitative groundwater problems (CWRDM, 1985; CGWB, 1992, 2002; Laluraj et al., 2005). Various studies have shown that groundwater quality in the shallow aquifers of the coastal plain is deteriorating rapidly, despite plentiful rainfall in plenty (Venkataraman, 1983; Ahmed et al., 1987; Dipanjali, 2000; Kumar, 2001; Kunhambu, 2003).

The Vembanad estuary (Figure 1) occupies a major portion of the study area (latitudes 9° 40′ and 10° 00′ N and longitudes 76° 15′ and 76° 35′ E), where tidal intrusion during non-monsoon months extends up to Tannirmukkam barrage, which regulates fresh water flow from the southern side of the backwater system. Hence, the western part of the coastal plain, covering the barrier island from Fort Cochin to Shertalai, is expected to be affected by intrusion of seawater from the Arabian Sea and brackish water from Vembanad estuary (Laluraj et al., 2005). The remaining zones of the coastal plain on the east experiences only brackish water intrusion. The Muvattupuzha River, which drains in the eastern crystalline terrain and is a major source for groundwater recharge. In the study area, groundwater is tapped from the phreatic weathered/fractured zone of the crystalline terrain and quaternary coastal alluvium (Girish and Seralathan, 2003, 2004a, 2004b; Laluraj and Girish, 2005). In the quaternary coastal alluvium, tapping of groundwater is mainly carried out through dug wells with depths ranging from 2 to 8 m (Raghava Rao, 1976). A previous attempt was reported for a smaller region in the study region to delineate the groundwater chemistry of one season (Laluraj et al., 2005). The present study extends the previous analyses for a systematic quantitative investigation to cover seasonal variations and different geologic formations.

Geology of the Study Area

An exploratory borehole study conducted within the coastal plain region by the Central Groundwater Board indicated the

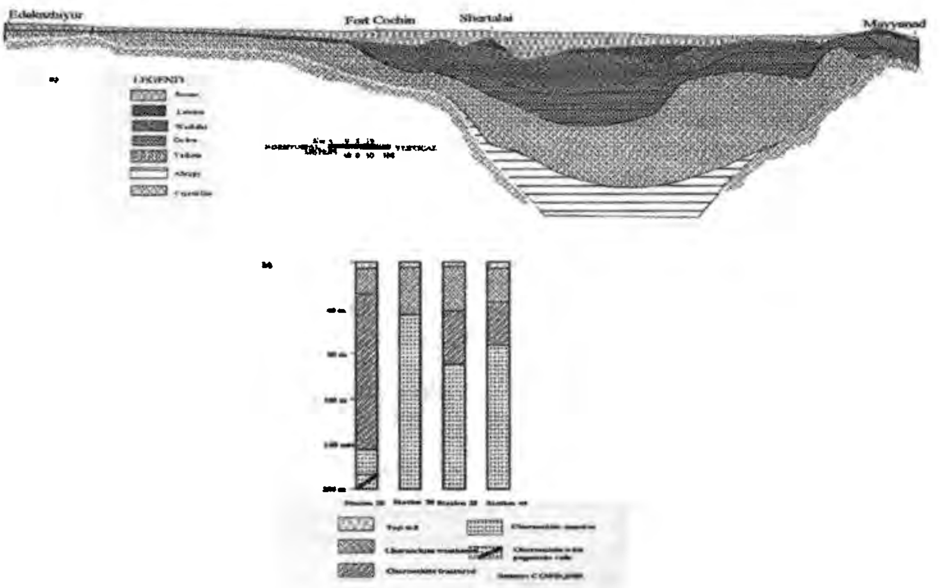

Figure 2. Subsurface lithology from bore well data (a) coastal plain (b) crystalline terrain.

presence of quaternary coastal alluvium (20 to 55 m) overlying tertiary sediments consisting of four distinct formations: the Warkali, Quilon, Vaikom, and Alleppey (Figure 2a). The Warkali Formation (approximately 80 m thick) consists of fine- to medium-grained semi-consolidated sandstone, coarse to very coarse sand, and variable clay with thin lenticular bands of lignite. The Quilon Formation (6 to 100 m thickness) is composed of ash-grey, hard, compact limestone; calcareous clay: and marl. The Vaikom Formation is composed of gravels, coarse to very coarse sands, clay, and carbonaceous beds. In several stretches, residual laterite is found lying between the quaternary alluvium and Warkali Formations (Raghava Rao, 1976). The sub-surface lithology further reveals that the Warkali Formation is absent beyond north of Fort Cochin (Figure 2a). The Alleppey Formation is composed mainly of highly carbonaceous clay and sandy clay beds. The coastal and offshore quaternary and tertiary sedimentary formations, otherwise known as *Kerala Basin*, uncomfortably overlie the Precambrian rocks of the crystalline terrain (Raghava Rao, 1976; Soman, 2002).

The Precambrian crystalline terrain consists of highly varied geological formations including laterites, charnockites, and hornblende gneiss. The charnockites comprise a major portion (approximately 85%) of the total. Borehole lithology from the basin gives a succession of top soil, weathered charnockites, fractured charnockites, massive charnockites, and charnockites with pegmatite veins (Figure 2b). Most of dug wells in the crystalline terrain of the study region lie within the weathered charnockites.

Materials and Methods

The study area is divided into four major zones: 1) the western (barrier island) coastal plain, 2) eastern coastal plain, 3) western crystalline terrain, and 4) eastern crystalline terrain. Conventional collection of groundwater in the study area is achieved through dug wells from phreatic aquifers. For this study, groundwater samples were collected from 44 dug wells (Figure 1) during premonsoon and postmonsoon periods of year 2002, covering the coastal plain (20 wells) and crystalline terrain (24 wells). These samples were analysed for their chemical constituents. The pH and electrical conductivity (EC) were measured at the sampling location, whereas the concentration of major cations, anions and *Escherichia coli* were analyzed in the laboratory, following standard analytical procedures (Grasshoff et al., 1983; APHA, 2002). The EC, measured in microsiemens/cm (μS/cm), provides a measure of salt content in the form of ions (Karanth, 1987). Na^+ and K^+ redundant were analyzed using flame photometry (Systronics FPM digital model Elico CL223-Flame Photometer). Ca^{2+} and Mg^{2+} were analyzed by ethylene diamine tetra acetate (EDTA) titrimetric method, whereas Cl^- was determined by argentometric titration using standard silver nitrate as the reagent. CO_3^{2-} and HCO_3^- concentrations of the groundwater were determined titrimetrically (Grasshoff et al., 1983; APHA, 2002). Sulphate concentrations were determined following the turbidity method (APHA, 2002) using a double-beam ultravoilet-visible spectrophotometer, the UV-VIS61 (Model U-2000, Hitachi, Tokyo, Japan). Analytical reproducibility was checked by performing duplicate analyses for each sample; thus final analytical data are presented as the average of triplicate values. The presence or absence of *Escherichia coli* in groundwater samples was determined by streaking the samples on Mac conkey agar plates. The brick-red bacterial colonies on the agar plate after incubation indicated the presence of *E. coli* (APHA, 2002). Groundwater-level data was collected for the year 2000 from National Hydrographic Station for the region maintained by the Central Groundwater Board, India, is used for the preparation of water level contour map for the premonsoon and postmonsoon seasons.

Results and Discussion

Tables 1 and 2 present the laboratory and field analytical results of the groundwater analysis conducted in the phreatic coastal plain and crystalline terrain.

Electrical Conductivity

In the phreatic coastal plain, EC of groundwater ranges from 124 to 5350 μS/cm during premonsoon season (Table 1), whereas it ranges from 111 to 2800 μS/cm (Table 2) postmonsoon. The EC value of groundwater in crystalline terrain varies from 40 to 356 μS/cm and 29 to 256 μS/cm respectively during premonsoon and postmonsoon periods. The EC of the groundwater of the western barrier island–coastal plain during postmonsoon is lower than that during premonsoon, indicating the high dilution during the monsoon. However, the relatively high EC values (> 3 times) in the western barrier island–coastal plain (well nos. 1–5, 8–10) during premonsoon and postmonsoon seasons compared with EC values in the eastern coastal plain indicates poor groundwater quality and non-equilibrium conditions at the interface between fresh and saline water, due to reduced recharge of fresh water. In addition, the groundwater in the northeastern coastal plain area (well nos. 14–17) shows moderate EC values during both the monsoons. In contrast, the crystalline terrain recorded low EC values throughout the year, indicating that the groundwater is of good quality. Samples with EC values < 100 μS/cm are more common during the postmonsoon than during the premonsoon period, which may be due to the dilution of soluble salts by infiltrating rainwater. The type and concentration of salts in groundwater depend on the geological environment and on the trends of movement of groundwater (Raghunath, 1987). Generally, higher concentrations of dissolved constituents are found in groundwater than in surface water because of its greater exposure to the soluble minerals of the geological formations (Todd, 1980).

pH

The dissolution of CO_2 and organic acids (fulvic and humic acids) that are derived from the decay and subsequent leaching of plant materials (Langmuir, 1997) gives the water an acidic character. The groundwater samples from the coastal plain during both seasons indicate alkaline nature that may be due to the presence of dissociated anions. The alkaline nature further shows the presence of high salinity in the shallow aquifer, which is well exemplified by the groundwater samples of western barrier-island–coastal plain. The small variation of pH among dug wells in the coastal plain indicates that the groundwater is being tapped from aquifers of a single formation (Langmuir, 1997). The pH of most of the groundwater samples from phreatic coastal plain, during both seasons, is within the desirable range (6.5 to 9.0) as prescribed for drinking purposes (ISI, 1983; WHO, 1984; Lloyd and Heathcote, 1985).

Most groundwater samples from the crystalline terrain are slightly acidic (Tables 1 and 2), and, in certain samples, the values are below the permissible limit listed previously. The low pH of the terrain is related to the wide distribution of lateritic soil for which the pH is always acidic (CESS, 1984). Another reason for the observed low pH could be related to the use of acid-producing fertilizers, such as ammonium sulphate and superphosphate of lime for agriculture (Dinesh Kumar, 1997; Rajesh Raghunath et al., 2001). Values of pH < 6.5 in water can cause corrosion to water-carrying metal pipes, thereby releasing toxic metals such as Zn, Pb, Cd, and Cu (Trivedy and Goel, 1986). This point should be taken into consideration while preparing future drinking water development plans in the study region.

Major Cations and Anions

Major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) and anions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, and Cl^-) of the groundwater samples of the premonsoon and postmonsoon seasons (Tables 1 and 2) show a marked spatial variation between the western barrier-island–coastal plain and the eastern coastal plain and temporal variation between the monsoons. A fourfold increase in Na^+, K^+ and Cl^-; 10-fold in Mg^{2+}; more than twofold in Ca^{2+}; and approximately twofold in $HCO_3^- + CO_3^{2-}$ have been found in the western barrier island–coastal plain compared with the eastern coastal plain. Further, higher values are observed in premonsoon than in postmonsoon. The crystalline terrain shows uniformly low values for these variables with only a small difference in the values between the monsoons. High concentration of Cl^- in groundwaters of the phreatic coastal plain has been attributed to seawater intrusion, natural brines, evaporated deposits and pollution (Junge and Wrby, 1958; Johnston, 1987). The high Cl^- content is generally taken as an index of impurity of groundwater. The groundwater in some of the dug wells of the western barrier island–coastal plain (wells 1–5, 7, 8) shows high concentration values of Na^+ and Cl^- (Tables 1 and 2) that are above the permissible limit of 250 mg/L (ISI, 1983, WHO, 1984; Lloyd and Heathcote, 1985). The high value is attributed to seawater intrusion. Compared with the coastal plain, Na^+ and Cl^- in the groundwaters of crystalline terrain for both seasons are found to be within the permissible limits (Tables 1 and 2). SO_4^{2-} and Mg^{2+} concentrations in groundwater of coastal plain and crystalline terrain, for both seasons, are also found to be within the permissible limit. However, Mg^{2+} content in groundwater of the western barrier island–coastal plain is 10-fold higher than that in the eastern coastal plain in both the seasons.

Table 1. Chemical and Escherichia coli *analysis of groundwater (premonsoon)*

		mg/L								
Well no.	μS/cm EC	pH	Ca	Mg	Na	K	$HCO_3 + CO_3$	SO_4	Cl	*E. coli*
Western Barrier Island–Coastal Plain										
1	535	8.3	67.0	17.3	410.3	28.4	282.3	2.1	587.0	+
2	2112	7.9	158.0	12.9	512.3	91.0	391.7	2.9	854.3	+
3	932	8.1	197.4	26.5	498.5	119.9	337.7	6.6	960.1	+
4	1115	8.4	135.4	15.1	516.7	87.4	389.4	4.5	886.2	+
5	5350	8.5	254.0	144.2	776.4	67.7	382.0	7.1	1734.0	+
6	212	7.6	67.8	19.8	125.4	41.3	313.4	3.0	189.6	+
7	312	7.5	96.7	23.7	367.4	115.1	276.4	4.1	717.8	+
8	610	7.5	101.2	14.9	486.4	55.5	209.7	4.0	812.1	+
9	1120	7.7	87.3	6.8	49.9	28.8	210.3	1.4	129.9	+
10	567	7.1	67.8	3.7	111.3	30.1	279.0	2.7	143.8	+
Average	1287	7.9	123.3	28.5	385.5	66.5	307.2	3.8	701.5	
Eastern Coastal Plain										
11	221	7.2	71.3	0.7	121.9	20.7	252.0	2.2	156.5	+
12	436	7.9	67.3	1.4	112.4	19.5	141.6	1.8	208.5	+
13	298	7.8	34.5	3.4	123.4	22.1	204.8	2.7	195.7	+
14	654	8.0	45.6	5.3	145.3	16.4	168.8	3.0	246.9	+
15	410	7.6	67.3	4.1	112.3	13.9	286.4	3.4	134.0	+
16	467	7.5	70.8	0.7	134.3	12.1	229.9	3.1	250.3	–
17	408	7.5	67.9	4.3	145.6	13.6	216.5	1.3	239.5	+
18	156	6.6	11.2	3.3	11.4	7.9	59.4	9.0	9.0	+
19	124	6.5	6.4	1.4	13.8	7.0	14.3	6.4	26.0	–
20	161	6.3	16.0	1.7	19.0	8.2	34.1	6.9	30.0	–
Average	333.5	7.3	45.8	2.6	93.9	14.2	160.8	4.0	149.6	
Eastern Crystalline Terrain										
21	153	7.3	8.0	2.1	21.0	3.5	60.5	5.8	8.0	–
22	52	6.2	4.1	1.5	6.8	1.0	25.1	4.1	24.8	–
23	124	7.2	14.4	0.4	5.2	5.5	59.4	4.9	5.0	+
24	186	7.4	16.0	3.0	6.0	0.7	62.7	8.0	11.0	+
25	56	6.7	4.0	1.5	4.2	1.1	16.5	4.9	5.0	+
26	142	7.3	20.8	2.2	3.0	1.9	48.4	9.2	6.0	–
27	52	6.6	4.0	1.5	3.2	0.7	15.4	6.2	7.0	–
28	52	6.3	0.8	3.0	3.8	0.9	20.9	5.6	9.0	–
29	53	7.1	6.4	0.0	4.9	1.1	17.6	7.3	5.0	+
30	40	5.9	1.6	0.8	4.1	0.7	14.3	6.4	9.5	+
31	55	5.7	3.2	0.7	5.2	0.4	12.1	5.6	7.0	+
43	112	6.3	6.4	5.3	13.0	1.2	17.6	5.6	19.0	+
44	69	7.3	5.6	0.5	3.2	0.8	22.0	5.6	6.6	–
Average	136	6.9	11.1	1.2	10.8	3.6	27.8	7.2	16.7	
Western Crystalline Terrain										
32	44	7.0	1.6	0.8	3.6	1.3	19.8	5.8	5.0	+
33	87	6.6	1.6	0.3	7.6	3.5	12.1	6.4	18.0	+
34	80	6.1	5.6	0.1	6.8	2.3	9.9	6.9	10.0	+
35	166	6.5	9.6	3.4	9.3	1.1	22.0	6.9	15.0	–
36	210	7.5	20.8	4.0	19.0	9.0	31.9	9.1	33.0	–
37	55	8.0	4.0	1.1	4.2	1.0	15.4	3.4	6.1	–
38	137	6.5	16.8	0.7	7.4	2.9	30.8	5.6	16.8	+
39	134	6.6	7.2	0.4	16.0	1.4	12.1	6.9	11.0	+
40	356	7.3	38.5	0.3	27.0	3.9	127.6	13.6	39.0	+
41	121	7.0	9.6	1.6	9.7	7.3	11.0	7.3	18.0	+
42	107	6.3	6.4	0.0	8.6	5.6	13.2	7.3	12.0	+
Average	88	6.7	7.4	1.8	6.4	1.5	30.2	6.1	9.5	

+ Presence of *E. coli*.
– Absense of *E. coli*.

Hill-Piper Diagram

Major cations and anions were discussed using the Hill-Piper trilinear diagram (Hill, 1940) and (Piper, 1944). The trilinear plot for the premonsoon and postmonsoon seasons (Figures 3 and 4) is explained using the facies classification of Back and Hanshaw (1965). The groundwater samples of the study fall into four hydrochemical facies depending on the dominance of cations and anions.

1) Facies 1: Ca^{2+}–Mg^{2+}–HCO_3^- groundwater type I
2) Facies 2: Na^+–K^+–Ca^{2+}–HCO_3^- groundwater type II
3) Facies 3: Na^+–K^+–Cl^-–SO_4^{2-} groundwater type III and
4) Facies 4: Ca^{2+}–Mg^{2+}–Cl^-–SO_4^{2-} groundwater type IV.

Table 2. Chemical and Escherichia coli *analysis of groundwater (postmonsoon)*

Well no.	μS/cm EC	mg/L							Cl	*E. coli*
		pH	Ca	Mg	Na	K	$HCO_3 + CO_3$	SO_4		
Western Barrier Island–Coastal Plain										
1	450	8.1	57.9	20.2	380.7	23.5	200.2	1.8	470.4	+
2	1110	7.7	117.7	10.3	457.1	75.2	321.9	2.4	640.3	+
3	767	8.0	190.4	22.7	480.4	110.0	334.1	5.6	749.4	+
4	800	8.2	122.0	11.2	546.0	72.2	276.9	3.8	757.4	+
5	2800	8.7	118.0	67.0	655.5	39.6	258.6	12.2	1120.4	+
6	111	7.5	50.8	15.3	110.6	38.3	203.6	2.5	128.2	+
7	213	7.6	87.0	22.8	339.0	95.1	187.4	3.5	541.6	+
8	512	7.4	70.2	11.0	445.9	45.9	160.1	3.4	612.0	–
9	848	7.6	70.0	5.0	34.2	23.8	160.5	1.2	111.0	+
10	495	7.1	55.3	2.0	98.0	24.9	213.0	2.3	122.9	+
Average	811	7.8	93.9	18.8	354.7	54.9	231.6	3.9	525.4	
Eastern Coastal Plain										
11	142	7.3	34.0	0.5	89.0	19.6	192.4	1.9	133.8	+
12	334	7.6	54.5	1.0	97.5	16.1	111.9	1.4	178.2	+
13	195	7.5	20.8	2.5	111.0	18.3	156.3	2.3	167.3	+
14	532	7.8	35.3	4.0	120.7	14.4	167.0	2.5	211.0	+
15	311	7.4	38.9	3.0	98.1	11.5	218.6	2.9	112.8	+
16	385	7.4	68.8	0.5	120.0	10.0	198.4	2.7	213.9	+
17	338	7.3	58.3	3.0	110.6	12.9	180.5	1.1	203.0	+
18	128	7.3	12.24	0.50	12.20	10.17	63.05	2.90	12.00	+
19	138	7.2	10.61	1.50	13.80	7.81	19.40	2.75	22.99	+
20	180	7.1	17.95	1.50	15.40	7.29	24.25	9.16	21.99	–
Average	268.3	7.4	35.1	1.8	78.8	12.8	133.2	3.0	127.7	
Eastern Crystalline Terrain										
21	29	6.4	4.9	0.5	4.8	1.5	29.1	2.6	8.0	–
22	72	6.1	3.3	0.5	7.9	2.2	19.4	3.3	10.0	–
23	55	6.8	4.1	1.5	7.4	2.5	34.0	2.8	9.0	+
24	97	7.4	16.3	1.5	5.7	0.6	63.1	2.8	5.0	+
25	45	7.1	3.3	0.5	5.8	1.7	29.1	2.6	5.0	+
26	86	7.4	13.9	1.0	5.2	1.5	53.4	2.6	3.0	–
27	45	6.6	4.1	1.0	5.0	0.6	24.3	2.6	4.0	–
28	43	6.4	3.3	1.0	5.0	1.1	34.0	1.3	6.0	–
29	46	6.6	4.1	1.5	6.5	1.3	34.0	3.3	6.0	+
30	41	5.9	2.4	0.5	6.2	2.2	29.1	2.9	12.0	–
31	54	5.6	3.3	0.5	6.4	1.1	24.3	2.8	11.0	+
43	87	6.8	5.7	1.0	11.5	2.2	29.1	2.8	17.0	+
44	61	7.0	7.34	0.50	4.60	2.01	38.80	2.75	6.00	–
Average	100	6.7	8.1	2.1	9.3	5.0	43.7	4.6	11.8	
Western Crystalline Terrain										
32	37	6.6	3.3	0.5	4.8	1.5	29.1	4.2	5.0	+
33	110	6.2	3.3	3.0	13.4	5.3	24.3	2.9	23.0	+
34	50	6.3	2.4	1.5	5.5	10.0	24.3	3.1	9.0	+
35	77	6.4	6.5	1.0	7.0	1.5	34.0	6.8	5.0	–
36	139	6.9	16.3	0.0	12.0	8.6	34.0	8.4	15.0	–
37	42	6.4	1.6	1.5	5.0	2.0	38.8	1.1	5.0	–
38	95	6.7	10.6	2.0	5.5	6.6	49.0	4.7	10.0	+
39	114	6.3	5.7	1.5	13.7	2.2	24.3	8.7	16.0	–
40	254	8.1	34.3	9.5	16.0	4.9	155.2	3.5	15.0	–
41	48	6.7	2.4	1.5	5.2	2.2	29.1	3.6	4.0	+
42	137	7.0	2.45	0.50	14.40	10.03	38.80	3.52	22.99	+
Average	59	6.6	5.8	0.9	6.3	1.6	34.0	2.7	7.8	

+ Presence of *E. coli.*
– Absense of *E. coli.*

Figures 3 and 4 show that a most samples in the coastal plain fall in type III (Na^+–K^+–Cl^- – SO_4^{2-}) followed by type II (Na^+–K^+–Ca^{2+}–HCO_3^-) for both the seasons. Most of the groundwater samples in phreatic coastal plain are characterized by type III (Na^+–K^+–Cl^- – SO_4^{2-}), which indicates seawater intrusion and poor groundwater recharge (Lloyd and Heathcote, 1985). While conducting groundwater salinity study in the shallow aquifers of central Kerala, Nageswara Rao (1975) inferred that seawater encroachment into shallow aquifers could be minimized by construction of tidal barriers. The removal of seawater Na^+ infiltrated into fresh water aquifer has been attributed to the action of ion exchange (Revelle, 1941; Piper and Garrett, 1953). The

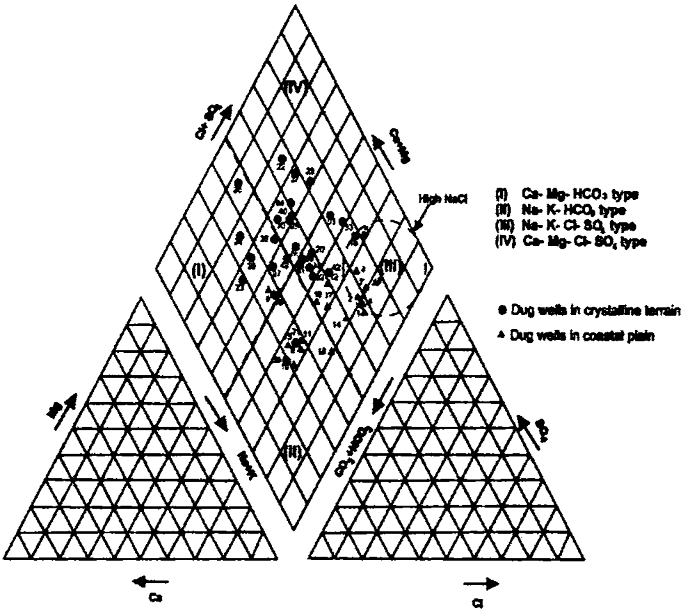

Figure 3. Trilinear diagram of dugwell samples (premonsoon).

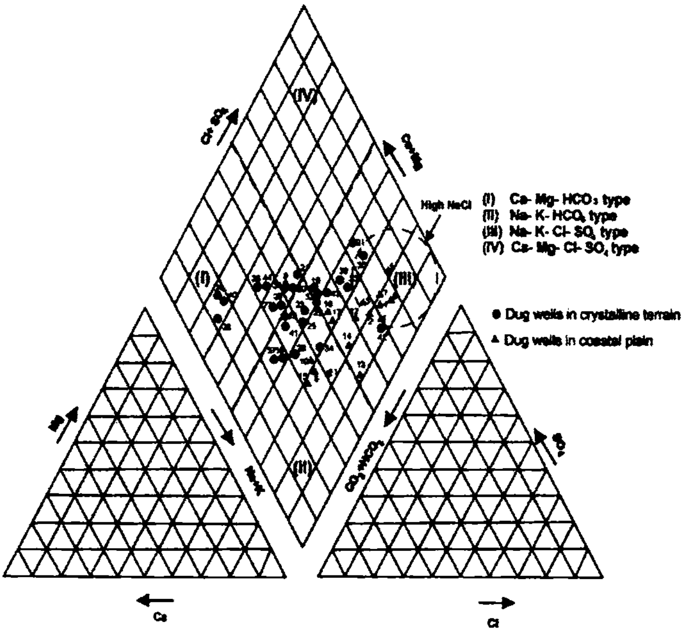

Figure 4. Trilinear diagram of dugwell samples (postmonsoon).

conversion of calcium bicarbonate water to sodium bicarbonate water in many aquifers has been attributed to ion exchange (Foster, 1942; Back, 1960; Appelo and Geirnaert, 1991).

Most groundwater samples in the crystalline terrain during premonsoon (Figure 3) are of type III (Na^+–K^+–Cl^-– SO_4^{2-}) followed by type I (Ca^{2+}–Mg^{2+}–HCO_3^-) type IV (Ca^{2+}–Mg^{2+}–Cl^-–SO_4^{2-}) and type II (Na^+–K^+–Ca^{2+}–HCO_3^-), whereas during postmonsoon (Figure 4) most samples are found to occupy in type I (Ca^{2+}–Mg^{2+}–HCO_3^-) followed by type II (Na^+–K^+–Ca^{2+}–HCO_3^-) and III (Na^+–K^+–Cl^-–SO_4^{2-}). Figures 3 and 4 show that the groundwater samples, which fall in type IV (S. No. 22, 25, 27–30, 40, and 44) during premonsoon have shifted position to type II (S. No. 22, 25, 28, and 29), type I (S. No. 27, 40, and 44), and type III (S. No. 30) during postmonsoon. The next predominant shifting of position is from type III (S. No. 19, 20, 31–34, 36, 41, and 42) to type II (S. No. 32, 34, and 41) and type I (S. No. 20 and 36). Other shifts are negligible. The seasonal shifting of facies from IV to II is mainly due to the weathering of feldspars in charnockites and gneissic rock as Ca^{2+} is replaced by Na^+. Further, it is also due to ionic exchange to exemplify or supplement rock water interaction. The characteristics of groundwater (hard or soft; mineralized or non-mineralized) depend on the reactions it makes with the country rock (Edmunds, 1994). The shift from facies IV to I is due to enrichment of bicarbonate in groundwater. According to Chandrasekharam (1989), the groundwater from lateritic terrain should be of bicarbonate nature as these have higher concentrations of HCO_3^- ions than SO_4^{2-} and Cl^- ions.

Escherichia coli

One of the most common and widespread health risks associated with drinking water is bacterial contamination caused either directly or indirectly by human or animal excreta. *E. coli*, a typical fecal coliform, is selected as an indicator of faecal contamination. The present study reveals that the majority of groundwaters of the coastal plain are contaminated with *E. coli* during both seasons (Tables 1 and 2), whereas in crystalline terrain only 50% of samples show the presence of *E. coli*. A high level of coliforms in the Muvattupuzha River waters (CGWB, 2002) is reported due to the open defecation and cattle bathing. These waters migrate slowly to the dug wells located adjacent to the drainage system. Migration of *E. coli* in the sedimentary formation is much easier than in hard rock terrains (Geldreich, 1972). According to Woods (1990), effluents from point sources such as septic tanks and improper solid waste disposal from farmyards are considered as the main sources of contamination of groundwater. The lack of protecting walls to dug wells may lead to the entry of contaminated runoff. The presence of *E. coli* in groundwaters of this study indicates a situation that warrants immediate attention.

Groundwater Level Analysis

It is found that groundwater level, expressed in meters below ground level, declines considerably during the premonsoon period compared with the postmonsoon period (Figure 5). Towards the coastal area, especially on the extreme west, the effect is less because this area is also a discharge area, as indicated by the concave contours. When compared with the premonsoon period, one of the interesting features of the postmonsoon season

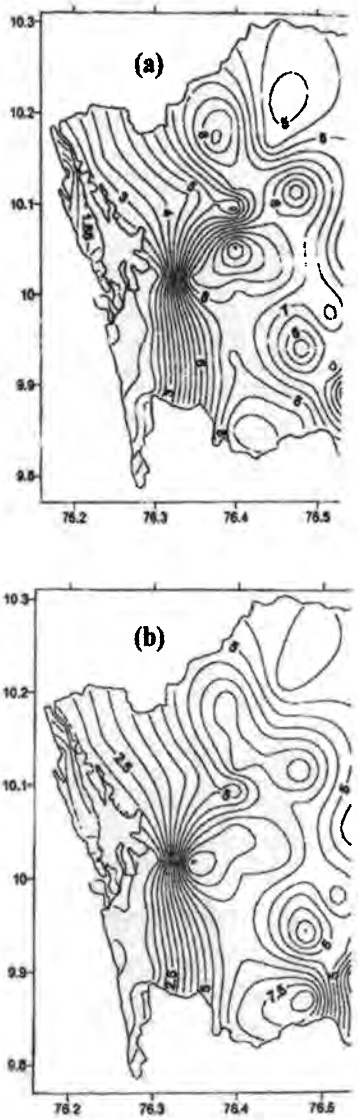

Figure 5. Groundwater level (meters below ground level) along the study region during (a) premonsoon and (b) postmonsoon seasons.

is that the contour lines also thicken towards the extreme south area, showing that monsoon brings another flow direction of groundwater in addition to the movement towards west. In general, there is a lowering of water level in premonsoon compared with the postmonsoon and these might have enhanced seawater intrusion into the coastal area.

Summary

Groundwater chemistry of phreatic coastal plain and crystalline terrain during premonsoon and postmonsoon seasons reveals that groundwater of the coastal plain has high EC whereas the groundwater of the crystalline terrains has an acidic nature with low EC values. Within the coastal plain area, the groundwater of the barrier island shows a marked increase in many of the variables in both the monsoons (11-fold rise in Mg^{2+}, 3- to 4-folds in EC, Na^+, K^+, and Cl^-, more than 2 times in Ca^{2+} and $HCO_3^- + CO_3^{2-}$) than the eastern coastal plain. Only pH and SO_4^{2-} show steady values without much fluctuation between the monsoons. In general, the groundwaters of the coastal area are of very poor quality and exceed the potable limit set by the World Health Organization (Geneva, Switzerland) and Indian Standards Institution (New Delhi, India). In contrast, the waters of the crystalline terrain is within the permissible limits. The Hill-Piper trilinear diagram reveals that during postmonsoon the groundwaters in crystalline terrain are enriched by Na^+ and HCO_3^-. Compared with the phreatic coastal plain, the shallow crystalline aquifer is geochemically good for drinking and domestic purposes (except for the presence of *E. coli*). Further, it is stressed that the coastal plain of the study area needs more attention to maintain optimum groundwater quality and the need to establish sound groundwater- management plans. Proper sanitation and waste disposal should be followed in the study area.

This study further reveals the need for groundwater monitoring over a seasonal or multi-seasonal time frame. Conclusions concerning the geochemical conditions of an aquifer cannot be made with one or two sampling events due to the variation in climatic conditions, especially in tropical zones where rain events can substantially alter the physical and chemical characteristics of water. It is recommended multiple sample events conducted seasonally be undertaken to address these issues.

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Environmental Analysis of Heavy Metal Deposition in a Flow-Restricted Tropical Estuary and Its Adjacent Shelf

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The geochemical condition of surface sediments in a tropical estuary and adjoining shelf region is discussed in terms of their elemental interactions using statistical methods. Principal component analysis separated two clusters comprising 1) heavy metals possessing significant correlation with texture (organic carbon, clay, and silt), which belong to sediments in the shelf region, and 2) heavy metals in high concentration showing poor correlation with sediment texture, which are of estuarine origin. Co-precipitation of iron hydroxide in addition to scavenging of other metals could be the principal mechanism explaining the accumulation of Cd, Cu, Pb, and Zn in the estuarine sediments. Discharge of industrial effluents has lead to the present level of metal contamination in the estuary. A hazard is associated because, in this state, the metals released during mineralization could be available to biota. The increased anthropogenic influence in the Cochin Estuary has probably resulted in a reduction in benthic biodiversity, where pollutant-tolerant species are found to take over the vacated niche. In contrast, the coastal environment is controlled by natural oceanographic processes, where the coastal currents and stable biogenic association normalize metal deposition. The source apportionment of metals by inorganic and biomediated interactions helps illuminate the processes controlling their depositional trends in pristine and impacted environments.

Keywords: Cochin Estuary, heavy metals, deposition, multivariate statistical analyses, organic and inorganic association, coprecipitation

Introduction

The conventional paradigm for the behavior of reactive materials in coastal marine ecosystems has been to identify the processes by which dissolved and particulate materials are associated with minerals settling to sediments. Because of the dynamic nature of these systems, estuarine processes are complex and their transformations often remain obscure. Turbulent mixing of fresh water and seawater can generate rapid changes in Eh, pH, salinity, and trace element concentrations (Feely et al., 1981). Superimposed on this variability are the biological processes acting on time scales of seconds to days (Hedges and Keil, 1999). Hence, it is difficult to understand the origins, pathways, and fates of dissolved and particulate materials in coastal marine systems, and especially in estuaries. Sediments are major repositories for metals and, in addition to providing the environmental status, they are also used to estimate the level of pollution in a region (Burton Jr. and Scott, 1992; Caccia et al., 2003).

Cochin Estuary, one of the largest tropical estuaries of India (256 km^2), is facing gross pollution problems following the release of untreated effluents from industries (0.104 × 10^6 m^{3}d^{-1}) and domestic sectors (0.26 × 10^3 m^{3}d^{-1}) (CPCB, 1996). The major polluting industries in the region include a fertilizer plant, an oil refinery, rare-earth processing plant, minerals and rutiles plant, zinc smelter plant, an insecticide factory, and an organic chemical plant. Reclamations over the past several decades have resulted in considerable shrinkage (40%) of the Cochin Estuary (Gopalan et al., 1983). Further, construction of hydraulic barriers on the northern and southern limbs of the estuary to prevent saline incursion into the upstream agricultural fields has imposed severe flow restrictions and increased sedimentation in the estuary (Menon et al., 2000; Balachandran, 2001). Sedimentary charts denote substantial transport of alluvium from rivers during monsoon (June through September), which are accumulated during postmonsoon (November through January), whereas silting environment prevails during the premonsoon (Mallik and Suchindran, 1984; Nair and Balchand, 1993).

Anthropogenic impacts have resulted in an accumulation of heavy metals in the estuarine sediments during winter monsoon (post-monsoon), whereas the coastal environment has remained essentially unaltered during the same season (Balachandran et al., 2003). This finding is interesting because, within different environments, there could be shifts in preferences of metals onto adsorption sites before sedimentation. The distribution of these metals in this environment is already discussed in Balachandran et al. (2005). The present study reviews the data with statistical methods and differentiates the natural and anthropogenic factors influencing the metal geochemistry in the two provinces.

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Materials and Methods

Sediments were collected using a Van Veen grab from the inner shelf of Cochin and from the lower estuary. Sampling was carried out in November 2000, covering 330 square kilometers in the shelf (15 stations and depths 5 to 30 m) and 90 square kilometers in the estuary (17 stations and depths 3 to 10 m) (Figure 1). Surface sediments were collected carefully by avoiding contamination and kept frozen until analysis. Textural characteristics (sand, silt, clay) were determined following pipette analysis (Krumbein and Pettijohn, 1938) and organic carbon of the composite samples using chromic acid digestion followed by back titration with ferrous ammonium sulphate (El Wakeel and Riley, 1957). For the heavy metal analysis, (total) finely powdered and dried (at 70°C) sediments were digested in a mixture of HF–$HClO_4$–HNO_3 (Loring and Rantala, 1992). Complete digestion was ensured by repeating the acidification until a clear solution was obtained and brought into solution in 0.5 M HCl (25 mL) using Milli-Q water. Samples were analyzed on a flame atomic absorption spectrophotometer (AAS) (AAanalyst 100, Perkin Elmer, Wellesley, MA) after calibration with suitable E-Merck elemental standards. For Cd analysis, a Graphite-AAS (ZL 4110 Perkin Elmer) was used. The precision of the analytical procedure was checked using a triplicate analysis of a certified reference material (BCSS-1) from the National Research Council of Canada. The Cd standard deviations (SDs) were typically ±5% for Cu and Pb; ±12% for Cr, Ni, Mn, and Zn, and ±21% for Cd, and Co (Table 1).

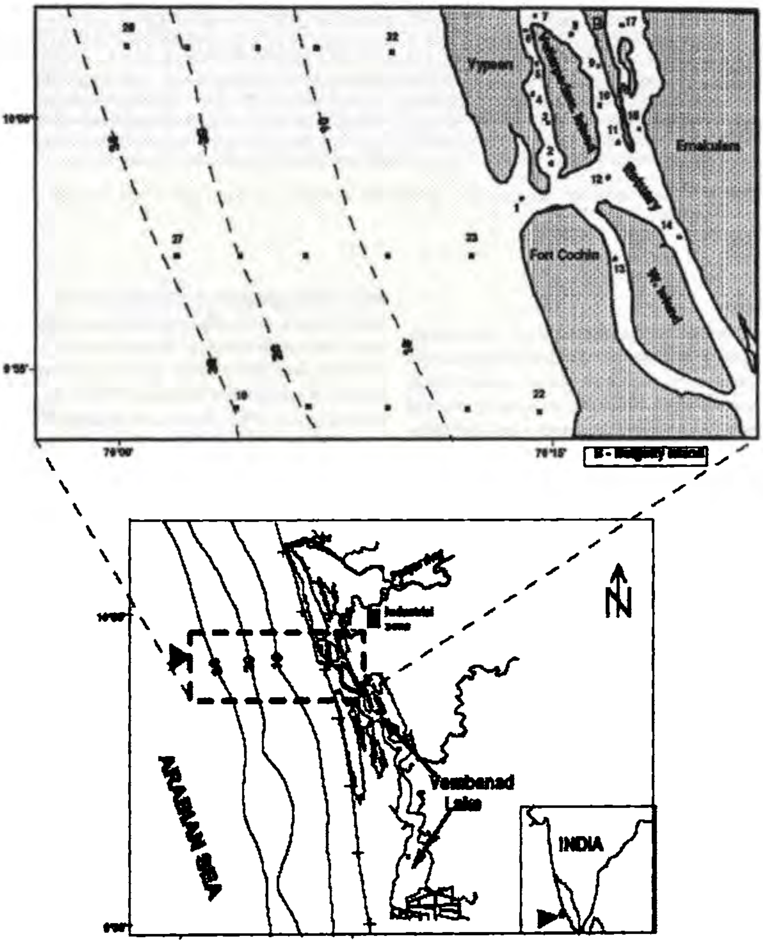

Figure 1. Study area showing station locations in Cochin Estuary (Vembanad Lake) and its adjoining marine area. Bathymetric depths are given in meters. *Source*: Balachandran et al. (2005).

Table 1. Metal extracted from the standard reference material BCSS-1 (n = 3)

Concentration	Pb	Ni	Co	Cr	Fe	Cu	Zn	Mn	Cd
Metals extracted[a]	22.70	55.3	11.4	123	—	18.5	119	229	0.300
Metals extracted[b]	23.98	60.9	13.86	108	29000	17.99	105.5	204	0.362
Accuracy (± %)	5	11	21	12	—	2.7	11	11	21

Source: Balachandran et al. (2005).

[a] Certified values corresponding to the total extraction of metals from the standard reference material BCSS-1.

[b] Values of the metals extracted from the standard reference material BCSS-1 in this study.

Results and Discussion

The results of the geochemical analyses are listed in Table 2. The sediments were generally rich in organic carbon and predominant in silty-clay fraction. The bar mouth (station 1) and northwest offshore region (station 28), however, was characterized by high sand fraction (Table 2). There was a sharp increase in heavy metal concentrations (Cd, Zn, Pb, Cu) in the estuary. In comparison with the earth crust (Wedepohl, 1995), the high level of Cd and Zn in the estuarine sediments is of major environmental concern because it is related to the anthropogenic inputs from upstream (Shajan, 2001; Balachandran et al., 2005). The coastal region did not show such a metal enrichment, probably because the prevalent northerly currents (Shetye et al., 1991) are capable of dispersing their deposition.

The organic carbon ranged between 0.04 and 4.07% in the estuary and between 0.59 and 4.28% in the shelf sediment, which are generally comparable. Relatively high organic carbon in the shelf samples (many sediments with >3%) suggest that despite the variable patterns of terrestrial supply and biological production, the retention of organic matter in sediment is governed by the type of clay minerals in respective environments. Geochemical studies from this region have shown that, on moving from river to the shelf environment, coarser illites and kaolinites (formed from leaching of laterites) are replaced by fine-grained

Table 2. Geochemical and textural properties of sediments in the study region

	(mg/kg dry wt)							(% dry wt)					
Station no.	Pb	Ni	Co	Cr	Cu	Zn	Mn	Cd	Fe	Organic	Sand	Clay	Silt
						Estuary							
1	19.3	16.0	5.6	15	5.4	92	151	0.594	1.41	1.88	64.7	24.5	10.8
2	28.3	48.0	16.8	103	21.5	245	337	7.707	3.87	2.65	36.6	62.3	1.1
3	35.4	49.5	15.9	81	22.6	245	182	4.150	3.71	3.17	32.9	62.7	4.4
4	35.4	40.2	15.0	70	22.9	276	141	1.782	3.40	3.06	39.3	50.2	10.5
5	42.9	63.2	22.6	78	37.0	743	206	4.980	5.11	4.07	9.6	46.5	43.9
6	43.1	66.5	20.9	117	36.1	529	266	4.819	5.37	1.08	4.9	40.6	55.5
7	40.7	63.5	26.1	104	30.9	540	263	2.695	5.17	1.91	3.1	40.2	56.7
8	71.3	63.1	22.6	121	53.2	1204	253	13.745	6.18	2.75	5.4	44.2	50.2
9	57.5	65.1	24.7	117	42.6	1183	223	11.446	5.91	2.58	35.3	59.9	4.8
10	64.1	64.6	24.5	101	42.3	1266	222	14.940	5.37	2.40	31.2	65.5	3.3
11	42.8	45.5	18.8	105	26.0	525	197	11.952	3.99	0.04	39.8	45.9	14.3
12	28.6	35.3	13.2	82	17.4	279	303	2.395	3.05	2.82	37.7	28.1	34.2
13	28.1	59.3	14.9	66	26.7	152	222	1.179	4.34	3.10	0.9	85.7	13.4
14	28.3	59.7	16.8	53	30.1	123	193	1.482	4.45	3.58	6.0	19.2	74.8
15	21.4	61.7	15.1	44	23.9	402	215	3.593	4.63	2.37	2.2	16.6	81.2
16	28.5	49.9	16.9	68	33.6	679	234	4.990	4.74	1.24	28.2	44.2	27.2
17	42.6	61.4	20.6	74	51.9	1076	287	8.036	5.35	2.66	9.0	62.8	28.2
						Coast							
18	39.6	60.3	20.1	168	21.8	64	184	2.590	2.89	3.35	2.0	36.5	61.5
19	26.0	61.1	19.8	158	23.4	72	197	3.270	3.10	1.24	2.0	48.4	49.6
20	39.5	66.9	21.6	53	25.7	83	181	2.210	3.42	3.38	2.0	54.5	43.5
21	39.5	63.6	20.1	181	26.7	77	170	1.840	3.27	3.56	1.0	78.6	20.4
22	19.7	61.8	17.0	169	27.6	70	152	1.840	3.09	1.42	9.0	64.8	26.2
23	38.2	58.2	17.9	167	22.0	132	167	2.140	2.91	4.28	42.0	40.8	17.2
24	13.1	54.9	15.4	151	25.5	88	179	1.470	2.82	0.59	1.0	70.3	28.7
25	26.4	71.9	21.6	176	32.6	99	171	1.470	3.27	3.63	8.0	63.5	28.5
26	33.3	69.3	18.7	186	27.9	90	165	1.490	2.82	2.45	0.1	90.	9.3
27	23.1	68.9	18.6	185	28.8	80	167	1.850	2.75	2.62	2.0	75.3	22.7
28	13.4	5.1	3.1	35	6.0	7	40	0.000	0.34	3.02	88.8	10.2	1.0
29	26.1	56.4	19.9	163	26.5	79	210	2.190	2.88	3.52	2.5	63.3	34.2
30	13.3	45.4	14.0	139	19.9	61	137	1.480	2.16	3.22	6.0	55.5	38.5
31	26.4	72.1	23.2	195	30.7	86	168	2.220	3.23	3.58	16.0	74.6	9.4
32	26.4	72.1	21.7	193	32.7	74	155	2.220	3.07	4.28	0.1	80.3	19.6

montmorrilonites (Reddy et al., 1992; Nath et al., 2000). These montmorrilonites in the coastal environments are hence responsible for greater accumulation of organic matter due to their larger surface area.

Source Apportionment by Multivariate Analysis

In the absence of a sequential extraction of metals in sediments, statistical procedures can be used for making inferences on the important pathways of elemental deposition (Isaac et al., 2005). The coastal and estuarine data were subjected to principal component analysis (PCA) to apply the hypothesis of geographically separating the sampling points in the study region. PCA identified two clusters (Figure 2) of shelf samples at the top (solid circle) and the estuarine samples at the bottom (hollow diamond). The major difference between these two clusters is the high metal content (Cu, Cd, Zn, Pb) in cluster 2 and their general inertness towards organic carbon, clay, and silt. The two clusters of PCA are generally indicative of a different trend for metal deposition in the two provinces. The two samples (stations 1 and 28), shown as outliers in Figure 2 differed in their texture (sand > 60%) from the remaining samples and were also impoverished in their metal content.

Geochemical Carrier

Pearson's correlation coefficients (significant at 99% level) were evaluated as an index of dependency among metals (Me) and texture in the two clusters (Table 3). A strong correlation between organic carbon and clay in the coastal region (r = 0.65) was in contrast to a weak correlation in the estuary (r = 0.07).

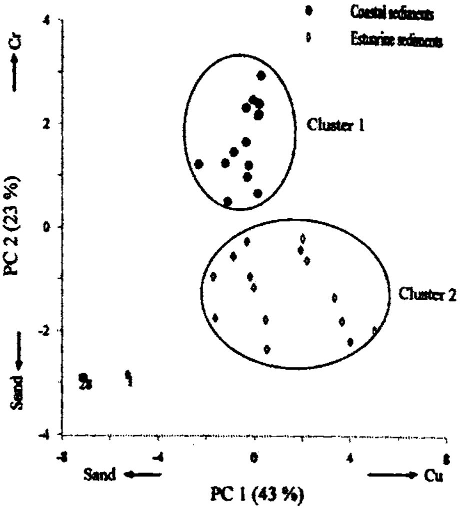

Figure 2. Principal Component scores for the coastal and estuarine sediments. The values in parenthesis denote the percentage variance accounted by each principal component.

Similarly, the strong correlations exhibited by clay towards Co, Fe, Cu, Mn, and Ni and organic carbon towards Ni, Co, Cu, and Mn in the shelf were not seen in the estuarine sediments. Silt fraction hosting Cd and Mn in the coastal sediments was quite

Table 3. Pearson correlation coefficient matrix for heavy metals, texture and organic carbon in sediments in the (a) Coastal region (n = 14) and (b) estuarine region (n = 16)

	Pb	Ni	Co	Cr	Cu	Zn	Mn	Cd	Fe	Sand	Clay	Silt
(a) Coastal region												
Ni	0.503											
Co	0.603	0.951										
Cr	0.183	0.712	0.632									
Cu	0.286	0.946	0.878	0.733								
Zn	0.478	0.725	0.677	0.549	0.648							
Mn	0.477	0.797	0.850	0.561	0.703	0.685						
Cd	0.509	0.675	0.777	0.466	0.506	0.469	0.820					
Fe	0.555	0.943	0.948	0.602	0.869	0.744	0.878	0.756				
Sand	−0.269	−0.820	−0.781	−0.588	−0.784	−0.441	−0.828	−0.643	−0.817			
Clay	0.122	0.766	0.630	0.689	0.848	0.469	0.511	0.243	0.647	−0.741		
Silt	0.240	0.234	0.348	−0.011	0.076	0.052	0.567	0.635	0.379	−0.528	−0.179	
Org.C	0.102	0.665	0.646	0.419	0.689	0.259	0.535	0.449	0.697	−0.727	0.647	0.247
(b) Estuarine region												
Ni	0.546											
Co	0.778	0.834										
Cr	0.756	0.547	0.783									
Cu	0.797	0.787	0.806	0.585								
Zn	0.866	0.565	0.752	0.569	0.870							
Mn	0.118	0.297	0.320	0.487	0.296	0.222						
Cd	0.835	0.396	0.616	0.678	0.659	0.827	0.235					
Fe	0.724	0.937	0.895	0.666	0.919	0.770	0.342	0.585				
Sand	−0.176	−0.816	−0.499	−0.205	−0.552	−0.187	−0.286	0.045	−0.692			
Clay	0.346	0.279	0.311	0.389	0.331	0.286	0.153	0.338	0.275	−0.034		
Silt	−0.118	0.396	0.142	−0.124	0.166	−0.069	0.100	−0.274	0.308	−0.704	−0.686	
Org.C	0.184	0.423	0.164	0.073	0.488	0.249	0.310	0.236	0.398	−0.538	0.075	0.338

Source: Balachandran et al. (2005).

unexpected as this feature was absent in the estuary. In the shelf, Fe established strong correlations with organic carbon (r = 0.70) and clay (r = 0.65), whereas they were weak (r = 0.40 and 0.27, respectively) in the estuary. The strong negative correlation between Fe and sand in the estuary (r = −0.82) and coast (r = −0.69) can be viewed as a dilution of the element by sand.

In the present approach, Fe is regarded as an element controlling the precipitation and redistribution of other elements, in the absence of data on other major elements such as Al, Ti, and K. Despite the fact that Fe was a major element in the mineral phase of sediments, its significant correlation with Al suggests that Fe is also of lithogenic origin (Nath et al., 2000). The behavior of Fe towards organic carbon, texture, and metals (Mn, Pb, and Cd) was found to be quite contrasting in the estuary and shelf. The geochemical properties in these two regions can be better explained using the Pearson's correlation of metals among all the phases. Accordingly, clay and silt are considered as geochemical phase, organic carbon as biogenic phase and, interaction with Fe as inorganic phase.

In the coastal region, the elements (Ni, Co, Cu) possess strong affinities towards Fe, clay, and organic carbon. Mn is coherent in all phases such as Fe, clay, organic carbon, and silt. Cd is associated with Fe and silt, whereas Cr has association with Fe and clay. Pb and Zn have association only with Fe. The preference of Mn and Cd towards the silt fraction is notable in the shelf region. In the case of estuarine sediments, the six elements (Ni, Zn, Cu, Cr, Pb, and Co) are associated only with Fe. Cr and Mn are independent to all the phases and so is the case for all metals with clay, silt, and organic carbon. A striking difference in the geochemical characteristics of the estuary from the shelf was the association of more elements with Fe and their inertness towards organic carbon and texture.

Environmental Significance

The previously noted variation in metals with respect to the carrier phases (clay, organic carbon, silt, and Fe) is indicative of a basic shift in the geochemical properties in response to the texture on moving from estuary to the shelf. In the shelf sediments, normalization of metals among the three carrier phases is probably masking their enrichment (Balachandran et al., 2005). The biogenic association is an effective binder of metals in the coastal sediments, especially in relation to the overlying biological production (Saraladevi et al., 1992). The intense organic production in Cochin Estuary coincides with the retreat of southwest monsoon, leading to the export of unconsumed phytoplankton to the sea during post-monsoon (Madhupratap, 1987). The settling of these organic materials in the coastal waters facilitates biogenic association of metals. The adsorption of metals onto Fe-Mn oxyhydroxides and Fe pyrites is commonly observed in marine sediments (Calvert, 1976). They are formed as coatings on the clay minerals or as individual particles and are normally observed in highly weathered environments (Isaac et al., 2005). The shelf sediments of this region are impoverished in sand but are rich in clay and organic carbon, which insulates oxygen penetration (Table 2). The prevalence of reducing condition in organic rich sediments favors the formation of iron sulfides (Rajamani, 1994) to the detriment of Fe-Mn oxyhydroxides (Pride et al., 1990; Jong and Parry, 2004; Isaac et al., 2005).

The situation is quite different in the estuary, where more than half of the sediment samples were rich in sand content (>30%). The high porosity of sand favors oxygenation and remineralization of organic carbon. In such conditions, the precipitated Fe oxyhydroxides are not converted to pyrite (Isaac et al., 2005). Thus, the elevated metal contents in the estuary and an increase in the number of elements associated with Fe suggest that coprecipitation of iron hydroxide along with scavenging of other elements could be the probable mechanism behind the accumulation of metals in the estuary. The intense chemical weathering of the estuarine environments also support this mechanism (Nath et al., 2000).

The estuarine sediments also showed an anomaly in spatially segregating the depositions of Fe and Mn, perhaps as a consequence of their flocculation properties dependent on salinity (Sholkovitz, 1978; Balachandran et al., 2005). Thus, Fe gets precipitated at low salinity (<20), whereas Mn requires salinity >20 for its precipitation (Feely et al., 1981). Pollutants released to flow-restricted water bodies can promote coagulation or coprecipitation of metals under the varying ionic (salinity) condition (Antonio and Prego, 2004). Studies elsewhere have shown that oxides of Fe^{+3} are bioavailable through bacterial mineralization and hence could be detrimental to benthic organisms on continued exposure (Lovely and Phillips, 1987; Phillips et al., 1993; Roden and Zachara, 1996).

Biogeochemical Processes

The degree of variation in the depositional patterns of elements with respect to a three-way mechanism in the sedimentary environment is summarized in Figure 3. The flowchart denotes the metal deposition in coastal environment controlled by the natural processes such as diffusion by coastal currents and normalization through geochemical, biogenic, and inorganic associations. In contrast, the estuarine environment is dominated by anthropogenic input (effluents), which induce fast coagulation and precipitation of iron hydroxide (inorganic) and, subsequent scavenging of other metals. The restricted flow modifies estuarine processes to form null zones, which favors metal deposition. Yet another factor contributing to the elemental make-up is the benthic flux, which varies with development of reducing condition in sediments.

Summary

In the present study, coastal and estuarine sediments of Cochin were examined with reference to heavy metal concentrations to identify the different processes of deposition. Factor analysis distinguished the estuary and shelf into two provinces behaving differently to the elemental deposition. Pearson correlation in the estuary indicated definite increase in the interelement

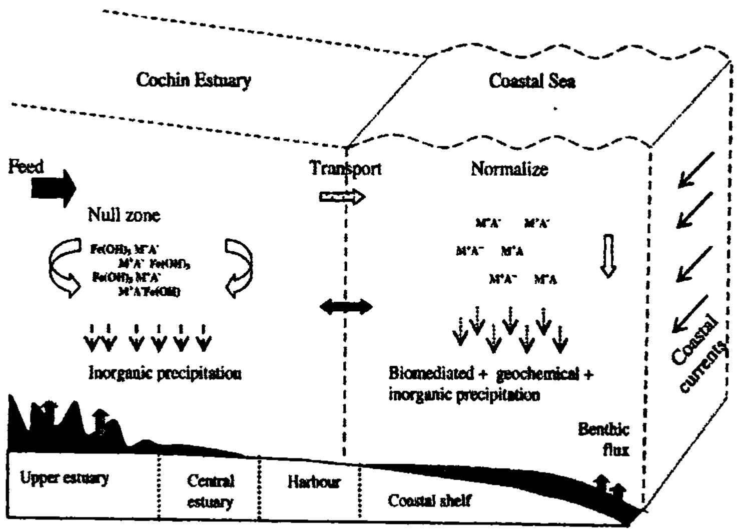

Figure 3. Schematic representations showing the active inorganic processes in the Cochin Estuary and bio-mediated processes in the adjoining shelf.

correlations irrespective of the sediment texture due to their common origin from effluents. Since the Fe-hydroxide depositions observed in the present study are detrimental, the estuary seems to be under stress (Isaac et al., 2005). The changes are noted in the estuary by an increase in the biomass of pollution-tolerant organisms (*Capitula cupitata*) replacing the vacated niche (Saraladevi and Venugopal, 1989; Saraladevi et al., 1992). In conclusion, the study shows that the geochemical behavior of the estuary is controlled by anthropogenic forces, whereas the coastal environment remained free from contaminants as the metals are rapidly removed by the coastal currents and biogenic association.

Acknowledgements

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ORIGINAL PAPER

Persistent volcanic signature observed around Barren Island, Andaman Sea, India

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Abstract This study delineates the formation of a warm pool (>34°C) of air to the west (downwind) of the active volcano of the Barren Island during October–November 2005. Barren Island is located in the Sumatra–Andaman region, about 135 km east of Port Blair, and lies within the Burma microplate, the southern tip of which experienced a submarine earthquake (M_w 9.3) causing a tsunami in December 2004. Barren Island is the only volcano, which has shown sustained eruptive activity since shortly after the Great Sumatran Earthquake of December 2004. Our observations require further corroboration to relate how submarine earthquakes activate volcanoes and how far these thermal emissions influence climate changes. Because it links global warming and climate changes to the frequent emissions from a volcano activated by submarine earthquakes, this case study is of special interest to the earth-ocean-atmosphere sciences community.

Keywords Andaman Sea · Barren Island · Volcano · Warm air pool · Global warming

Introduction

The causes of the global surface air temperature warming in the previous century remain a topic of debate (Shiogama et al. 2006). Although it is known that increase in greenhouse gases and solar irradiance changes are responsible for the rise in the surface air temperature (Stott et al. 2003), recent studies suggest that natural forcing such as volcanic activity, along with solar irradiance changes may be the most important factors influencing global warming (Hegerl et al. 2003; K-I Model Developers 2004; Nozawa et al. 2005). Understanding the forcing functions of the past climate change is much needed to improve the global circulation model and to predict future climate changes precisely. In this study, we present observational evidence of a warm air pool supporting the relative importance of volcanic emissions on surface air heating in the Bay of Bengal, a region of tropical cyclones (Pankajakshan et al. 2002; Shenoi et al. 2002). On 24 December 2004, this region experienced a devastating tsunami caused by a submarine earthquake, the deadliest disasters in modern history (Javed and Murty 2005; Waltham 2005; Bandopadhyay et al. 2006; http://www.volcano.si.edu/reports/usgs/index). The very fact that a warm air pool was observed in the Andaman Sea where the Stratovolcano (Barren Island) erupted soon after the Great Sumatran Earthquake, makes this study important to models linking climate and solid Earth tectonic and magmatic activity.

Materials and methods

Hydrographic observations were made during an oceanographic expedition (FORV Sagar Sampada, cruise No.SS 239) in the Andaman Sea during October–November 2005 (Fig. 1). On noticing the volcano in the Barren Island emitting fumes (Fig. 2, photo-

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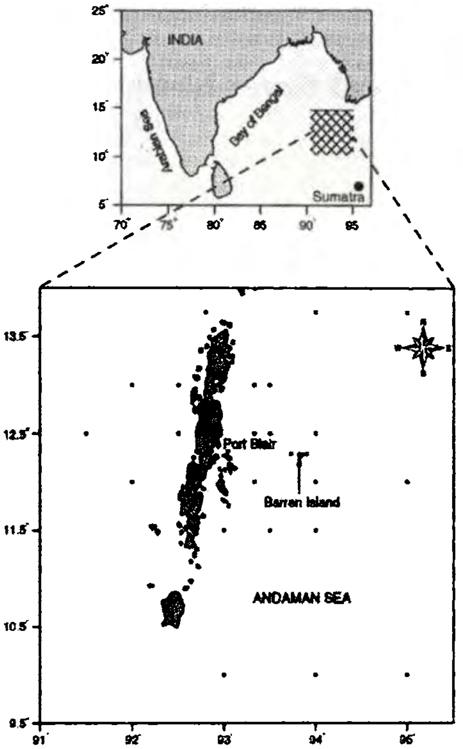


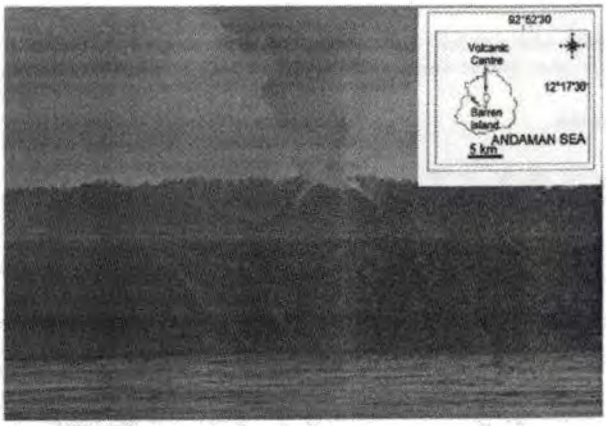
Fig. 1 Study region in the Bay of Bengal, showing Andaman Sea, Port Blair (filled right arrow head), Barren Island (pointed by arrow) and the Sumatra Island (Station locations are shown as solid dots)

graph taken from the ship when it was west of the island on 30 October 2005), we made site-specific observations around the island to evaluate the atmospheric and oceanographic disturbances in the vicinity of an active volcano. Atmospheric temperature was recorded using the ship-mounted automatic weather station (AWS, model YSI 44202, accuracy, ± 0.15°C; 10-min interval), as was weekly wind velocity (R.M. Young wind monitor 05103, range 0–60 m/s) and sea surface temperature using the Conductivity-Temperature-Depth profiler (CTD, Seabird Electronics, accuracy ± 0.001°C) available onboard the research vessel. In order to avoid diurnal variability in the air temperature, only data recorded during 10:00–14:00 h was used in the present study. Similarly, in order to describe the meteorological features of the region, wind velocity (monthly average) were retrieved from the available satellite-derived source (ftp://ftp.ssmi.com; QuickSCAT, Savannah, GA, USA, resolution 25 × 25 km^2). In order to put our findings into context, we use the oceanographic and meteorological data of the region collected on two occasions for comparison; one observation taken prior to the volcanic eruption (cruise No. SS 220, December–January 2004) and the second represents a recent observation (cruise No. SS 243, March–April 2006).

Results and discussion

The QuickSCAT diagrams over the Bay of Bengal indicate that in general, winds shifts from a southeasterly to a northeasterly direction as the season changes from October to November (Fig. 3a, b). Distribution of

Fig. 2 Barren Island and its active volcanic vent (Photograph taken from FORV Sagar Sampada on 30 October 2005). The view of the volcano is seen from the western side. Inset shows the Barren Island in Andaman Sea



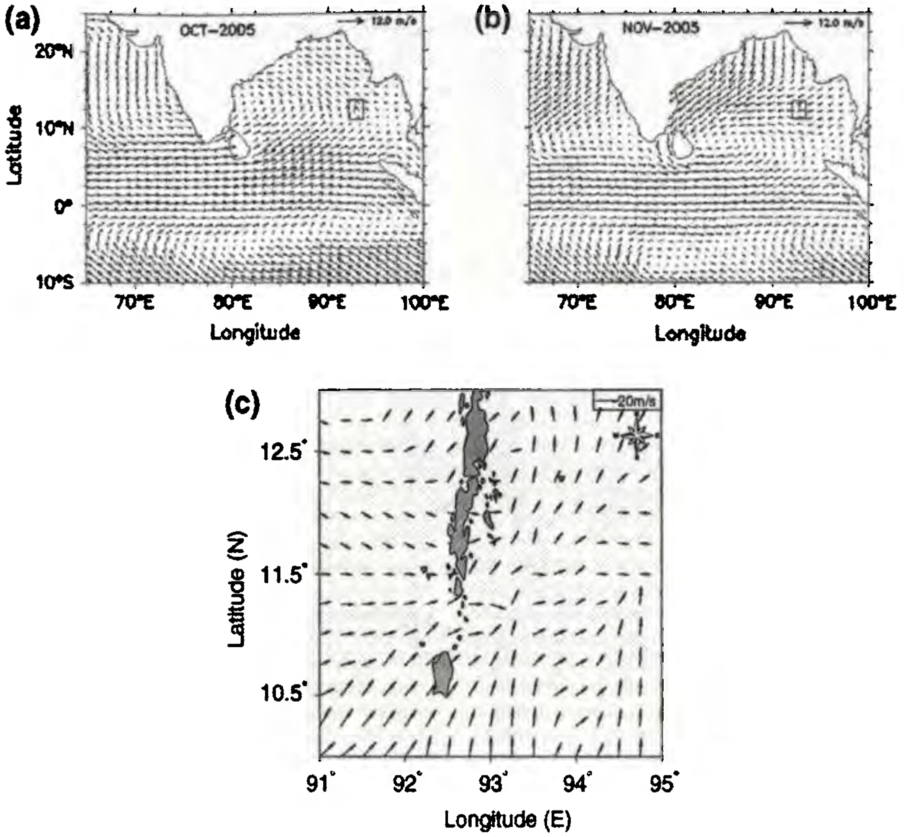


Fig. 3 Average wind velocity (m/s) in the Bay of Bengal during (a) October and (b) November (c) Average wind velocity (m/s) in the Andaman Sea during 25–30 October 2005

air temperature indicated a thermally elevated region (>34°C) surrounding Barren Island (Fig. 4c). This warm air pool is unusual because corresponding plots for the same region during the previous winter season (cruise No. SS 220. December-January 2004, Fig. 5) did not show such an anomaly. The heat wave emanating from this region is seen as a plume oriented in the north-northwest direction as well as in the north-northeasterly direction. The spread of the warm pool in the north-northwest direction matched the monthly averaged wind velocities (Fig. 3a, b), but could not explain the drift towards the north-northeast. In order to illustrate this, we averaged the wind velocity in the Andaman Sea during the period 25–30 October 2005. It is evident that during this period, the local winds were weak and northerly (Fig. 3c), consistent with the orientation of the warm air pool. The heat source feeding the warm air mass may be above the sea level, as the slightly warmer surface waters (>29.4°C) may be an artifact of this warm air (Fig. 4d). The vertical distribution of temperature measured at different locations around Barren Island using the CTD Profiler also indicated a steady decrease with depth below sea level. From the distribution pattern of air temperature and the sea surface temperature, we suggest that the source of this warm air is the Barren Island volcano, probably the volcanic emission. The following facts regarding Barren Island are also provided to support and substantiate our findings.

Barren Island (area 10 km^2, summit elevation 335 m) has experienced several phases of volcanic activity in the past; i.e. during 2000, 1994–1995, 1991,

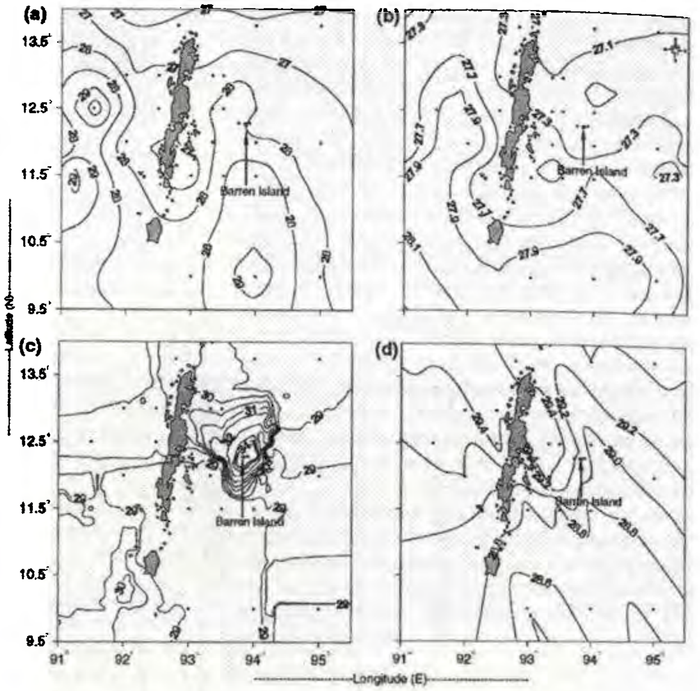


Fig. 4 Distribution of (**a**) air temperature and (**b**) sea surface temperature during December–January 2003–2004, prior to volcanic eruption and (**c**) air temperature and (**d**) sea surface temperature during October–November 2005, during the volcanic eruption in the Andaman Sea. All the units are given in degree Celsius (°C). Stations are shown as solid dots

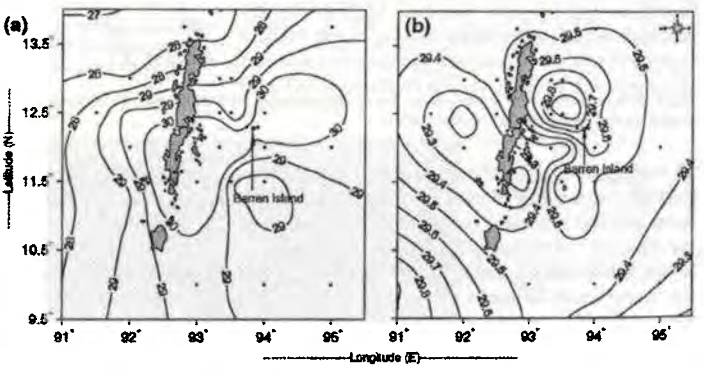


Fig. 5 Distribution of (**a**) air temperature and (**b**) sea surface temperature in the Andaman Sea during March–April 2006. There is a feeble, but persistent warm air pool around the Barren Island (>30°C). All the units are given in degree Celsius (°C). Stations are shown as solid dots

1852, 1803–1804, 1795, 1789 and 1787 (http://www.geos.iitb.ac.in/dchandra/biexp/; Raina 1987; Haldar 1989; Haldar et al. 1992, 1995; Ravi et al. 2001; Haldar and Luhr 2003). The recent eruption of this volcano on 28 December 2004 was followed by a series of eruptions in January, May and October 2005 with greater intensities (Bandopadhyay et al. 2006; http://globalrumblings.blogspot.com/2005 01_01globalrumblings_archive.html). Generally, volcanic eruptions are followed by very high-thermal evolution (>1,000°C), which extruded large volumes of rocks, emitting tephra and other trace gases that must have heated the air

(Cadle et al. 1976). The intensity and movement of this hot air mass depends on the strength and endurance of eruption and the winds (Mass and Portman 1989). Persistence of a warm air pool in the Andaman Sea, especially in the winter season is significant because of its closeness in space and time to the Great Sumatran Earthquake of December 2004. It would be worthwhile to know whether the sustained eruption of this volcano since January 2005 was a manifestation of this earthquake, indicating seismic-magmatic connectivity. Process-related studies on earthquakes have pointed out the existence of a close relationship between seismic and volcanic activities (Thomas and Steven 1984; William et al. 1991; Hill et al. 2002; Bandopadhyay et al. 2006). In Sumatra Island, there is a fault zone extending towards Barren Island, indicating the volcano overlying a seismically active zone (Javed and Murty 2005; Waltham 2005).

Volcanic emissions are found to influence surface warming and climate change (both heating and cooling) on different timescales (Rampino and Self 1992; Zielinski 2000; Nozawa et al. 2005; Shiogama et al. 2006). The climate response to large eruptions lasts for several years. The aerosol clouds produce cooling at the surface but heating in the stratosphere (Robok 2000). Volcanic eruptions that inject large quantities of sulphur-rich gases into the stratosphere have the capability of cooling global climate by 0.2–0.3°C for several years after the eruption (Zielinski 2000). Equatorial eruptions will impact global climate, whereas mid-latitude eruptions can cool climate in the hemisphere of origin (Rampino and Self 1992). Magnitude of cooling varies by latitude and it is possible for warming to occur in certain regions, primarily during the winter (Shiogama et al. 2006). Furthermore, the role of sea surface temperature in the genesis and intensification of tropical cyclones has been well demonstrated (Emanuel 1999; Trenberth et al. 2003; Trenberth 2005; Webster et al. 2005). Sea surface temperatures of >28°C are generally considered favourable for the development of tropical cyclones (Saunders and Harris 1997; Whitney and Hobgood 1997; Shapiro and Goldenberg 1998) and in the Bay of Bengal: the surface temperature remained higher than 28°C (Anwar 1999; Lal 2001). At present, there is no evidence to suggest that these volcanic activities influence atmospheric warming in the Bay of Bengal but this remains to be elucidated. However, it has been observed that there was an increase in the number of cyclonic systems developed in the Bay of Bengal during the northeast monsoon of 2005 (Five cyclonic depressions compared to an average 3.5 cyclonic depressions for the same period during 1971 (Ramakrishnan 2005: http://en.wikipedia.org/wiki/2005_North_Indian cyclone season). An important point to be mentioned here is that, Barren Island volcano continues to be active even in May 2006 (http://www.volcano.si.edu/reports/usgs/archive. cfm?volcano = barren#mar2006). We have an evidence in support of this volcanic activity, as our recent observations in the Andaman Sea (cruise No. SS 243, March–April 2006) still show a feeble, but persistent warm pool in this region (Fig. 5).

The Bay of Bengal has some climatic features including high precipitation, sea surface temperature and low-surface salinity that cause density stratification, all of which lead to frequent cyclonic depressions (Murthy et al. 2000; Pankajakshan et al. 2002; Shenoi et al. 2002; Vinayachandran et al. 2002; Jayu and Prasannakumar 2006). These are generally illustrative of a basin in which, a complex interplay of diverse processes takes place. The frequent atmospheric perturbations in this region are to be investigated carefully in relation to the occurrence of seismic-volcanic activities and their influence on cyclonic depressions. With a possession of 36 medium and large size volcanoes in the Sumatra–Myanmar subduction zone, their emissions are expected to influence the surface air temperature substantially. Because volcanic eruptions and their subsequent climatic change represent a large perturbation to the climate system over a relatively short period, volcanic emissions should be considered in global circulation models to predict the regional climatic responses, as suggested by Shiogama et al. (2006).

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Change Detection Studies of Sagar Island, India, using Indian Remote Sensing Satellite 1C Linear Imaging Self-Scan Sensor III Data

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ABSTRACT

DINESH KUMAR, P.K.; GOPINATH, G.; LALURAJ, C.M.; SERALATHAN, P., and MITRA, D., 2007. Change detection studies of Sagar Island, India, using Indian Remote Sensing Satellite 1C Linear Imaging Self-Scan Sensor III data. *Journal of Coastal Research*, 23(6), 1498–1502. West Palm Beach (Florida), ISSN 0749-0208.

The coastal zone of Sagar Island, India, is subjected to various cyclic and random processes that continuously modify the region. The shoreline and land-use/land cover changes have been studied using *Indian Remote Sensing Satellite 1C* (IRS 1C) linear imaging self-scan sensor (LISS) III satellite data from 1998 and 1999. A comparison between a topomap of 1967 and satellite data of 1999 established that during these years about 29.8 km of coastline was eroded, whereas the accretion is only 6.03 km². A comparison of satellite data from 1998 and 1999 showed that the island had undergone severe erosion of about 3.26 km², while the accretion was just about 0.08 km². Change detection studies based on land-use patterns of the region revealed that the areal extent of mangrove vegetation of the island during 1998 and 1999 was 2.1 km² and 1.3 km², respectively. The areal extent of agricultural fields during these periods was 130.4 km² and 118.6 km², respectively. These results can be used to develop an index for temporal land-use changes in the region as an aid to quantify the extent and nature of the development change and to understand the surrounding environment, which in turn may help the planning agencies to develop sound and sustainable land-use practices.

ADDITIONAL INDEX WORDS: *Land-use pattern, mangroves, satellite data, Sagar Island, India.*

INTRODUCTION

The vast Indian coastline, about 7500 km, supports a large number of island ecosystems, which are unique and scientifically interesting. These zones also have immense biological diversity and are often rich in living resources. By virtue of their location, their high productivity, and the services they offer, island ecosystems are often subjected to severe ecological pressures. Environmental issues of these zones are highly complex, and resource use and management systems often confront multiple conflicts. As the hinterland becomes crowded and resources get used up and exploited, greater attention is often being paid to the development of these zones. The complex interactions between natural and man-made processes of island ecosystems thus must be well understood so that adverse effects on natural environment and ecology can be avoided or minimized. Because of the complexity and their variations from sector to sector, a great deal of site-specific research is needed to predict the extent of geomorphic and ecological changes that will occur. In the present study, an investigation has been carried out in Sagar Island, India, to delineate the shoreline and land-use/land cover changes.

ENVIRONMENTAL SETTING

Sagar Island—which forms part of the Sundarbans biosphere and is the largest island of the Sundarbans deltaic complex, has been selected for the present study. The island is situated in the estuarine environment of Hooghli River. It is bounded by the Hooghli River to the north and west, the Muriganga River to the east, and the Bay of Bengal to the south (Figure 1). It extends from 21°37′21″ to 21°52′28″ N and 88°2′17″ to 88°10′25″ E. The length of the island in the north–south direction is 30 km, and it has a maximum width of 12 km. It is 6.5 m above mean sea level (Mukherjee, 1983). The coast is tide dominated and is characterized by tidal creeks, mudflats/salt marshes, mangroves, and sandy beaches. Fluvial, marine, tidal, and Aeolian processes are the chief agents in shaping the narrow coastal belt.

Over the centuries, the island has been affected several times by tropical cyclones. As per the nomenclature of Davies (1964), the coast of Sagar Island falls under the tidally dominated coast, having a tidal range of over 6 m. This island was formed in the lowermost part of the Hooghli River. In the region, local sea-level rise has been estimated as 2.6 mm per year. Previous studies invariably established that the island has been subjected to erosion by various processes (Bandyopadhyay, 2000; Ghosh, Gopinath Bhandari, and Sugata Hazra, 2001; Girish Gopinath and Seralathan, 2005; Paul and Bandyopadhyay, 1987). In the last 140

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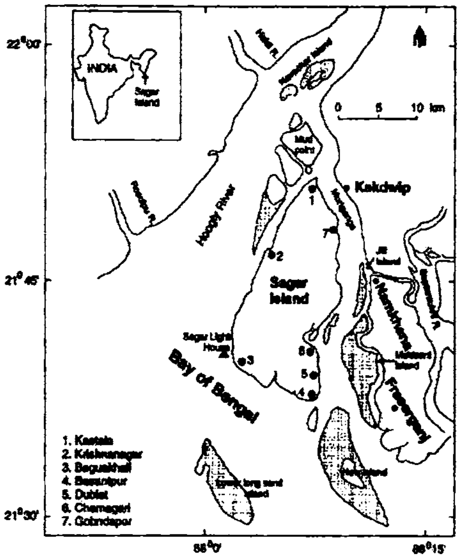

Figure 1. Location map of Sagar Island.

years, one-fourth of the area of Sagar Island (70.8 km^2) has been reported eroded (Bandyopadhyay, 2000). The geomorphological changes observed in the region are due to the change in the estuarine hydrodynamics caused by both natural and anthropogenic activities (Ghosh, Gopinath Bhandari, and Sugata Hazra, 2001).

MATERIALS AND METHODS

Satellite data of December 1998 and October 1999 (*Indian Remote Sensing Satellite 1C* IRS 1C linear imaging self-scan sensor (LISS) III, digital and geocoded false colour composite) available for the region were collected from the National Remote Sensing Agency, Hyderabad (Table 1) and were analyzed for the present study. The satellite data procured for erosion/accretion study represent days of equal tidal level. The tidal height was obtained from survey of India (SOI) tide table. Geocoded data were used in the field to obtain ground control points. Digital data were processed in the laboratory using digital image processing and Erdas Imagine software. The satellite images were then rectified with reference to ground control points and topomap of SOI 79C/1 and 79C/2. The rectified images were classified (supervised) on the basis of ground truth observations. Area covered by different classes was estimated by multiplying with spatial resolution. An accuracy test was also performed using Erdas Imagine software for different classes to confirm the accuracy of the procedure.

Table 1. *Details of satellite data. Abbreviation: SWIR, short wave infrared.*

Data	Data Details	Description
Satellite data (*IRS* 1C LISS III)	Path and row: 108/57	Spatial resolution: 23.5 minutes
	Date: 11 October 1999	Spectral resolution:
	Path and row: 108/57	Green: 0.52–0.59 μ
	Date: 3 December 1998	Red: 0.62–0.68 μ
		Near infrared: 0.77–0.86 μ
		SWIR: 1.55–1.70 μ

Table 2. *Shoreline changes of Sagar Island based on topomap and satellite data of 1998 and 1999.*

	Area (km^2)	
	1967–1999	1998–1999
Erosion	29.80	3.36
Accretion	6.03	0.08

Change detection studies pertaining to erosion/accretion and coastal vegetation status were undertaken. For this purpose, a band 4 image was extracted from rectified images. These images were classified into two classes, representing water and land. By subtracting one image from the other (1998–1999), the differences obtained by this procedure revealed the areal extent of erosion and accretion. Similarly, the 1967 topomap and classified image of 1999 were used for estimating areal extent of erosion and accretion (Table 2). Supervised classification procedure was followed for change detection of land-use pattern of Sagar Island and the areal extent of each class estimated (Table 3).

RESULTS AND DISCUSSION

Analysis of the multitemporal satellite data showed that from 1998 to 1999, the island had undergone erosion of 3.26 km^2, whereas the accretion was only 0.08 km^2. A comparison between a topomap of 1967 and satellite data of 1999 indicated that about 29.8 km^2 of the island got eroded, whereas the accretion was only 6.03 km^2 (Figures 2 and 3). Thus, the net eroded zone was quantified as 23.77 km^2.

A major environmental issue confronting the island is the degradation of mangrove forests, which has an adverse impact not only on marine bioresource productivity but also on the socioeconomic status of the rural coastal community. The areal extent of mangrove forests during 1998 (Table 2) has been estimated as 2.1 km^2. However, in the 1999 the mangrove forest coverage decreased to 1.3 km^2. Total area covered

Table 3. *Changes in land-use and land cover during 1998 and 1999.*

Classes	Area (km^2)	
	1998	1999
Casuarina	7.4	7.2
Mangrove	2.1	1.3
Sandy beach	1.2	1.2
Land vegetation	64.68	74.3
Agriculture fields	130.4	118.6
Total area	205.76	202.6

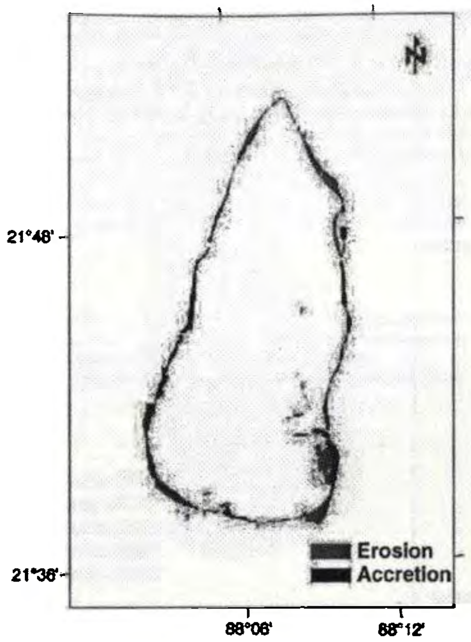

Figure 2. Shoreline changes of Sagar Island (1967–1999). For a color version of this figure, see page 1473.

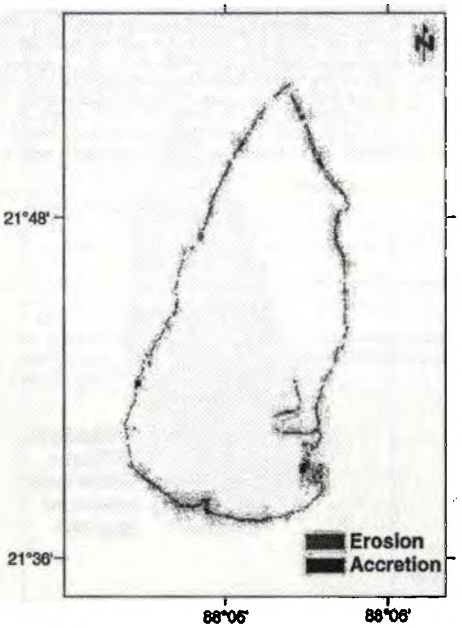

Figure 3. Shoreline changes of Sagar Island (1998–1999). For a color version of this figure, see page 1473.

by Casuarinas during 1998 and 1999 was 7.4 km² and 7.2 km², respectively, whereas the areal extent of sandy beach remained the same in both years at 1.2 km². The area covered by paddy fields in 1998 and 1999 was estimated. It was 130.4 km² in 1998 and 118.6 km² in 1999 (Table 3). From this estimation it can be seen that the areas of agricultural field are shrinking gradually. From Figures 4 and 5 it is evident that agricultural fields were replaced by land vegetation.

Being dynamic, the ecosystem is subjected to severe changes due to its strategic location in the Bay of Bengal. The island has been subjected to erosion since its origin. During the last 140 years, one-fourth of the total area (70.8 km²) has eroded (BANDYOPADHYAY, 2000). A comparison between the topomap of 1967 and the satellite imagery of 1999 showed that the northern part of the island and the southeastern and southwestern corners of the island were subjected to severe erosion over the past three decades. The present study confirmed the trend. It is found that about 29.8 km² has been lost due to erosion, whereas the accretion was only 6.03 km². The southwestern part of the island near Beguakhali has also been subjected to large-scale erosion in the past. The old lighthouse, which is now about 100 m offshore of the island (Figure 1), is a testimony to the retreating shoreline along this part of the island. Likewise, the sandy beaches and muddy shores exposed to the Muriganga estuary on the eastern side of the island are eroding at a faster rate. As evidence of this, remnants of bricks used for seawall construction were found in a linear pattern on the low water line near Dublat and Basantpur during a field survey. It appears that after the destruction of the first seawall, another seawall would have been built on the high water line, which is also subjected to wave erosion. It was found during the field survey that the second one has also been destroyed in places. Another cause of coastal erosion along this side of the island is mining of clay from the near shore zone. The clay is mined mainly for brick manufacturing and seawall construction. Mining of clay leads to increase in depth of near shore water, which in turn is responsible for waves breaking directly on the seawalls. Usually, sandy beaches get eroded faster than muddy beaches, but in the study area some of the muddy beaches along the Muriganga (eastern side) are severely eroding due to high flood velocity during monsoon period and tidal activity in the Hooghli estuary. GHOSH, GOPINATH BHANDARI, and SUGATA HAZRA (2001) have stated that between 1969 and 1995 the island lost 3.88 km². Further, from 1995 to 1999 the island has registered a faster rate of land loss, which was found to be 16 km². In addition to this, wave and tidal current activities also contribute to erosion of this side to a certain extent.

Deposition is noticed not only on the northern tip, but also

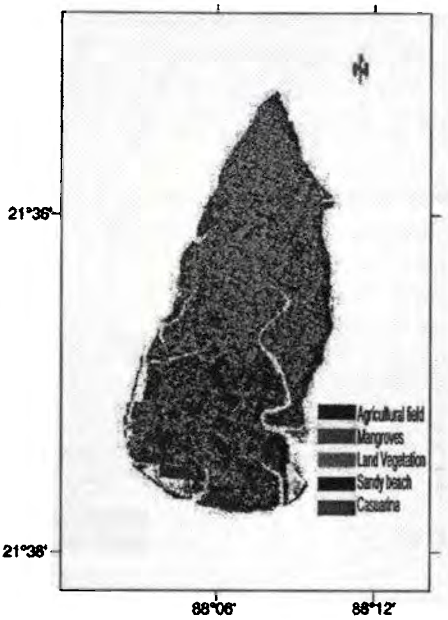

Figure 4. Land-use pattern of Sagar Island during 1999. For a color version of this figure, see page 1474.

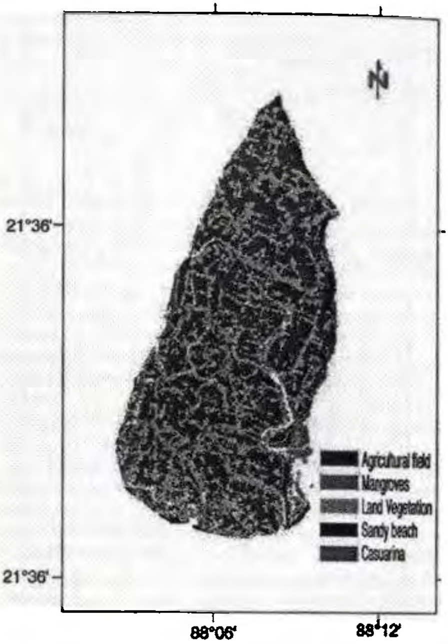

Figure 5. Land-use pattern of Sagar Island during 1998. For a color version of this figure, see page 1474.

in the southern part and on either side of the island. The field surveys showed that behind the beaches, many sand dunes have developed. PAUL and BANDYOPADHYAY (1987) have conducted a detailed study on the geomorphology of Sagar Island. They concluded that the causes of deterioration of the deltaic environment were human settlement, reclamation of lowland, indiscriminate resource use, and mangrove destruction. Their study also reveals that all the sides of the island, except north, are undergoing erosion. Deposition of sand, silt, and clay from south to north is a characteristic feature of this deltaic island.

At places where coastal erosion is severe, the condition of coastal vegetation, especially the mangroves, is critical. The total area of mangrove forests in 1998 was 2.1 km². However, in 1999, the area of mangrove forests had been reduced to 1.3 km², possibly because of human interference and coastal erosion. It is reported that during the last hundred years an area of 150,000 hectares has been lost in Sundarbans due to land reclaimed for agriculture, settlement sites, and road networks for an ever-increasing coastal population (MASTALLER, 1996). Thus, immediate steps should be taken for the conservation of mangrove forests. The increasing human population and the influence of the Hooghli and Muriganga rivers could be the major causes of degradation of the morphology and the ecosystem of the coastal stretches of the island. The population of the island in 1864 was only 1488 *i.e.*, 5.2 persons per km² (DAS, 2000). Given the total island area of 1999 and the 2001 census population figure (185,301), the human population density is estimated as 914.6 persons per km². Since the availability of natural resources is limited, it is clear that at least a part of the environmental degradation can be attributed to human stress along with the other factors. These changes over centuries have brought about as the currently described anthropogenic (cumulative and evolving) changes.

CONCLUSIONS

Sagar Island is characterized by the changes in the estuarine hydrodynamics, causing continuous erosion and deposition, and by anthropogenic activities. The areal extent of coastal vegetation and agricultural lands has declined. The major coastal vegetation, including mangroves and casuarinas, is under human threat, and immediate steps are needed. The net rate of erosion from 1967 to 1999 is estimated as 0.74 km²/y. Further, natural and anthropogenic activities are causing severe changes to the island, especially in the northern, southeastern, and southwestern faces. Since the availability of natural resources is limited, it is clear that at least a part of the environmental degradation can be attributed to human stress.

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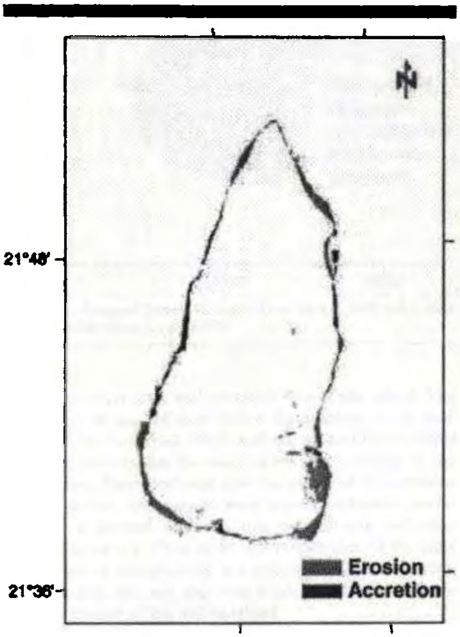

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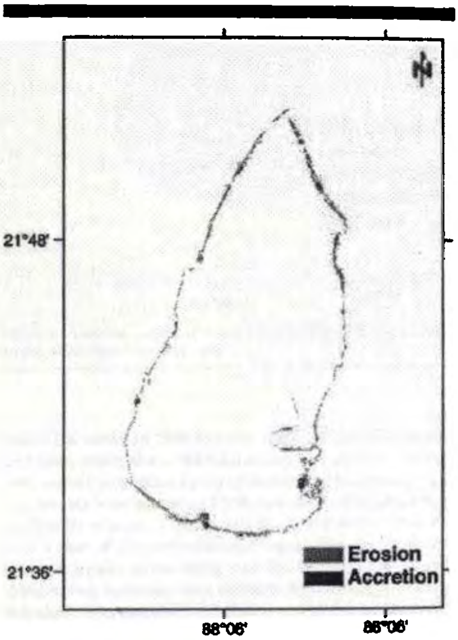

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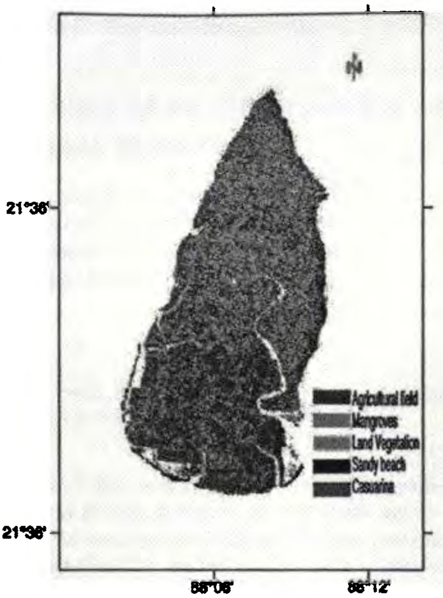

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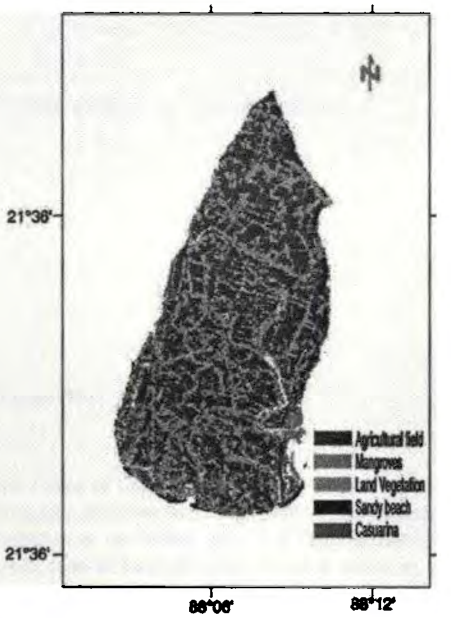

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ORIGINAL ARTICLE

Recovery of an estuary in the southwest coast of India from tsunami impacts

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T. Joseph · M. Nair**

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Abstract Water quality in the Cochin Estuary, southwest coast of India during the tsunami attack was assessed and compared with the pre and post tsunami characteristics. From the results obtained, it is evident that a drastic change in hydrography has been inflicted by the energy transferred through the tsunami, which disturbed the entire estuarine embayment. However, the post tsunami water quality showed normal levels indicating that the region has recovered from the tsunami impacts.

Keywords Cochin Estuary · Southwest coast of India · Tsunami impacts · Water quality

1 Introduction

The great Indian Ocean Tsunami of December 2004 generated due to the Earthquake off the west coast of Sumatra, Indonesia was among the deadliest disasters in modern history. This tsunami devastated the shores of Indonesia and several Southeast Asian countries including India. A significant enrichment in nutrients in the coastal waters of Dakshin Kannada (west coast of India) has been reported following the tsunami (Reddy *et al.*, 2005). Cochin Estuary (connected to the Arabian Sea through a 450 m wide opening at Cochin) has also experienced the ferocity of this tsunami. An attempt has been made here to assess the impacts of tsunami on the hydrochemistry of Cochin Estuary.

2 Data and methodology

The study area (Lat. 09°54′ & 10°00′E and Long. 76°15′ & 76°21′N) comprises of the barmouth (station 1) in the harbour area, Bolghatty (5 km northeast of barmouth; station 2) and Thevara (10 km southeast of barmouth; station 3) in Cochin estuary (Fig. 1). Hydrographic observations were carried out at these stations on 30th December 2004. At station 1 sampling was carried out over two consecutive tidal cycles (two samples each during ebb and flood tide). The tide gauge record at Cochin Port showed unusual water level variations due to tsunami at frequent intervals with varying amplitudes from 26 to 30 December 2004 (Fig. 2). Hence, the observations on 30th December 2004 are considered to represent the tsunami period.

Water samples were collected from 0.5 m below surface using Niskin Sampler and kept in freeze till analysis in the shore laboratory. The light transparency

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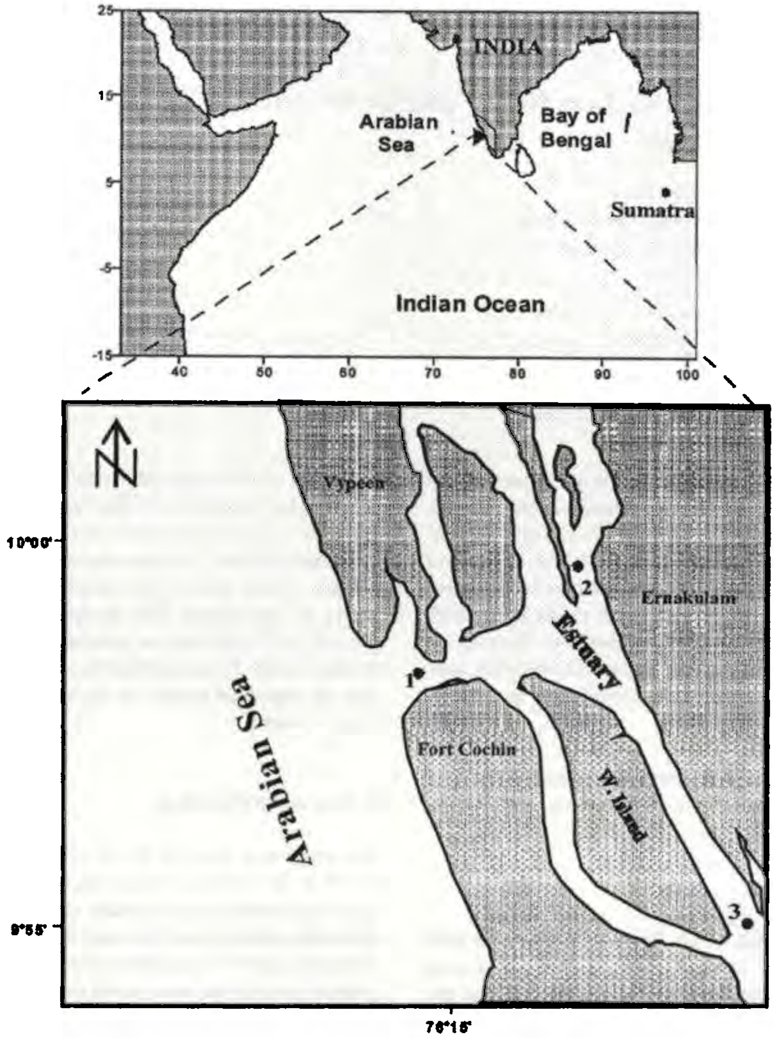

Fig. 1 Study region showing station locations in the Cochin Estuary

was measured using a secchi disc. Salinity was determined using electrodeless induction salinometer (DIGI AUTO 3G, accuracy ± 0.001). For pH measurements, an ELICO LI 610 model pH meter (accuracy ± 0.01) was used. Dissolved oxygen was estimated using Winkler titration method. Water samples were filtered and analysed for nitrate, nitrite, silicate, phosphate and ammonia using spectrophotometer (Shimadzu UV-1650PC) following standard procedures (Grasshoff *et al.*, 1983). Analytical reproducibility was checked by performing triplicate analyses for each sample and is presented here by the average value. The water quality characteristics of Cochin Estuary during the tsunami period are compared with the data available from the same region before tsunami (December 2003 and 22nd December 2004) and after tsunami (March,

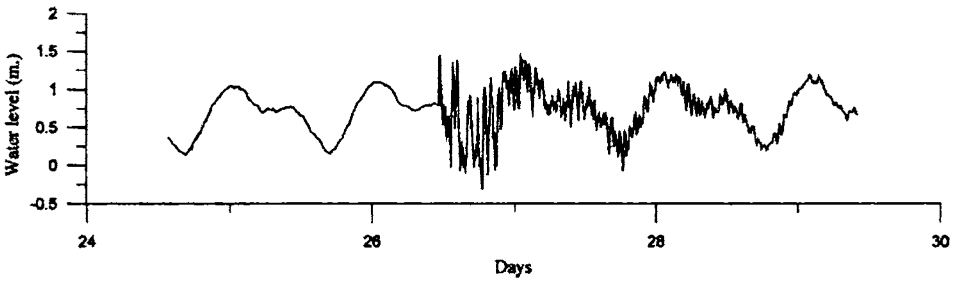

Fig. 2 Changes in mean sea level during December 2004, recorded at Cochin Harbour

2005) periods collected from the ongoing modeling studies.

3 Results and discussion

The water quality data of the study region during pre and post tsunami periods are presented in Fig. 3.

The water column generally remained thermally homogenous (average 29.8°C) in correspondance with air temperature (average 29.9°C, Fig. 3). The water temperature was lowered considerably during tsunami (average 27.7°C) as compared to air temperature (average 29.9°C). The surface salinity gradually decreased from barmouth towards st. 2 and 3 during pre and post-tsunami periods (20.5–35.8). But the tsunami erroded this gradient quickly, as the entire estuarine region was dominated by high saline water mass (34.2–35.2). The high turbidity caused by the tsunami is evident from the reduced water transparency during tsunami (secchi depth: 0.3 m to 0.8 m) compared to pre tsunami (1.7 m to 3.0 m) and post tsunami (1.3 m to 1.8 m). pH also showed a marginal increase during tsunami (8.28–8.45, Fig. 3). However, when compared to pre-(4.7–5.3 ml/l) and post-tsunami (4.6–5.0 ml/l) periods, the changes in dissolved oxygen level were marginal (4.0–4.5 ml/l) during tsunami.

There was a sharp rise in the phosphate concentration during tsunami (2.5–4.7 μM) as compared to pre-tsunami (0.9–1.5 μM) and post-tsunami (0.7–1 μM) periods. The nitrate concentration was also conspicuously high during tsunami (26.6–30.4 μM) as compared to those during pre tsunami (6.3–9.9 μM) and post tsunami (5.2–9.1 μM) periods. Silicate showed similar trends with higher values (35.0–42.2 μM) during tsunami period than the values during pre (9.8–23.4 μM) and post tsunami (10.2–13.4 μM) periods. The high ammonia (87.9–93.3 μM) in the entire study area during the tsunami compared to the levels before and after tsunami (4.1–68.8 μM and 6.3–43.2 μM respectively) is conspecusous. Cochin Estuary is reported to contain variable concentrations of nutrients (Haridas *et al.*, 1973; Qasim and Madhupradhap, 1979; Sarala Devi *et al.*, 1979, 1983, 1991; Sankaranarayanan *et al.*, 1986; Dinesh Kumar *et al.*, 1994; Balachandran, 2001.). In contrast, the homogenous water mass containing consistantly high concentrations of these nutrients in the entire study region during tsunami event could indicate the extent of local disturbance it created. However, the post tsunami observation showed normal levels indicating that the region has recovered from the tsunami impacts.

4 Conclusion

The present study observed drastic changes in estuarine water quality (high saline, turbid, cool and nutrient-rich water mass) generated by the tsunami through a massive inflow of coastal waters and the local disturbance it created. The turbidity was caused by the churning up of the sea bed by the intense energy transferred by tsunami. The withdrawal of sea before the advancement of the tsunami could be another factor supporting the bedload sediments to get suspended along with lashing waves. This turbid waters as it advanced into the estuary, released excess nutrients into the water column. Hence, the effect of tsunami on biological activities will be an interesting aspect to examine. An enhancement in the primary and secondary production could be expected following the nutrient enrichment in the study region. Even though

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Hydrodynamic and Geomorphic Controls on the Morphology of an Island Ecosystem in the Vembanad Lake, West Coast of India

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ABSTRACT

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Textural characteristics of the surficial sediments around Perumbalam Island located within the Vembanad Lake, southwest coast of India, were studied on a seasonal basis to understand the geomorphic response of the region. Sediment grain size increased from the northern to southern end of the island, indicating a progressive sorting by tidal currents. In contrast, an increase in the clay and organic carbon content in the sediments of the northern part of region suggests that their distribution is controlled by the productivity of the overlying water column. The evolution of this island is believed to be due to fluvial inputs from Muvattupuzha River. The braid shape of the island is attributed to the high-energy flow along the wedge of the estuary facing the river mouth, which has resulted in a build up of land along the southern boundary. The intense accretion on the southeastern and western sides of the island observed through satellite imagery reveals the fluvial influence on the evolution and morphology of this coastal lagoon.

ADDITIONAL INDEX WORDS: *Hydrodynamic condition, geomorphology, texture, organic carbon, Vembanad Lake, west coast of India.*

INTRODUCTION

Estuaries along the southwest coast of India are dynamic regions that never maintain a morphological equilibrium (KUNTE, 1995). Morphological characteristics of estuaries are generally the result of long-term changes in sedimentological and hydrodynamic features which tend to attain steady state. Several factors, including the topography, wave activity, tides, storms, river discharge, hydrodynamics, and human impacts, seem to influence the morphology of an estuary. The estuaries on the southwest coast of India were formed as the result of a series of transgression and regression events during the Holocene period (BLACK and BABA, 2001). Observations of shoreline changes in the coastal zones and estuaries have generated concern because these regions remain highly vulnerable in the future. Shifts in river courses observed in this region may be linked to the closure of existing outlets and formation of new lagoons in the coastal belt associated with tectonic processes. During monsoon, these estuaries overflow discharging sizeable quantities of sediments into the sea, whereas during other periods, seawater enters into the estuaries over considerable distances and modifies sediment deposition. A typical example is the Vembanad Lake, which is presently subjected to severe modifications by various kinds of natural and human interference (BALACHANDRAN *et al.*, 2005; LALURAJ *et al.*, 2006). In addition to a drastic reduction in volume (~40%; GOPALAN *et al.*, 1983), the establishment of the Cochin Port (1936) and hydraulic barriers (1976) have considerably changed the estuarine circulation. These factors are probably responsible for the emergence of new islands in the southern Vembanad Lake. Sediment texture analysis is one of the efficient tools that can be used to differentiate various depositional environments of a region (MANSON and FOLK, 1958; NORDSTROM, 1977). Although textural characteristics of sediments from various parts of Vembanad Lake are available (VEERAYYA and VARADACHARI, 1975; MALLIK, 1975; PADMALAL and SERALATHAN, 1994), a proper interpretation linking the hydrodynamics, geomorphology, and coastline changes to this estuary has not been completed.

The objective of this study is to understand the changes in the texture of sediments under varying energy conditions around an island (Perumbalam) in the Vembanad Lake in relation to its morphology and evolution. This will provide useful information regarding future changes expected in the region.

ENVIRONMENTAL SETTING

The Vembanad Lake is one of the largest tropical estuarine systems in India, extending to about 90 km, and it acts as a

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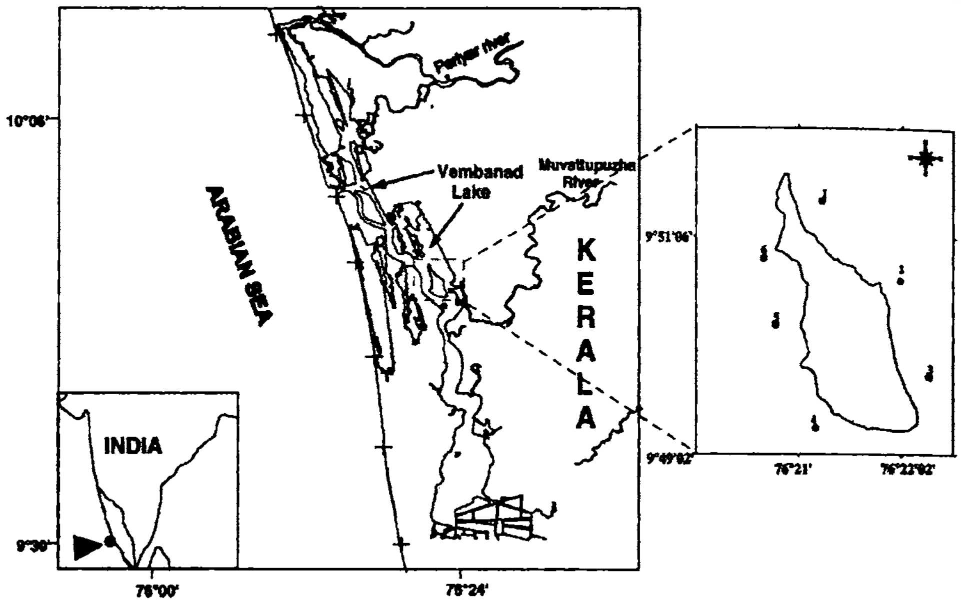

Figure 1. Base map of Cochin backwaters showing sample locations around Perumbalam Island.

major burial ground for Quaternary deposits (NARAYANA *et al.*, 2002). It is believed to have attained its present configuration in the fourth century AD. In its early configuration, it was primarily a marine environment with an alluvial bar boundary running parallel to the coast and interrupted at places by the Arabian Sea. In AD 1341, a catastrophic cyclone occurred that made the river Periyar change its course; this resulted in the formation of a number of islands and separated a distinct water body from the sea that yet maintained its connection with the sea (MENON, 1913). According to the definition of estuaries given by PRITCHARD (1967), the Vembanad Lake conforms to "bar-built estuary." Peat deposits have been identified at different depths in the boreholes between sandy clay and clayey sand sedimentary facies (NARAYANA *et al.*, 2002). Pollen analysis of peat has revealed the existence of mangrove vegetation and evergreen forest, suggesting humid climate during that time.

The emergence of several islands in the lake from the time of its formation is a clear indication of siltation of fluvial supply from rivers. The rate and mode of accretion depend on the transportation, quality, and deposition of sediments, tidal influence, and prevailing hydrodynamic conditions. During southwest monsoon (June–October), the estuary receives enhanced supply of alluvium, which is accumulated as bed sediment. The well-known clam fishery of this watershed, both live and dead, evidences the transformation of an originally marine environment into an estuary (PRESTON, 1916). The hinterland is composed of Archaean crystalline rocks, Tertiary sediments, and rocks with laterite capping (MALLIK *et al.*, 1987). In the south Vembanad region, the swampy areas (Kari lands) with black peaty soil, which has a high proportion of carbonaceous wood, represent areas that were dense mangroves in the past.

Perumbalam Island, located within the central part of the Vembanad Lake (09°48'–09°53' N, 76°18'–76°23' E), is wedge shaped and points toward the bar mouth (Figure 1). Southern and northern parts of the island are sandy, whereas the western side is muddy in nature. The sediment characteristics around the island are highly variable, probably due to the tidal influence (PADMALAL and SEERALATHAN, 1994). The length of the island is about 5 km, and the width narrows down from 400 m in the south to 200 m in the north. The tapering nature of the island toward the north is suggestive of the high fluvial supply from rivers, especially from the Muvattupuzha River. It has an average fluvial discharge of 722 Mm^3 during monsoon and 297 Mm^3 during postmonsoon (CUSAT, 1999). During the premonsoon period, the region is dominated by tides, whereas during other seasons, river flow is found to dominate. The average depth around the island varies between 3 and 8.5 m (MALLIK and SUCHINDRAN, 1984). The average range of tides during monsoon and postmonsoon seasons is 47 cm and 43 cm, respectively (SRINIVAS *et al.*, 2003). The currents are low (~15 cm s^{-1}) during Oc-

Table 1. *Textural classification and hydrodynamic subdivisions of the sediments from the study region.*

Location	Months	Code (Flemming, 2000)	Textural Classification
1	July	D-IV	Clayey slightly sandy mud
	Aug	D-IV	Clayey slightly sandy mud
	Sep	D-IV	Clayey slightly sandy mud
	Nov	D-IV	Clayey slightly sandy mud
	Dec	D-IV	Clayey slightly sandy mud
2	July	B-III	Clayey sand
	Aug	B-IV	Very clayey sand
	Sep	B-III	Clayey sand
	Nov	C-III	Silty sandy mud
	Dec	C-III	Silty sandy mud
3	July	A-I	Slightly silty sand
	Aug	A-I	Slightly silty sand
	Sep	B-II	Silty sand
	Nov	B-I	Very silty sand
	Dec	B-II	Silty sand
4	July	A-II	Slightly clayey sand
	Aug	C-IV	Clayey sandy mud
	Sep	B-IV	Very clayey sand
	Nov	C-IV	Clayey sandy mud
	Dec	C-IV	Clayey sandy mud
5	July	D-IV	Clayey slightly sandy mud
	Aug	D-IV	Clayey slightly sandy mud
	Sep	D-IV	Clayey slightly sandy mud
	Nov	D-IV	Clayey slightly sandy mud
	Dec	D-IV	Clayey slightly sandy mud
6	July	B-III	Clayey sand
	Aug	B-III	Clayey sand
	Sep	B-III	Clayey sand
	Nov	B-II	Silty sand
	Dec	B-II	Silty sand

Table 2. *Grain-size proportions and organic carbon (OC) content (%) in the sediment.*

Location	Months	Sand	Silt	Clay	OC
1	July	20.03	31.1	48.87	2.9
	Aug	21.87	29.56	48.57	2.7
	Sep	10.12	30.8	59.08	3.2
	Nov	12.98	28.06	58.96	3.5
	Dec	11.99	27.8	60.21	3.4
2	July	71.25	8.1	20.65	1
	Aug	73.12	6.21	20.67	1.9
	Sep	74.44	7.83	17.73	1.99
	Nov	48.14	30.13	21.73	1.04
	Dec	37.1	33.16	29.74	0.66
3	July	81.11	10.66	8.23	1.8
	Aug	74.83	14.9	10.27	1.3
	Sep	70.18	16.85	12.97	1.2
	Nov	61.39	29.15	9.46	0.8
	Dec	58.1	27.17	14.73	1.04
4	July	76.7	6.76	16.54	1.3
	Aug	72.56	8.68	18.76	1.6
	Sep	73.97	5.86	20.17	1.8
	Nov	45.44	10.66	43.9	2.1
	Dec	41.54	12.5	45.96	2.3
5	July	8.97	33.6	57.43	3.4
	Aug	7.82	29.5	62.68	3.6
	Sep	9.58	26.93	63.49	3.81
	Nov	7.41	25.6	66.99	4.3
	Dec	9.21	24.4	66.39	4.8
6	July	67.64	15.2	17.16	1.1
	Aug	65.46	14.2	20.34	1.5
	Sep	65.48	15.2	19.32	1.9
	Nov	61.17	19.2	19.63	1.4
	Dec	62.07	20.06	17.87	1.5

tober–December and increase to 45 cm s^{-1} during February–May (SRINIVAS *et al.*, 2004).

MATERIALS AND METHODS

Surface sediment samples were collected from six locations around Perumbalam Island for six months (July to December) using a Van Veen grab (area 0.45 m^2). Samples collected during July to September (monsoon) and November–December (postmonsoon) were compared for their seasonal change. The textural properties were analysed following FOLK and WARD (1957) and CARVER (1971). The organic content of the sediment was estimated by the wet digestion method (EL WAKEEL and RILEY, 1957). The energy condition was evaluated following the classification made by PEJRUP (1988), and their textural classification was made according to FLEMMING (2000). Satellite data from Indian Remote sensing Satellite-IC Linear Imaging Self Scanning III (geocoded False Color Composite) of the study area were obtained from National Remote Sensing Agency, Hyderabad. The morphological changes in Perumbalam Island were evaluated by comparing the topographic map of 1968 and the geocoded data of 2001.

RESULTS AND DISCUSSION

Textural Facies

The sediments generally showed variable textural facies, such as clayey slightly sandy mud, very clayey sand, clayey sand, *etc.* (Table 1). Their textural characteristics and organic carbon content are given in Table 2. The textural distribution under the different hydrodynamic subdivisions facilitates a depositional environment. The sorting of sediments with respect to hydrodynamic energy conditions are given (Figure 2) as a ternary diagram (FLEMMING, 2000). Except at stations 3 and 6, sediments were muddy in nature. The tapering end of the island (station 6) and near the mouth of the river (station 3), also were sandy. Station 2 and 4 were sandy only during monsoon, which afterward changed to muddy. The silt and clay content at stations 3 and 6 were enhanced after monsoon with a clear gradient from the river mouth. The Muvattupuzha River, entering at the southern part of the island, is considered to be the source of large-grained sediment in that area. The abundant supply of sediment during monsoon leads to the accretion of sediments along the southeastern margin as well as on the western side of the island. The study region showed more affinity towards clayey and silty facies during postmonsoon. The similarity in the nomenclature of sediments collected in different periods (stations 1 and 6) reveals that the environment changes were almost consistent.

The grain-size distribution provides a measure of energy conditions during deposition. Grain-size distribution of sediments is influenced by channel morphology, source, weathering, abrasion, corrosion, sorting, and deposition of settlements. In the present study, the sediment grain size generally decreased from the broad southern side of the island to

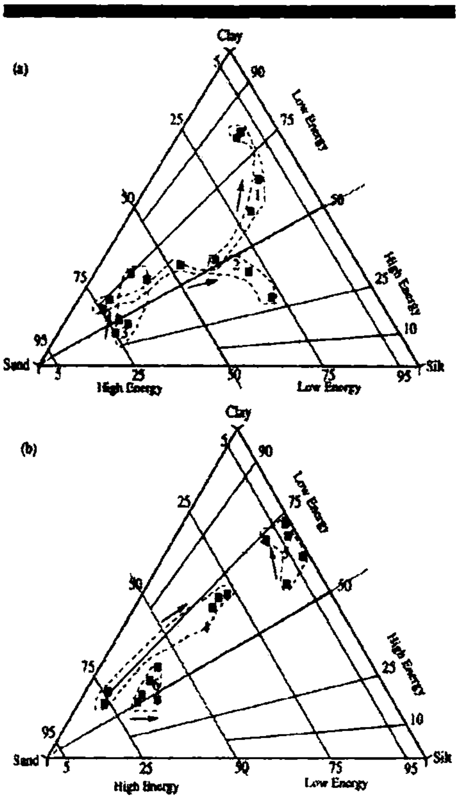

Figure 2. Ternary diagrams on the basis of sand/silt/clay ratios showing the textural trend of six locations during monsoon and postmonsoon (indicated by arrows: monsoon to postmonsoon). (a) Locations of stations 1, 2, and 3 and (b) locations of stations 4, 5, and 6 (after Fleming [2000] and Pejrup [1988]).

the tapering northern end. As the river flow wanes out, coarser sediments get deposited immediately while fine sediments are transported seaward. The grain size and the texture of sediments in the region are presented in Tables 2 and 3. Sand was generally high during monsoon at all stations due to the high-energy conditions that prevail in the region. Similarly, clay was very high compared to silt except at the river entrance (stations 2 and 3). However, during postmonsoon, fluvial nature of stations 2 and 3 indicated good supply of silt.

Hydrodynamic Environment

The textural characteristics of an estuarine environment are influenced by the hydrodynamic condition that prevails over the region. This can be described using a trilinear diagram that indicates the textural qualities of the region during monsoon and postmonsoon (Figure 2). During monsoon, the river mouth remained highly energetic and rich in suspended sediments, which gradually decreased afterward. This was reflected in a shift in the sediment texture toward silt during postmonsoon as the result of the decreased river flow containing suspended sediments. A weak-energy condition at stations 1 and 5 during postmonsoon is indicated by a shift in the texture toward the clay axis. The relatively deeper station 4 showed a markedly low-energy condition (steadiness), which favoured the deposition of clay during postmonsoon. However, there was no appreciable variation in energy condition at the northern end because the tidal activity at the convergence of two channels encouraged uniform deposition. At station 6, disturbance was still low, and sediments remained more or less undisturbed in both seasons.

Table 3. *Textural parameters of sediments.*

Location	Months	Phi Mean Size	Standard Deviation	Skewness	Kurtosis
1	July	5.86	2.63	−0.19	0.92
	Aug	6.42	3.22	−0.07	0.99
	Sep	7.11	2.77	−0.18	1.19
	Nov	7.08	2.82	−0.2	1.19
	Dec	7.09	2.8	−0.2	1.19
2	July	3.17	3.45	0.4	1.42
	Aug	3.16	3.55	0.36	1.56
	Sep	3.38	3.39	0.14	1.48
	Nov	4.14	2.87	0.08	0.93
	Dec	3.81	3.53	−0.05	0.98
3	July	2.46	2.24	−0.19	1.64
	Aug	2.82	2.59	0	1.3
	Sep	3.38	2.64	0.16	1.23
	Nov	3.41	2.6	0.15	0.94
	Dec	3.12	3.06	0.03	0.99
4	July	3.43	3.23	0.2	1.99
	Aug	3.46	3.39	0.16	1.49
	Sep	3.12	3.58	0.38	1.58
	Nov	4.55	3.39	0.1	0.74
	Dec	4.88	3.4	−0.13	0.74
5	July	7.1	2.64	−0.14	1.08
	Aug	7.39	2.42	−0.08	1.07
	Sep	7.14	2.62	−0.16	1.07
	Nov	7.41	2.4	−0.09	1.44
	Dec	7.4	2.43	−0.09	1.47
6	July	3.76	3.12	0.31	1.46
	Aug	3.8	3.15	0.31	1.42
	Sep	3.81	3.13	0.31	1.42
	Nov	3.81	3.15	0.3	1.42
	Dec	3.77	3.13	0.29	1.42

Statistical procedures can be used for classifying the depositional environment based on the sediment grain size (Table 3). In general, the high values of phi during postmonsoon indicate low-energy conditions, which decreased upstream. The skewness (0.41 to 0.19) ranged from near symmetrical to very finely skewed. The kurtosis ranged from 0.74 to 1.99, *i.e.*, platy kurtic to very platy kurtic. The kurtosis fluctuated between stations and between seasons, but at station 6, it did not vary considerably due to a steady-energy environment around it. The phi standard deviation varied between 2.24ϕ and 3.58ϕ, indicating poorly sorted sediments under low-energy conditions. During monsoon, high river flow transported large amounts of fine and coarse sediments that settled im-

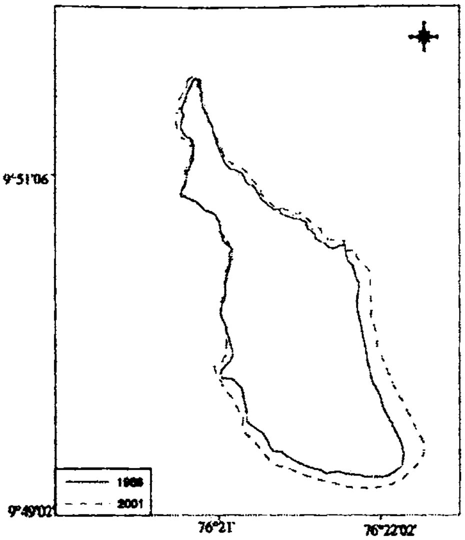

Figure 3. Morphological changes in Perumbalam Island (1968–2001).

mediately, which is an indication of poor sorting of the sediments.

The extent of morphological changes in the study region was estimated by comparing the topographic map of 1968 and satellite imagery of 2001 (Figure 3). It is evident that during this 33 y period, the island Perumbalam has undergone considerable change in morphology by accretion of land area, especially on the southeastern part of the island where the Muvattupuzha River enters. The hydrodynamic condition revealed that the sediments brought by rivers are generally deposited along the southeastern parts of the island as compared to the tapering northern end of the island. This is because the energetic hydrologic environment of the southern part (stations 3 and 4) induced by river flow and tidal activity favoured deposition. It was further noticed that station 5 was also characterised by high-energy conditions caused by tidal influx. Based on Figures 2a and 2b, a shift in the energy condition around the island from higher (monsoon) to lower (premonsoon) intensities can be assumed. This supports the view that the monsoon cycle plays an important role in the supply and distribution of suspended sediment and, therefore, modifications to the morphology of the island. The sediment supply from Muvattupuzha River and its further modifications in the estuary by tidal activity probably have contributed to the deposition and growth of Perumbalam Island.

Organic Carbon

In addition to the tidal and hydrological forces that control the deposition of sediments, the distribution of organic carbon in the lagoon was mainly controlled by overlying productivity. In Vembanad Lake, it has been observed that productivity remains consistently high throughout the year (Murthy and Veerayya, 1972). In the present study, the organic carbon ranged from 0.66 to 4.8%. Highest values were observed at stations 1 and 5 (Table 2), which were impoverished in sand content. In general, an increase in organic carbon was accompanied by decrease in mean grain size of sediments (Table 2). Similar to the consistent behaviour in the sediment texture, organic carbon also did not vary much at station 6, indicating the steady depositional environment that prevailed in that region.

CONCLUSIONS

This study showed that the formation of Perumbalam Island in Vembanad Lake was mainly the result of fluvial input from Muvattupuzha River and its subsequent modifications brought about by estuarine circulation. The wedge shape of the island indicates a linear flow through the braided lagoon resulting in sediment accretion at the southern side. Accretion mainly occurred toward the southeastern and western side. High-energy conditions at the river mouth favoured deposition of sand on the southeastern side, but the deeper channels on the western side of the island encouraged deposition of silt and clay. In summary, seasonal variation in the river flow and tidal activity has played a vital role in the evolution of numerous islands of similar type in Vembanad Lake.

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FRESH WATER INFLUENCE ON NUTRIENT STOICHIOMETRY IN A TROPICAL ESTUARY, SOUTHWEST COAST OF INDIA

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Abstract. Cochin backwaters, a micro tidal estuary, undergo a characteristic transformation from a river-dominated system during summer monsoon to a tide-dominant system during pre-monsoon season. The present study observes that as the river flow weakens after monsoon, the flushing of the estuary diminishes and the nitrogen and phosphorous loadings through anthropogenic activities (industries) and sediment re-suspension alter the nutrient stoichiometry substantially. The increased tidal activity during pre-monsoon changes the estuary into a vertically mixed, eutrophic and flow-restricted system supporting an enhanced organic production. This implies that monsoon-induced hydrology plays an important role in regulating the nutrients, secondary production and even the migrant fauna of the estuary. The system is delicately poised, as continuous release of pollutants including nutrients into this estuary would suppress fish and shell fish production, where only pollution tolerant species can exist.

Keywords: *nutrient stoichiometry, Cochin backwaters, Southwest coast of India*

Introduction

Dissolved nutrients are the raw material for the marine trophic chain and estuaries are the main entry for nutrients coming from continental drainage to the marine environment [1, 5]. The nutrient supply is greater in estuaries that are near densely populated regions, due to the entry of domestic and industrial waste, urban drainage, and agricultural effluents. The increase of nutrient concentrations in estuarine and coastal waters causes several environmental modifications, such as increases in productivity and fishing yields [6, 8, 9, 10]. However, anthropogenic inputs frequently cause excessive eutrophication in the environment, especially where the circulation is restricted, such as in estuaries and coastal regions. Several alterations in chemical characteristics and water quality in such water bodies occur as a result of varying river flows. Such alterations can lead to various ecological consequences like changes in species composition, blooms of phytoplankton and decrease of oxygen concentrations.

Cochin backwaters, one of the largest tropical estuaries of India (256 km^2), are facing gross pollution problems following the release of untreated effluents from industries (0.104 x 10^6 m^{3}d^{-1}) and domestic sectors (0.26 x 10^{3}m^{3}d^{-1}) [12]. Reclamations over the past several decades have resulted in considerable shrinkage of the Cochin backwaters [13]. The hydraulic barriers constructed to prevent saline incursion into the upstream agricultural fields imposed flow-restrictions and increased sedimentation in the estuary [2, 6, 14]. The monsoon-derived alluvium accumulates in the estuary during post-monsoon, whereas silting environment prevails during the pre-monsoon [15, 16]. The natural and anthropogenic factors influencing the geochemistry of sediments in the Cochin backwaters and the adjacent coast have been reported [2, 17]. Many studies have assessed the environmental changes caused by anthropogenic input of nutrients and other materials in this estuarine system, albeit, systematic study over a region covering tidal cycles are not yet reported.

The present study explains the variability in the nutrient distribution and stoichiometry in the lower reaches of Cochin backwaters, as observed during two contrasting seasons. The observations are mainly based on two time-series measurements conducted along 5 locations in the northern limb of the estuary during October 2003 (high river flow) and March 2004 (low river flow).

Materials and methods

The observations were carried out as a part of the programme "Ecosystem Modelling of Cochin backwaters". The northern limb of the Cochin backwaters was selected as the study area because of its increased anthropogenic disturbance [2, 8, 18,]. Five stations in an approximately 5 km stretch were occupied for simultaneous time-series measurements during October 2003 and March 2004. Station 1 was situated closer to the inlet and station 5 towards the north estuary in the River Periyar *(Figure 1)*.

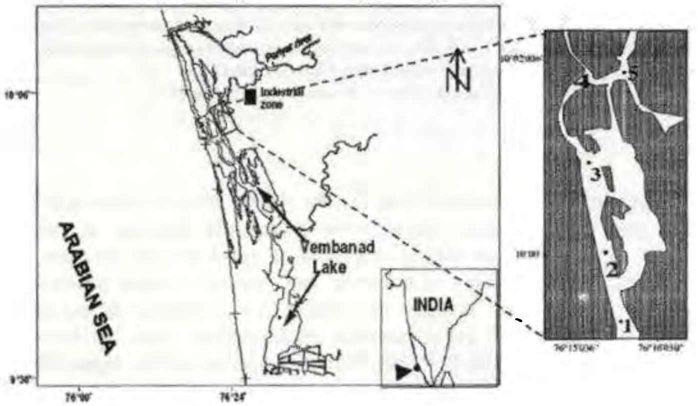

Figure 1. Study area in the Cochin backwaters showing the station locations for the time-series observation.

Variation in water levels, flow, salinity and temperature were recorded from all these five locations at every 10 minutes interval using tide gauges (Valeport) and current meters (RCM9) moored for 30 days continuously during both occasions. Details regarding the sampling and hydrodynamic model development are discussed early [19]. Water samples were collected from 0.5 m below the surface and from 2 m depth of these stations at 3 hourly intervals for 30-h period on 4 occasions, each during October 2003 and March 2004. The samples were subjected to various physico-chemical analyses within an hour of collection (This was possible because the study region was very close to our laboratory). Salinity was determined using a Digi Auto Salinometer (model TSK, accuracy ± 0.001) and the pH using an ELICO LI610 pH meter (accuracy

± 0.01). Samples for dissolved oxygen were fixed on board and later, estimated following Winkler method [4]. Samples for nutrient analysis (nitrate, nitrite, ammonia, silicate and phosphate) were filtered and analysed in a UV-VIS Spectrophotometer (1650 Shimadzsu) following standard procedure [4]. 250 ml of water sample was filtered through GF/F filter paper, extracted with 90 % acetone for 24 hr, centrifuged and analyzed for chlorophyll *a* by measuring the extinction at 630, 645, 665 and 750 nm against a reference blank using a spectrophotometer [11].

Results

Climatic conditions and hydrography

In order to explain the hydrography and nutrient distribution of the region, we consider a set of observations made during two contrasting seasons. October 2003 was generally a rainy season and (28th October was cloudy with cold winds of speed 4 m/s). The water column was comparatively turbid, as the secchi depth was < 0.7 m due the high influx of river-born suspended sediments. In contrast, 22nd March 2004 was a sunny and warm day with weak winds and as a consequence, the water transparency increased to 1 m. The variations in the different environmental parameters at surface and bottom of the study region during both seasons are furnished as contour diagrams *(Fig.2-5)*. The presentations of figures are in such a way that the x-axis represents the station locations (approximately 1 km apart) and the y-axis represents the time of collection, which always starts at 6:00 hrs on each day. Even though station 5 was situated in an adjacent channel, we have considered it to be approximately 1 km north of station 4, as the tide at this point was found to lag behind station 4 [19]. The dominant fresh water flow on 28th October was indicated by the near zero salinity towards the seaward end of the study area, which however showed saline incursion (6-18) at bottom during high tide *(Figure 2)*. During pre monsoon (March 2004), increased tidal activity brought in a vertical mixing, as the salinity increased (18–30) in the study region and water was warmer by 4°C (28° to 32.2°C) as compared to the previous season *(Figure 3)*. The salinity variation generally shows that the region experiences semi-diurnal mixed tides, which was more intense during March, as observed early [10]. The river discharged lowered the pH below 6 in October, but the pre monsoon season indicated a recovery, when the pH increased considerably (7.4 to 8).

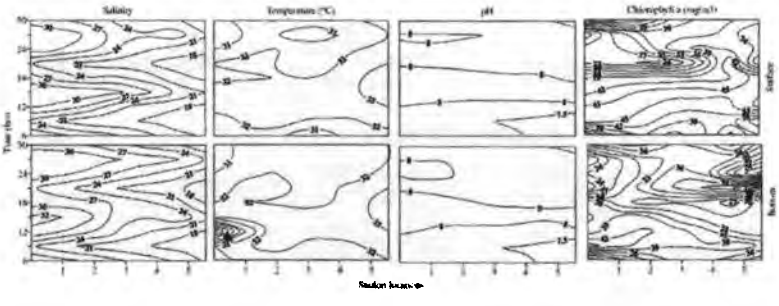

***Figure 2.** Time-series variation in salinity, temperature (°C), pH and chlorophyll (mg/m³) at surface and bottom waters on 22nd March 2004.*

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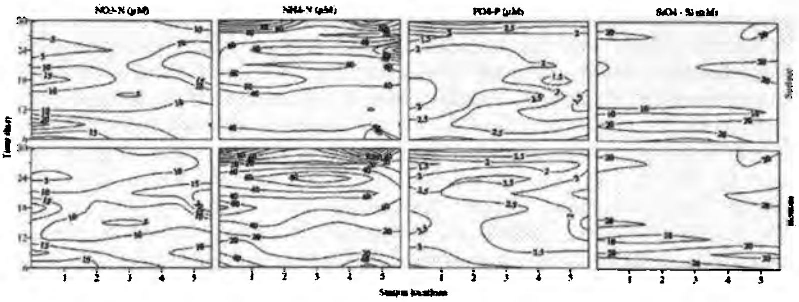

***Figure 3.** Time-series variations in nitrate (µM), ammonia (µM), phosphate (µM) and silicate (µM) at surface and bottom waters on 22nd March 2004.*

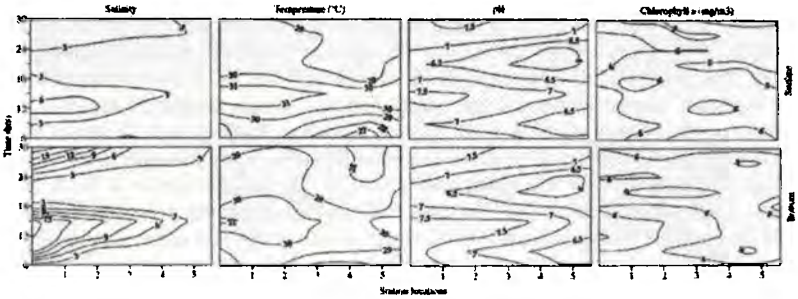

***Figure 4.** Time-series variation in salinity, temperature (°C), pH and chlorophyll (mg/m³) at surface and bottom waters on 28th October 2003.*

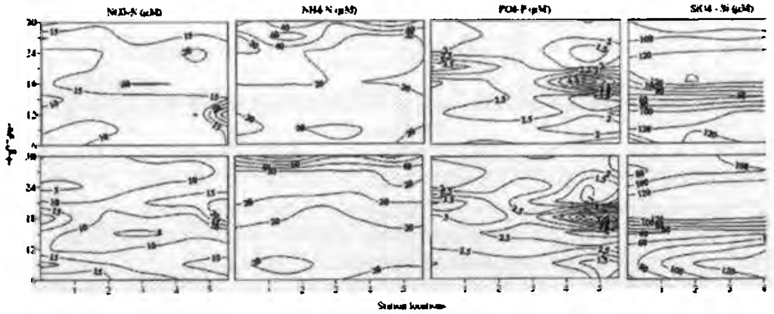

***Figure 5.** Time-series variations in nitrate (µM), ammonia (µM), phosphate (µM) and silicate (µM) at surface and bottom waters on 28th October 2003.*

Dissolved inorganic nutrients and chlorophyll a

During March, the increased tidal activity ensured a vertical mixing, as evidenced by a uniform distribution of nutrients *(Figure 2-5)*. Ammonium (NH_4^+) represented 80% of dissolved inorganic nitrogen (DIN), and its highest values were always associated with fresh water inflow. Phosphate was moderately high (1.5 - 4.5 µM) in October, whereas the concentrations decreased towards upstream (1.5 µM) in March. Fresh water flow enhanced the nitrate and silicate levels during the post monsoon (NO_3 10-30 µM, SiO_4 60-130 µM, ***Figure** 5*) indicating their upstream origin. Chlorophyll *a* concentrations were low during October, possibly due to the reduced light intensity and swift currents, which probably exported the productive estuarine waters to the sea [20]. The chlorophyll *a*, which was low during October (< 10 mg/m^3), increased during March, especially towards upstream (> 45 mg/m^3). Another important observation was that, even with low transparency of the water column, the chlorophyll concentrations at sub surface (2 m) were fairly close to that in the surface waters on both occasions. Increased residence time of the estuary is probably resulting in an enhanced productivity in the Cochin backwaters during March [6].

Dissolved inorganic nutrients generally showed an inverse relationship with salinity, where the highest concentrations were recorded during the periods of lowest salinity *(Figure 6, 7)*. Significant positive relationship (n = 90) was found between salinity and pH ($P > 0.01$, $r^2 = 0.51$) during October, whereas it was low during March ($r^2 = 0.40$). Nitrate and phosphate showed insignificant and inverse correlation with salinity ($r^2 =$ 0.03, 02) during March and October ($r^2 = 0.08$, 02) respectively. Because of the extraneous input of ammonium compounds, the N/P ratio was high during March (60) as compared to October (< 20).

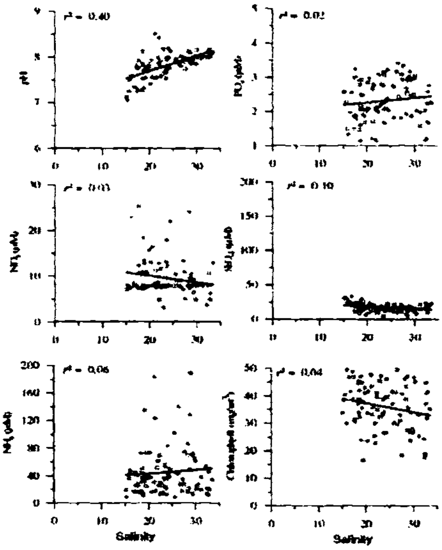

Figure 6. Scatter plots showing the linear correlation between salinity and different parameters in the study region during March 2004 (n = 90).

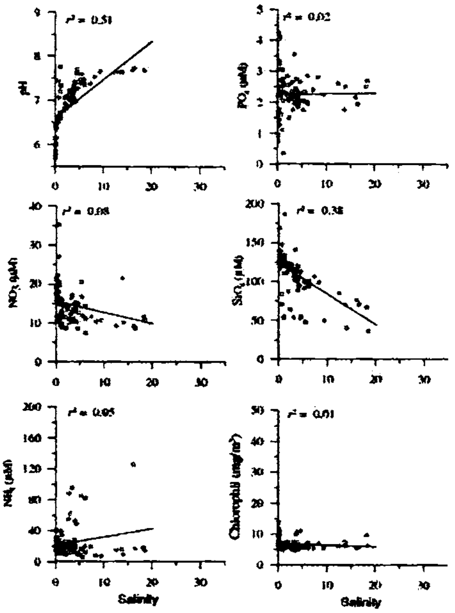

Figure 7. *Scatter plots showing linear correlation between salinity and different parameters in the study region during October 2003 (n = 90).*

Silicate was high only during October which showed negative correlation with salinity (r^2 = 0.38). The generally vide scatter observed in the distribution of nutrients against salinity could be due to their excess loading into the region. The nutrients in general, maintained higher levels during March, but ammonia was high during October. Correlation between salinity and chlorophyll *a* was also insignificant on both occasions (r^2 < 0.04) indicating that phytoplankton production in the estuary is not limited by these nutrients during all seasons.

Discussion

It is evident that high saline waters in the Cochin backwaters during March are supporting enhanced organic production. The river discharge is considerably reduced (2 %) during this period, whereas during October, the region receives approximately 12 % of the annual discharge [10]. During October, high P loading was observed from upstream. But pre monsoon season promoted an increased re-suspension in the water column, which released the adsorbed P at higher salinities in the lower estuary [7, 9]. As a consequence, N/P ratio, which was > 80 during October, was lowered to < 30 during pre monsoon season. From the sediment trap experiments conducted during the same periods, it was observed that removal of P on to suspended matter during high river flow periods and their subsequent release to water column during lean river flow periods under high saline conditions are the characteristics of the phosphorus dynamics in the Cochin backwaters. The N/P ratio during post monsoon season was close to the

Redfield ratio (16:1), mainly caused by a proportional increase in the phosphate input. With a considerable reduction in the fresh water flow from October to March and without much change in the nutrient input, the system was seen to transform into vertically mixed and eutrophic [6]. The enhancement of nutrients favoured high primary production owing to the prevalent solar insolation and sluggish movement of the estuarine waters [3].

Conclusion

The present dataset documents that anthropogenic activities are increasing nutrient loads to the backwaters in regions of escalated population growth, leading to many associated changes in environmental quality. This implies that changes in the hydrology induced by monsoon play an important role in regulating the nutrients, secondary production and even the migrant fauna of the estuary. The elevated inorganic and likely organic nutrient loadings are moving into and changing the pelagic food web. The significant variation in nutrients and their stoichiometric ratio; especially during post monsoon season is definitely a cause of concern regarding the health of the estuary. Trend analysis has shown that continuous release of nutrients and other pollutants into this estuary has not only inhibited the survival of higher predators including fishes, but also supported the proliferation of pollution tolerant species [2].

The hydrodynamically complex nature of the backwater system with increased renewal times as well as pollutant trapping efficiency, makes Cochin backwaters a delicately poised sensitive ecosystem. The region is undergoing an explosive development including an exclusive economic zone, container terminal, LNG terminal, single buoy mooring platform, international transshipment base, marina to attract tourists etc. In view of the alarming rate at which the population in this region is growing (0.6×10^6 in 1975 to 3×10^6 in 2002 and an expected 5×10^6 by 2025), there should be proper environmental conservation plans to minimize the excessive pollution, keeping pace with developmental impacts that are inevitable [2]. The most important control measures that should be prioritized are the indiscriminate reclamation of this wetland leading to its reduced flushing quality and, discharge of pre-treated industrial and domestic sewage causing eutrophication in water and contamination in sediments. The sampling program described here is to be continued to provide a useful field test of the functional relationships between nutrient loading, productivity and composition of pelagic ecosystem.

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Step-up multiple regression model to compute Chlorophyll *a* in the coastal waters off Cochin, southwest coast of India

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Abstract The interaction effects of abiotic processes in the production of phytoplankton in a coastal marine region off Cochin are evaluated using multiple regression models. The study shows that chlorophyll production is not limited by nutrients, but their physiological regulations (responses to nutrients, pH, temperature and salinity) are mainly responsible for the increased biological production. The model explaining 77% of variability for chlorophyll *a* production is indicative of preconditioning of the coastal waters. The phytoplankton production is found to be sensitive to the environment, which varies seasonally. Further, the study suggests that supply of organic matter and grazing of zooplankton (not included) would improve the model efficiency. Despite this, the good agreement in the computed and measured chlorophyll *a* values shows that step-up multiple regression model is a useful tool to understand the influence of environmental variables on the production of phytoplankton in these coastal waters.

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Keywords Multiple regression analysis · Chlorophyll *a* · Phytoplankton · Nutrient interactions · Cochin backwaters · Southwest coast of India

Introduction

The availability of nutrients in the euphotic zone and its subsequent biochemical response is the basis of any biological properties of marine systems. It is recognized that the water quality plays an important role in selecting the size of the phytoplankton community (Malone 1980; Platt et al. 1983; Chavez 1989; Legendre and Le-Fevre 1989). Biomass of phytoplankton in terms of chlorophyll *a* concentration, is one of the most widely accepted methods in the study of biological production as it indicates total plant material available in the water at primary level of food chain (Weyhenmeyer et al. 1999). The spatial and temporal gradients in environmental parameters offered by the coastal waters off Cochin make it suitable for examining the relationship between physico-chemical parameters and phytoplankton, which forms the main objective of the present study. The coastal region of Cochin (~2,500 km^2) is studied for changing seasons to derive the salient features that characterize its biological productivity. The study aims to understand the (a) controlling and interactive factors of phytoplankton production and (b) interrelationship between nutrient and chlorophyll *a* in the coastal waters off Cochin with respect to seasonal periodicity. In order to achieve this, multivariate statistical approach is adopted. Chlorophyll *a* can be related to the environmental parameters by means of linear regressions, though it provides only the prediction efficiency of a single factor at a time. The inclusion of interaction effects excites the study as in the formulation of an ecological model: a number of factors jointly controlling the bioactivities are to be considered. The first order interaction effects between parameters are highly critical since in biological activities, competition between abiotic species (difficult to measure) can be replaced by interaction between nutrient factors.

Environmental setting of the study region

Cochin is the second largest city along the west coast of India situated at the tip of one of the largest wetlands of the country (Vembanad Lake). The lake was formed in the fourteenth century A.D. following a catastrophic deluge modifying the drainage area of the six rivers to the present state, retaining its pristine glory for rich biodiversity till the later part of 19th century (Gopalan et al. 1988). There has been a growing deterioration in the environmental condition of this lake since 1970s, particularly towards the lower reaches of the lake known as Cochin backwaters, due to increased human settlements and industrialization (Balachandran 2001; Balachandran et al. 2005). The coastal waters of this region are hence, significant in two ways, as the recipient of approximately 1.9×10^{10} m^3 of fresh water annually from the Cochin backwaters (Srinivas 2000) and as the unique region occupying the well-known *mud banks*, which are store houses of primary nutrients, attracting immense fishery during southwest monsoon (Varma and Kurup 1969; Sylas 1984; Mathew et al. 1995; Balachandran 2004).

Materials and methods

The present study is based on the environmental properties of coastal waters of Cochin, surveyed during three critical seasons viz; October (fall inter monsoon), November (winter monsoon) and February (late winter monsoon) between 1997 and 2000. The locations of stations were so selected that during October, as many as 56 stations of seven transects were sampled from about 500 km^2 (between 9°51′and 10°09′N lat. 76° and 76°18′E long.) area of coastal region (Fig. 1). During October (transition period), the currents reverse their direction from south to north and the presence of upwelling combined with fresh water discharge from the backwaters cause stratification in the coastal waters. As the stratification is not felt once the monsoon withdraws, study area has been extended to the southern region, stretching to about 2,500 km^2 area during February and November (between 9°12′ and 10°12′N lat. 76° and 76°24′E long.) and 45 stations of nine transects. The duration of survey was five stations per day, thus consuming about 9–10 days to cover the entire region.

Sampling and analytical procedures

For the hydrographic survey, water samples were collected from surface, mid and near-bottom using a 5-l Niskin sampler (Hydrobios-Kiel). Temperature and pH were recorded in situ and samples for dissolved oxygen were collected separately. Water samples for the analysis of salinity and nutrients were collected in pre-cleaned polythene bottles and kept in iceboxes till analysis at the shore laboratory, within hours of collection. For chlorophyll *a* analysis, samples filtered through Whatman GF/F filters were extracted with cold 90% acetone and estimated spectrophotometrically (UNESCO 1966). The nutrients (nitrite, nitrate, phosphate, ammonia and silicate) were analyzed immediately after filtering through Whatman no.1 filter papers, following standard procedure (Grasshoff et al. 1983) using a double beam spectrophotometer (Hitachi U-2000) after proper calibration.

Statistical analysis using step-up multiple regression model

Method of choosing the minimal set of environmental variables that can explain the variation in the affected parameter (Pedersen et al. 1995). and the Monte Carlo permutation test that replaces the *F* test or the test in forward selection in univariate multiple regressions were adopted earlier (Ter Braak 1990). It has been stated that modeling the dependent variable on the individual effects of the environmental parameters alone would become an artifact on the production relation (Evonne et al. 1995). A modern approach to

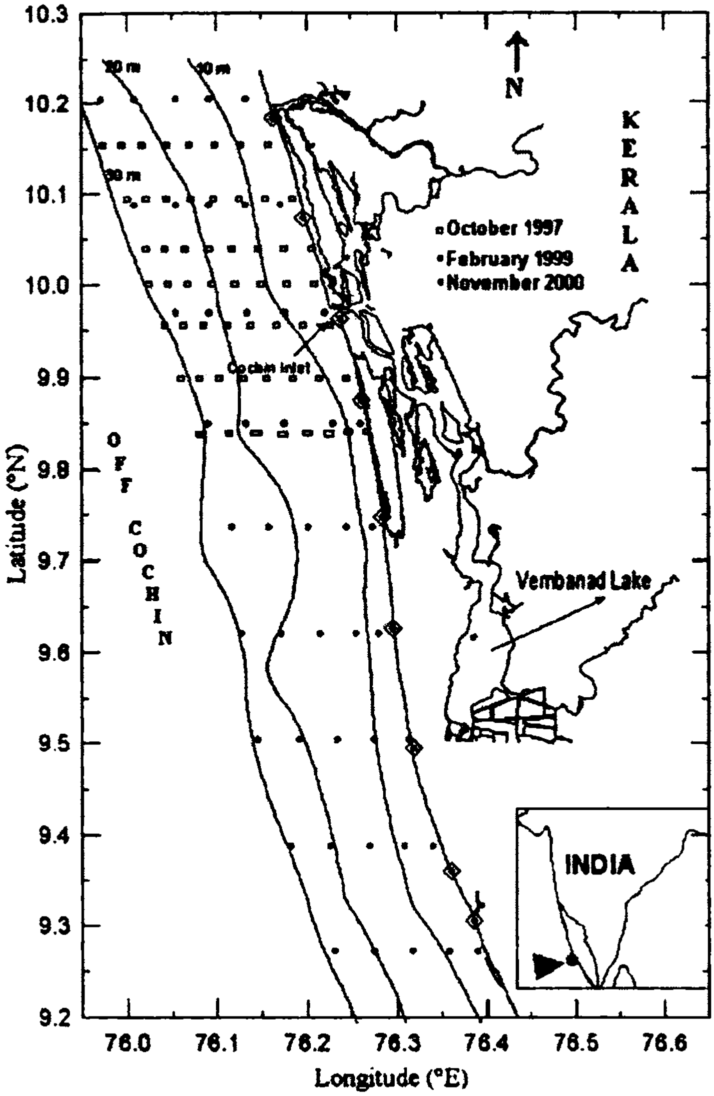

Fig. 1 Study area showing station locations in Arabian Sea

explore the possible influence of various environmental variables on phytoplankton dynamics is the application of a multivariate statistical analysis (Lau and Lane 2002). These methods are widely used in ecological studies and have proved to be useful for understanding interactions between ecological factors that influence phytoplankton production. Here, an attempt is made to include the individual factors and first order interaction effects of the environmental parameters viz: temperature, salinity, dissolved oxygen, nitrite, nitrate, ammonia, phosphate, silicate and pH to relate chlorophyll *a* concentration in the predictive model. A step-up multiple regression analysis is applied using phytoplankton (chl. *a*) as the dependent variable and direct and first order interaction effects of the above listed environmental parameters as the independent variables, to examine the controlling role of any particular parameter or group of parameters on phytoplankton biomass. The multiple regression model fitted is of the form

$$Y = a_0 + \sum_{i=1}^{k} a_i X_i + \sum_{i=1}^{k}\sum_{j=1}^{k} (X_i \times X_j) bij \qquad (1)$$

Where a_i and b_{ij}, $i, j = 1, 2, \ldots\ldots\ldots k$, $i<j$ are the regression coefficients. Independent variables as well as dependent variables are standardized using the transformation,

$$Z_i = (X_i - \mu_i)/\sigma_i \qquad (2a)$$

$$Z = (Y - \mu)/\sigma \quad \text{for dependent variable} \qquad (2b)$$

where μ_i (μ)=arithmetic mean (mean of X_i [Y]) and σ_i (σ) is the standard deviation of X_i (Y). The regression coefficients are called standard partial regression coefficients or the relative importance of the independent parameters. The model has been fitted by least square method considering the parameters and also their interaction effects of first order as the independent variables. The significance of the regression coefficients are tested using the Students' *t* statistic

$$t_i = d_i \big/ S_{ei} \ \ and \ \ t_{ij} = b'_{ij} \big/ S_{eij} \qquad (3)$$

where a'_i is the estimated value of the *i*th regression coefficient and b'_{ij} is the estimated value of the *ij*th interaction effect, S_{ei} and S_{eij} are the standard errors of the regression coefficients.

$$S_{ei} = S(C_{ii})^{1/2} \qquad (4)$$

where S^2 is the deviation mean square and C_{ii} is the *i*th diagonal element in the inverse of the matrix of sum of squares and products (Snedecor and Cochran 1967).

When k parameters are considered there will be $k(k-1)/2$ interaction effects and total number of parameters for the model will be $k+k(k-1)/2$, i.e.; $k(k+1)/2$ and total number of regression models fitted is (2^k-1). The regression model of Y (dependent variable) on all the parameters (individual effects only) is also determined. From these 2^k predictive models (2^k-1+1), that model with highest value for the explained variability (V.E) calculated as.

$$\mathrm{V.E} = (1 - \mathrm{MDSS/MTSS}) \times 100 \qquad (5)$$

where MDSS=mean deviation sum of squares and MTSS=mean total sum of squares. is considered.

Table 1 Best fitted model equation in terms of nine environmental variables and their significant interaction effects

Month (Eq. no.)	Best fitted model equations
October-Surface (8)	$\log \mathrm{Chl}.a = (0.36 + 0.38\mathrm{PO_4} + 0.35\mathrm{pH} \times \mathrm{DO} + 0.52\mathrm{pH} \times \mathrm{NO_3} + 0.32\mathrm{pH} \times \mathrm{SiO_4} + 0.35\mathrm{S} \times \mathrm{DO} + 0.38\mathrm{S} \times \mathrm{SiO_4} + 0.42\mathrm{DO} \times \mathrm{NO_3} + 0.51\mathrm{NO_3} \times \mathrm{SiO_4}) - (0.29\mathrm{pH} + 0.59\mathrm{S})$
October-Bottom (9)	$\log \mathrm{Chl}\ a = \{0.01 + 0.06\mathrm{DO} \times \mathrm{NO_2}\} - \{0.35\mathrm{DO} + 0.38\mathrm{NO_2}\}$
February-Surface (10)	$\mathrm{Chl}\ a = (1.22\mathrm{pH} + 0.81\mathrm{NH_4} + 1.10\mathrm{pH} \times \mathrm{NO_2} + 0.75\mathrm{pH} \times \mathrm{NH_4} + 0.20\mathrm{DO}{*}\mathrm{NO_2}) - (0.82\mathrm{S} \times \mathrm{DO} + 0.34\mathrm{S} \times \mathrm{NO_2} + 0.29\mathrm{DO} \times \mathrm{NH_4} + 0.47\mathrm{NO_2} \times \mathrm{NH_4} + 0.42)$
February-Bottom (11)	$\sqrt{\mathrm{Chl}.a} = (2.32\mathrm{T} + 6.63\mathrm{pH} + 3.01\mathrm{PO_4} + 13.45\mathrm{T} \times \mathrm{pH} + 3.90\mathrm{T} \times \mathrm{S} + 2.86\mathrm{T} \times \mathrm{DO} + 5.21\mathrm{T} \times \mathrm{PO_4} + 2.35\mathrm{T} \times \mathrm{SiO_4} + 5.86\mathrm{pH} \times \mathrm{NO_3} + 4.51\mathrm{DO} \times \mathrm{NO_3} + 2.63\mathrm{DO} \times \mathrm{PO_4} + 3.84\mathrm{NO_2} \times \mathrm{NH_4}) - (4.18\mathrm{T} \times \mathrm{NH_4} + 3.62\mathrm{NO_2} + 9.94\mathrm{pH} \times \mathrm{DO} + 3.32\mathrm{pH} \times \mathrm{NO_2} + 5.24\mathrm{pH} \times \mathrm{SiO_4} + 2.34\mathrm{DO} \times \mathrm{SiO_4} + 3.09\mathrm{NO_2} \times \mathrm{PO_4} + 0.38)$
November-Surface (12)	$\log \mathrm{Chl}.a = (0.61 + 5.09\mathrm{NO_3} + 3.90\mathrm{PO_4} + 9.23\mathrm{T} \times \mathrm{S} + 5.94\mathrm{T} \times \mathrm{DO} + 4.51\mathrm{T} \times \mathrm{NO_2} + 7.69\mathrm{T} \times \mathrm{SiO_4} + 10.63\mathrm{pH} \times \mathrm{DO} + 6.03\mathrm{pH} \times \mathrm{NH_4} + 8.22\mathrm{S} \times \mathrm{DO} + 6.65\mathrm{S} \times \mathrm{NO_2} + 11.55\mathrm{S} \times \mathrm{NO_3} + 6.15\mathrm{DO} \times \mathrm{PO_4} + 6.85\mathrm{DO} \times \mathrm{PO_4} + 8.85\mathrm{NO_2} \times \mathrm{NH_4} + 5.10\mathrm{NO_2} \times \mathrm{PO_4} + 4.75\mathrm{NO_3} \times \mathrm{NH_4}) - (7.43\mathrm{T} + 5.86\mathrm{pH} + 9.61\mathrm{NO_2} + 3.70\mathrm{SiO_4} + 17.25\mathrm{T} \times \mathrm{pH} + 4.56\mathrm{pH} \times \mathrm{NO_3} + 8.57\mathrm{pH} \times \mathrm{SiO_4} + 6.02\mathrm{S} \times \mathrm{NH_4} + 8.8\mathrm{S}'\mathrm{SiO_4} + 1.98\mathrm{DO} \times \mathrm{NO_3} + 7.26\mathrm{NO_2} \times \mathrm{SiO_4} + 4.36\mathrm{NO_3} \times \mathrm{SiO_4})$
November-Bottom (13)	$\sqrt{\mathrm{Chl}.a} = (0.75\mathrm{pH} + 0.72\mathrm{NO_3} + 0.70\mathrm{T} \times \mathrm{NH_4} + 0.82\mathrm{pH} \times \mathrm{S} + 0.51\mathrm{pH} \times \mathrm{DO} + 0.71\mathrm{S} \times \mathrm{DO} + 0.83\mathrm{S} \times \mathrm{NO_3} + 0.74\mathrm{DO} \times \mathrm{NO_2} + 0.58\mathrm{DO} \times \mathrm{NO_3} + 0.96\mathrm{DO} \times \mathrm{NH_4} + 0.62\mathrm{NO_3} \times \mathrm{PO_4} + 0.60\mathrm{pH} \times \mathrm{NH_4}) - (1.33\mathrm{T} \times \mathrm{PO_4} + 0.72\mathrm{pH} \times \mathrm{PO_4} + 0.65\mathrm{S} \times \mathrm{NO_2} + 0.85\mathrm{DO} \times \mathrm{PO_4} + 0.88\mathrm{NO_2} \times \mathrm{NO_3} + 4.76)$

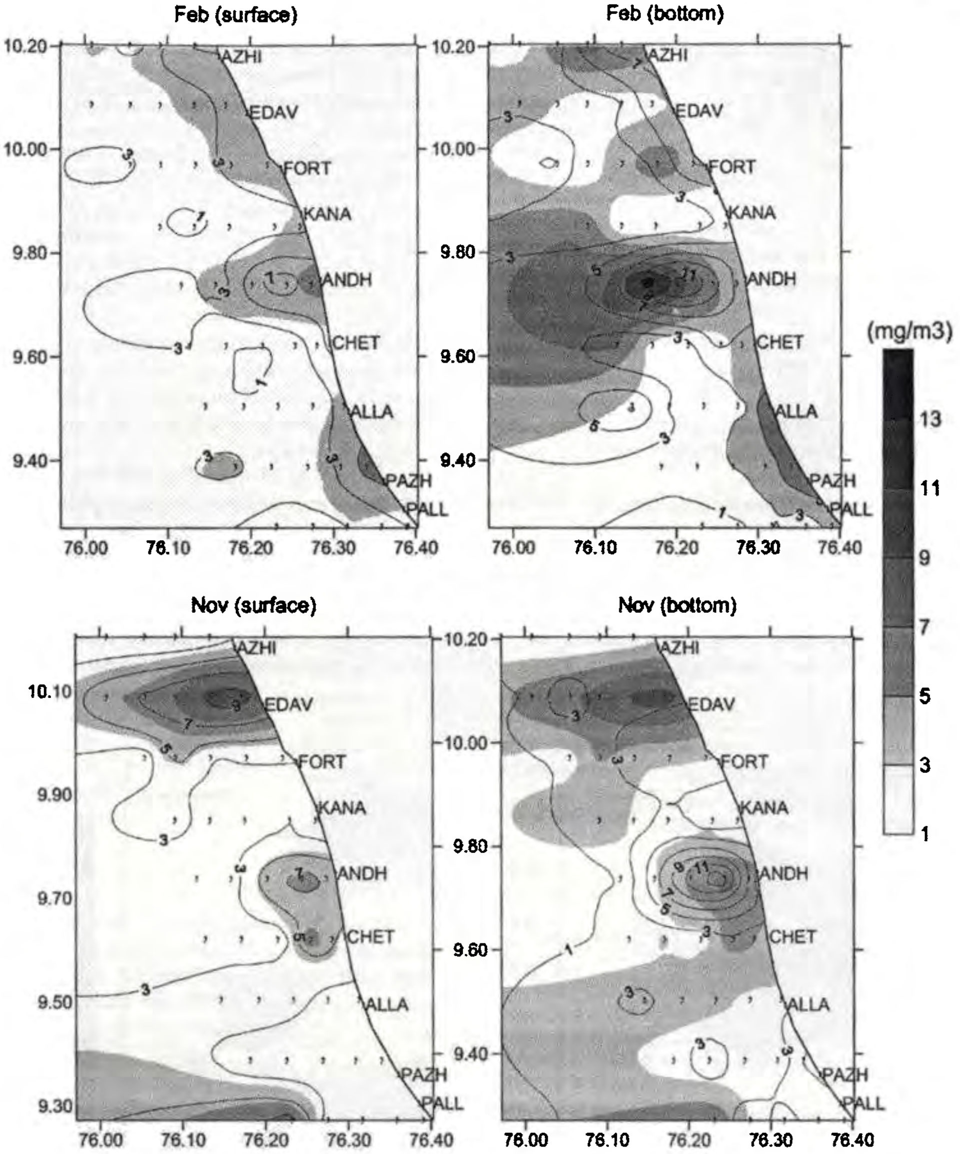

Fig. 2 Chlorophyll *a* (mg/m^3) distribution for February and November (observed value as *contour line* and predicted value as *filled contours*), based on Eqs. 10 and 11 (February) and Eqs. 12 and 13 (November) in Table 1, respectively

Further, the above analysis is repeated with different transformations for Y and X_i^s as

Y on X_i^s log Y on X_i^s log Y on log X_i^s

$\sqrt{Y}$ on X_i^s $\sqrt{Y}$ on $\sqrt{X_i^s}$ Y on $\sqrt{X_i^s}$

Thus, a variety of $2^9 \times 6 = 3{,}072$ models are altogether fitted to choose the best predictive model for each case. Among these that model which explains the maximum variability is considered as the best predictive multiple regression model where the insignificant regression coefficients (parameters) get deleted based on the t statistic.

Results: the step-up multiple regression model

The predicted chlorophyll a values based on Eqs. 10 to 13 (Table 1), respectively are superimposed as filled contours for respective layers in Fig. 2, along with the observed chlorophyll a (lines). Surface chlorophyll concentration for February (S) showed much deviation, as it explained only 37% variability. Generally, there is good agreement between the observed and predicted values especially during February (B) and November (S and B), with the explained variability of 69.21, 77 and 77.42%, respectively.

A predictive phytoplankton model for these coastal waters for all seasons emerged insignificant, as the combined analysis of environmental data for the three seasons ($n=300$) gave only 13% explained variability ($F_{15,284}=2.89$, $P<0.05$). The main reason for this may be due to the seasonal variability, where the west coast of India experiences upwelling during June to October (Naqvi et al. 2000). A generalization for the non-monsoon months (February and November, $n=188$) also could explain only 19% of the variability, possibly indicating that the nutrient availability and their interactions are very sensitive.

Alternatively, pooling all the surface and bottom water quality during each period evolved an empirical model given by Eqs. 6 and 7 (Fig. 3), predicting the observed chlorophyll a values during both November (VE=31.27%, $r=0.49$) and February (VE=30.95%, $r=0.48$). The relation for February (Eq. 6) is based on standardized values of square root transformed values of chlorophyll a on standardized values of square root

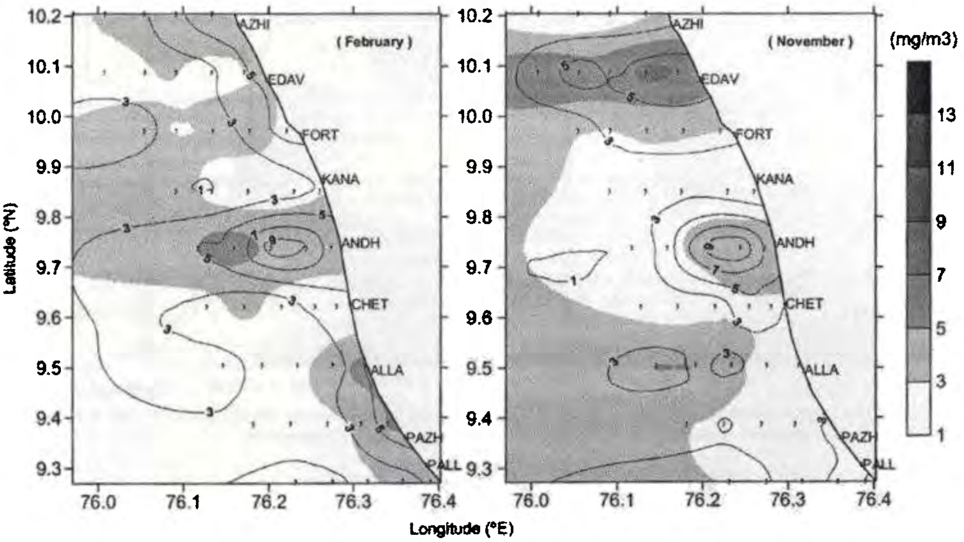

Fig. 3 Chlorophyll a distribution (average of surface and bottom) of observed (*line*) and predicted (*shaded*) value during February and November (mg/m3). Predicted values are based on Eqs. 6 and 7, respectively

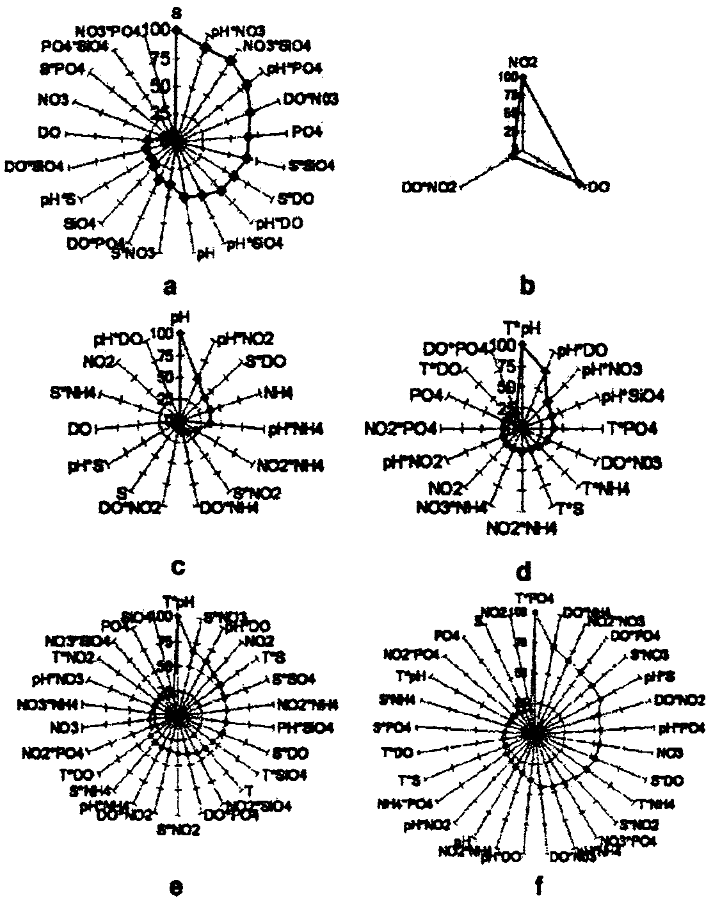

Fig. 4 Relative importance (>20%) of the model parameters predicting chlorophyll a during October **a** surface (variability explained, VE=49%), **b** bottom (VE=22%), February **c** surface (VE=37%), **d** bottom (69%) and November **e** surface (VE=77%), **f** bottom (VE=77.4%)

transformed values of parameters ($F_{28,65}=2.51$, $P<0.05$, $n=94$) and for November (Eq. 7) based on standardized values of log-transformed values of chlorophyll *a* on standardized values of log-transformed values of parameters ($F_{21,72}=2.98$, $P<0.05$, $n=94$).

$$\begin{aligned}\mathrm{Chl}.a &= \left\{\begin{array}{l}0.66\mathrm{pH}+0.46\mathrm{NO_2}+0.21\mathrm{NO_3}+\\ 0.24S\times\mathrm{NH_4}+0.29\mathrm{PO_4}+0.61\mathrm{pH}\times\\ \mathrm{S}+0.83\mathrm{pH}\times\mathrm{DO}+0.60\mathrm{pH}\times\mathrm{NO_2}+\\ 0.36\mathrm{pH}\times\mathrm{NO_3}+0.11\mathrm{NO_3}\times\mathrm{NH_4}\end{array}\right\}\\ &-\left\{\begin{array}{l}1.36\mathrm{pH}\times\mathrm{NH_4}+0.39\mathrm{pH}\times\mathrm{PO_4}+\\ 0.45\mathrm{S}\times\mathrm{DO}+0.28S\times\mathrm{NO_2}+0.22\mathrm{S}\times\\ \mathrm{NO_3}+0.19\mathrm{DO}\times\mathrm{NO_2}+0.49\mathrm{DO}\times\\ \mathrm{NO_3}+0.47\mathrm{S}+0.23\mathrm{DO}+0.28\end{array}\right\}\end{aligned} \tag{6}$$

$$\begin{aligned}\mathrm{Chl}\ a &= \left\{\begin{array}{l}0.09+0.23\mathrm{NH_4}+0.24\mathrm{T}\times\mathrm{pH}+0.12\mathrm{T}\times\\ \mathrm{NH_4}+0.36\mathrm{pH}\times\mathrm{SiO_4}+0.15\mathrm{PO_4}\times\mathrm{SiO_4}\end{array}\right\}\\ &-\left\{\begin{array}{l}0.36\mathrm{NO_3}\times\mathrm{PO_4}+0.14\mathrm{T}+0.18\mathrm{pH}+\\ 0.32\mathrm{NO_3}+0.56\mathrm{SiO_4}+14\mathrm{pH}\times\mathrm{NO_3}\end{array}\right\}\end{aligned} \tag{7}$$

It is to be noted that both Figs. 2 and 3 show a regional shift in the distribution of peaks in the predicted and measured chlorophyll values. The mismatch is attributed to the inconsistency in measuring the real impact of nutrient-chlorophyll transformation, since the life cycle of phytoplankton is only a few days (Reynolds 1984). Lohrenz et al. (1990) have observed that the transit time for the entrainment of fresh nutrient-rich water to the salinity range where biomass and productivity peak is very short relative to the nutrient uptake. It has been argued that even time-series data, collected through monitoring programs, inherently have characteristics that violate basic assumptions of parametric procedures (Momen et al. 1996). Our sampling scheme was such that; each survey was spanning about 9–10 days (five stations in 1 day). However, the step-up multiple regression analysis is reliable to detect both abrupt and gradual patterns (Ludwig and Reynolds 1988). The low variability explained also cautions that apart from seasonal changes, vertical gradients are to be considered for attaining perfection in coastal ecosystem modeling.

Discussion

Control of abiotic processes

The multiple regression analysis using Eq. 1 generally shows the significant influence of environmental (abiotic) variables and their interactions on the production of chlorophyll *a*. In order to explain this, the model results are furnished based on their relative importance (>20%) to chlorophyll during different seasons (Fig. 4). It can be seen that in the distribution of chlorophyll *a*, the direct effect of each environmental variable is insignificant, but their interaction effects (×) are more important. The overall results showing more number of variables during November and February, is an indication of their increased activity. The interaction of PO_4 with NO_3 determines the inter-specific competition at different nutrient concentrations, because their intakes are species specific (Kautsky 1981). The absence of this interaction during the present study indicates that the chlorophyll production in these coastal waters is not controlled by nutrients. Temperature is obtained as an important factor during February and November (Fig. 4d,e,f), suggesting an optimal metabolic activity of warm waters (Fisher and Gray 1983). This also underlines the fact that primary productivity is a function of solar irradiance (Platt 1986). The unexplained variability of <25% during November suggests that the physiological variability (responses to nutrients, temperature and salinity) has primary control while photoperiod has a secondary control on phytoplankton production (Cole and Cloern 1987). In some cases, as inferred in Tables 1 and 2, limiting factors are found to be more important than controlling factors. Thus, salinity during fall intermonsoon (October) was a dominant factor limiting the production of phytoplankton, as evident from the increased estuarine input freshening the surface layers to <25 psu (Balachandran 2001). During the same period, persistent upwelling in the sub-surface layers was characterized by oxygen-deficient (<1.4 ml/l) and nitrite-replete (>1.2 µM) waters. These features possibly infer the

Table 2 Variance explained (VE%) and relative importance of the first 10 model parameters on Chlorophyll *a* based on Eqs. 2a and 2b

Month	Relative importance (controlling/limiting parameters)	*F* ratio	VE (%)[a]	VE (%)[b]
October (surface)	$S>pH\times NO_3\times>NO_3\times SiO_4>DO\times NO_3>PO_4>S\times SiO_4>S\times DO>pH\times DO>pH\times SiO_4>\mathbf{pH}$	$F_{21,34}=3.49$; $P\leq 0.05$	28.52	48.69
October (bottom)	$\mathbf{NO_2>DO}>DO\times NO_2$	$F_{3,52}=5.59$; $P\leq 0.05$	17.54	20.00
February (surface)	$pH>pH\times NO_2>\mathbf{S\times DO}>NH_4>pH\times NH_4>\mathbf{NO_2\times NH_4>S\times NO_2}>\mathbf{DO\times NH_4}>DO\times NO_2>S$	$F_{15,31}=2.81$; $P\leq 0.05$	12.63	37.11
February (bottom)	$T\times pH>\mathbf{pH\times DO}>pH>pH\times NO_3>\mathbf{pH\times SiO_4}>T\times PO_4>DO\times NO_3>\mathbf{T\times NH_4}>T\times S>NO_2\times NH_4$	$F_{45,1}=3.30$; $P\leq 0.05$	31.24	69.21
November (surface)	$\mathbf{T\times pH}>S\times NO_3>pH\times DO>NO_2>T\times S>\mathbf{S\times SiO_4}>NO_2\times NH_4>\mathbf{pH\times SiO_4}>S\times DO>T\times SiO_4$	$F_{45,1}=4.42$; $P\leq 0.05$	9.66	77.00
November (bottom)	$\mathbf{T\times PO_4}>DO\times NH_4>\mathbf{NO_2\times NO_3}>\mathbf{DO\times PO_4}>pH\times S>pH>DO\times NO_2>\mathbf{pH\times PO_4}>NO_3>S\times DO$	$F_{36,10}=5.38$; $P\leq 0.05$	14.89	77.42

Limiting parameters are typed in bold.

[a] For only the nine environmental parameters

[b] For the nine environmental parameters and their interaction effects

limiting conditions for DO and NO_2 in the bottom waters (Table 1). Since ($NO_2 \times NO_3$) interaction is obtained as one of the limiting factors during November (Fig. 4f), it follows that the growth of phytoplankton is often controlled to a certain extent, by the supply of ammonium excreted by zooplankton and members of higher trophic levels (Kiefer and Atkinson 1984). Since nitrogen compounds and DO are obtained as important factors (Fig. 4), it means that they are also brought into the medium by decomposition of particulate organic carbon (Robinson et al. 1982). The controlling effects of pH and the interaction effects of pH with NH_4^+, NO_2, DO, T and NO_3 are also found to be vital factors in primary production. In the present study, pH and salinity are found to be dominant interaction factors (Table 2; Fig. 4f), a feature not found in the Arabian Sea (Jayalakshmy 1998). This can be attributed with the greater land–sea interaction and also due to the fact that the biological production induced by chemical changes in coastal zones far exceed that of the oceanic region.

It is worth mentioning here that while this predictive model for the Arabian Sea (Jayalakshmy 1998) could explain only less than half the variability in primary production (for 21 parameters and excluding pH), the same analysis in the present study during non-monsoon period could explain more than 70% of the variability (Fig. 2). Higher variability explained implies a more stable environment. This indicates that, in spite of strong seasonality, these coastal waters are pre-conditioned for the primary production during most of the time as compared to oceanic region.

Conclusions

The study shows that in the distribution of chlorophyll *a*, the interaction effects of different environmental parameters are more important than their individual effects. The more number of interactive variables is an indication of increased biochemical activity during non-monsoon periods. Even though chlorophyll production is not limited by nutrients, their physiological regulations (responses to nutrients, pH, temperature and salinity) are the most important factors responsible for the increased biological production of these coastal waters.

Considering the uncertainties in computing forcing functions on biological parameters, the agreement shown by the model indicates that the step-up multiple regression analysis is a useful tool to compute chlorophyll *a* biomass using environmental variables. The seasonality in the trophic inter-relationships cautions the inclusion of biotic components to address the complex phytoplankton community structure. The variability can be further improved by including biotic factors like growth, grazing, mortality and mineralization of bacteria, phytoplankton and zooplankton. A precise prediction of ecological processes necessitates the need of continuous monitoring data on a long-term basis.

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Nutrient environment of red tide- infested waters off south-west coast of India

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Abstract The bloom-infested waters along the south-west coast of India were assessed to bring about the probable cause related to the excessive algal production. Low nitrate and silicate concentrations were concomitant with slightly higher levels of phosphate. The silicate depletion in the bloom area is possibly an indication of community succession (diatom to dinoflagellate), since it was completely utilized by the preceding diatom blooms. The dinoflagellates in this region could have been advected from the northern regions where it was noticed during the previous months.

Keywords Red tide · Nutrient characteristics · South west coast of India · Arabians Sea

Introduction

Red tides, a natural phenomenon, are now common in many coastal waters. Various factors contribute to red tide formation such as insolation, wind, rain, salinity and nutrient input from land or by upwelling. Nitrogen and phosphorus are involved in phytoplankton proliferation, which, in excess lead to the occurrence of red tides. It has been suggested that natural succession and biological competition are the major factors regulating harmful algal bloom outbreaks. Silicon supply is another factor regulating bloom occurrence, but unfortunately, there has been little research in this area. The Red Tide phenomenon noticed off Kollam (lat. 8°56′N, long. 76°57′E) and Vizhinjam (lat. 8°22′N, long. 76°57′E) along the south west coast of India in September 2005 had created panic, as people living in the coastal belt of Kerala, started vomiting and were feeling nausea following a mysterious foul smell from the sea (Ramaiah et al. 2005). The affected area within almost 6 km radius, consist of many fishing hamlets. A report made in this regard revealed that there were no toxic elements or other pollutants in the sea apparently due to discharge of effluents from factories or land drainage, but the existence of holococcolithophore bloom along this coast during this period was noticeable (Ramaiah et al. 2005)

According to UNEP, 'toxic algae bloom is an indicator of an upset in the environmental conditions. Toxic blooms indicate the declining health of the water body, which is why the phenomenon should be viewed seriously. Inflowing water from rivers and atmospheric fall out transport nutrients and trace elements, which are especially beneficial for plant life in the illuminated surface layers of sea. It has

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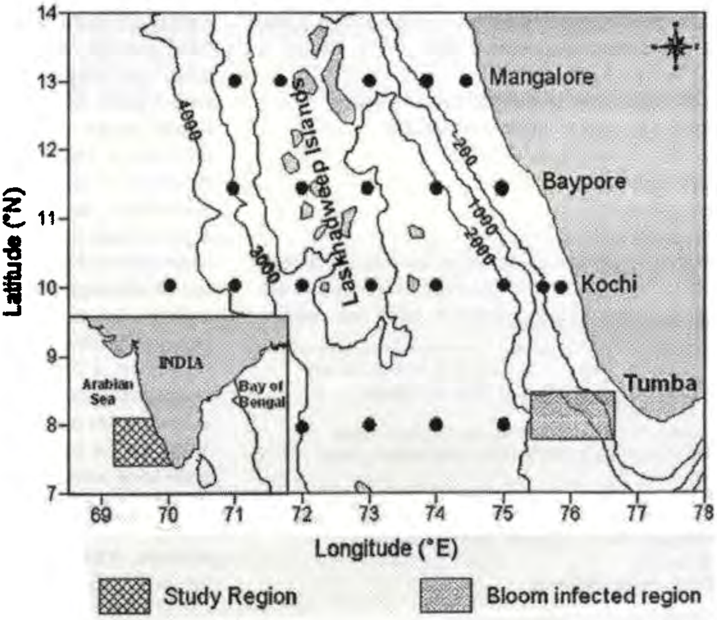
been suggested that vertical migratory behavior is shown by some flagellates to form red tide by absorption of nutrients near the bottom and effective utilization of light energy near the surface (Eppley et al. 1968; Heaney and Eppley 1981). Since systematic investigations are fundamental in understanding the consequences of this event, an attempt has been made to evaluate nutrient content of the red tide -infested waters off Thumba (Lat. 8°34'N, Long. 76°49'E; Fig. 1). It was first observed during an earlier study (FORV Sagar Sampada) after 2 weeks of which, this study was undertaken. We analyze the environmental data and look for a link between dinoflagellte blooms and nutrients during red tide outbreaks in this region.

Materials and methods

A research cruise on board FORV Sagar Sampada through the Arabian Sea (Fig. 1) during September-October, 2004 provided an opportunity to investigate the nutrient environment associated with a brilliant and exhaustive display of surface water discolouration (Fig. 2). The notable features were the extreme calmness of the sea, a clear sky and a strong sunshine. *Noctiluca miliaris* was first reported as the causative species of the red tide occurrence off Thumba (lat. 8°34'N. long. 76°49'E), on 29th September 2004 (Sahayak et al. 2005). A red tide bloom was earlier reported from the coastal areas of Kollam and Vizhinjam on September 17, 2004. Recent reports available on *Noctiluca* blooms in the Indian subcontinent area include (Katti et al. 1988; Nayak and Karunasagar 2000) on the west coast and Dharani et al. (2004) on the east coast.

We examined the bloom region as well as other stations for many relevant hydrographical and biological parameters. Seawater samples were collected from standard depths using CTD rosette sampler fitted with 1.8 l Niskin bottles. Measurements were made for Sea surface temperature, salinity, pH, dissolved oxygen and nutrients (nitrite, nitrate, phosphate and silicate). The sea surface temperature was measured using bucket thermometer and salinity was measured using an Autosal. Dissolved oxygen was analyzed by Winkler's method and nutrients by the segmented flow Auto Analyzer (SKALAR) on board using standard procedures (Grasshoff et al. 1983). Chlorophyll *a* measurements were carried out from two stations in each transect representing coastal and

Fig. 1 Base map showing station location along the west coast of India. Bathymetric depth are given in meters



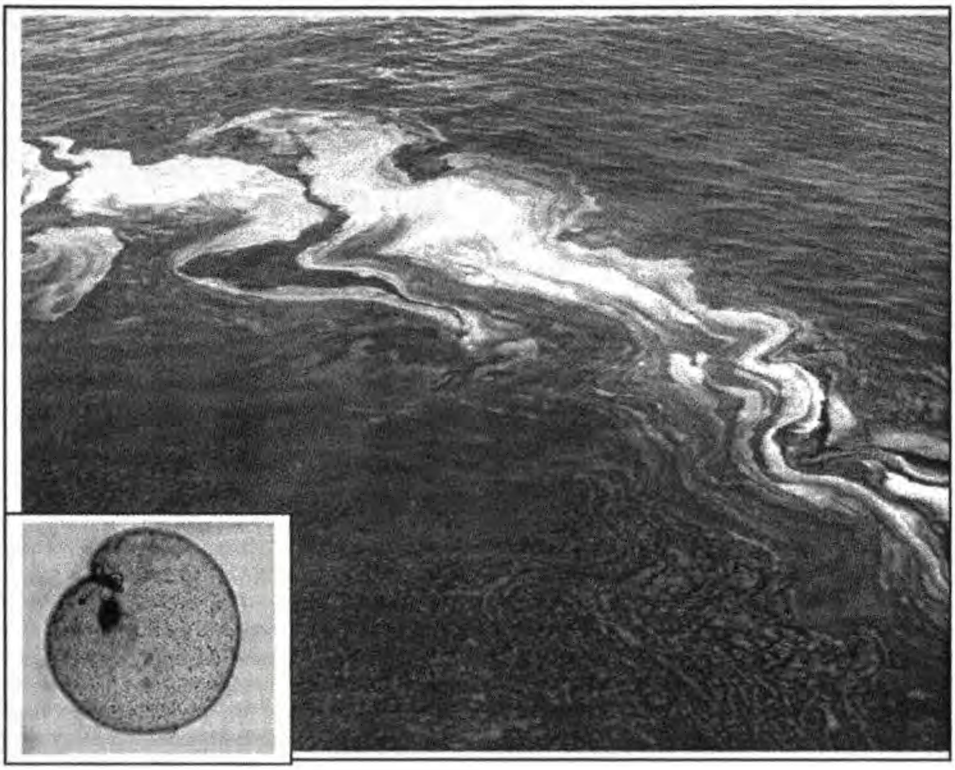


Fig. 2 Bloom of *Noctiluca milaris* and its photomicrograph (insite) observed at the bloom infected area

oceanic regions respectively. One litre of water sample from each depth was filtered through GF/F filters (pore size 0.7 μm) for measuring Chl 'a'. Chl a estimation was carried out using a spectrophotometer (UV-1650PC Shimadzu), after extracting with 10 ml 90% acetone in the dark (Strickland and Parsons 1972).The concentrations of various parameters at surface and 10m depths have been taken into account for the present study.

Results and discussion

The distribution of environmental parameters during the period is presented (Figs. 3 and 4). The sea surface temperature (27.8°C) and the air temperature (28.5°C) recorded at bloom-infested station were slightly warmer as compared to the other stations of the same latitude. The salinity values remained unaltered with other stations of the same latitude. The dissolved oxygen levels were 211 μM at the surface and 210 μM at 10 m depths, quite comparable with the levels generally found in the Arabian Sea. The low concentrations of silicate-Si (1.07 μM at surface and 1.17 μM at 10 m depth) in the bloom-infested waters are noticeable (Figs. 3 and 4). The nitrate concentrations were also low as compared to the other stations along the transect, which is indicative of the utilization of this nutrient element for the establishment of the bloom. Nitrate, a limiting nutrient to phytoplankton production in many oceanic environments, can enter the euphotic zone directly through rainfall (Willey and Paerl 1993). The availability of different forms of nitrogen and their relative rates of utilization are important factors contributing to the phytoplankton blooms (Dharani et al. 2004).

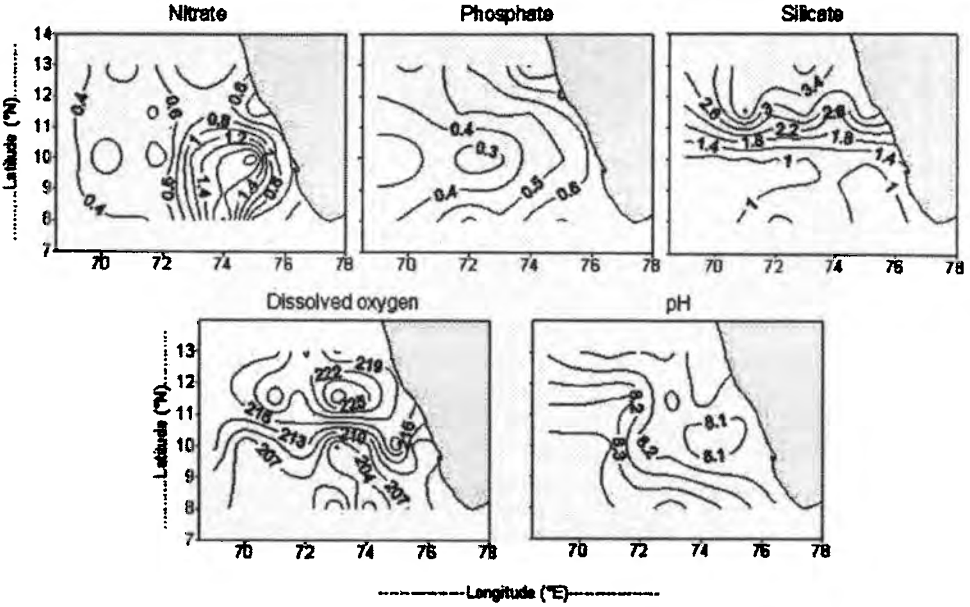


Fig. 3 Surface distribution of nitrate, phosphate, silicate, dissolved oxygen (all in μm M) and pH along the study region

There was a slight increase in the dissolved phosphate levels as compared to other stations of the same latitude. The trends in nitrate and phosphate were almost similar to the observations made at Port Blair region (Dharani et al. 2004). The temperature, salinity, dissolved oxygen and pH did not change drastically and were typical of the upper few meters of tropical oceanic water. But silicate-Si followed an opposite trend with strikingly low concentration differentiating this study area from that off Port Blair where high levels of silicate was observed during the peak bloom. The causative species for the red tide at Port Blair was found to be *Noctiluca scintillans* (Dharani et al. 2004). Diatoms and dinoflagellates are the two groups of the phytoplankton, and with an increase in the density of diatoms there was a decline in the dinoflagellates and vice versa. Recent findings indicate that even the competition between diatoms and dinoflagellates shouldn't be overlooked. Silicon comprising around 5% dry weight of diatoms, is an essential element for diatom growth (Werner 1977) and hence, silicate must have played a significant role in determining the dominant species and the magnitude of red tide along this region. The silicate-Si concentration was very low in this region, indicating that *dinoflagellate* growth must have been promoted by the exhaustion of silicate supply and the resultant reduction of diatoms.

The earlier study made on board FORV Sagar Sampada during last week of July along the coastal areas of Kollam (lat. 8°56'N, long.76°34'E) Vizhinjam (lat. 8° 56'N, long. 76°57'E) reported high levels of nutrients and Chl a (Cruise report, FORV SS. No.227). The record on species of *dinoflagellates* causing the red tide at places along the south west coast for a few weeks must be the different succession stages of the phytoplankton and *dinoflagellates*. The region had experienced heavy rains during this period and the high river discharge enriched the waters with nutrients, primarily as nitrates. Dinoflagelltes are some of the most adaptable organisms in these conditions, because they can perform photosynthesis even under adverse conditions.

The Chl-a in the surface waters between Vizhinjam and Purakkad indicated bloom conditions Sahayak et al. (2005). The absence of any fish catch at stations off Kollam was also reported. Commercial fishes, especially the shoaling population generally avoid

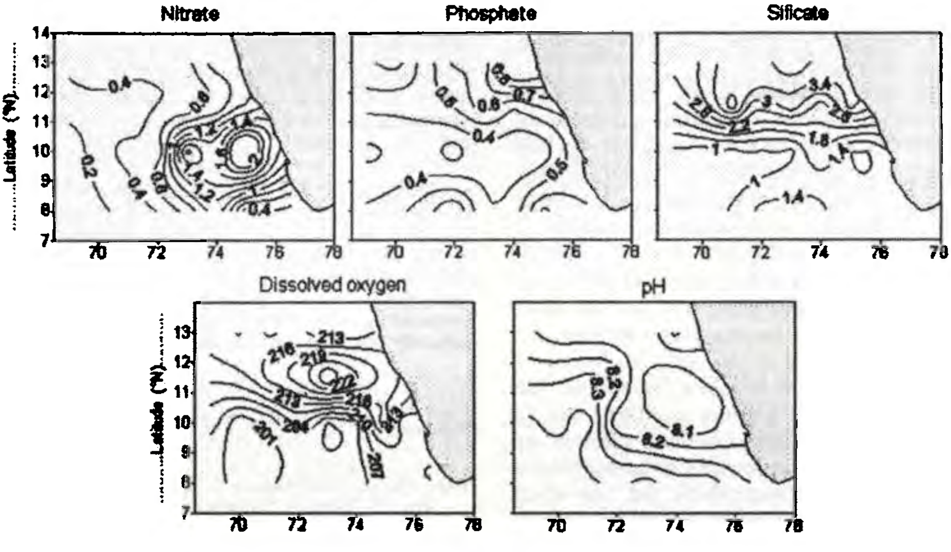


Fig. 4 Horizontal distribution (10 m) of nitrate, phosphate, silicate, dissolved oxygen (all in µm M) and pH along the study region

Noctiluca bloom (Prasad and Jayaraman 1954). Also, the period of study is known for the occurrence of coastal upwelling, which brings in large quantities of nutrients to the surface waters. The nutrient data (Figs. 3 and 4) during this study did not show such an intense upwelling in this region, but the Chl-a levels were high (Table 1) indicating an intense utilization of nutrients. Red tide once established at low levels of nutrients, could grow rapidly if it is transported into an area rich in nutrients caused by upwelling or anthropogenic inputs. The dependence of the dinoflagellates to the deeper waters for their high nutrient requirement for the establishment of the bloom, is also possible. The bloom observed off Kollam must be the combined effect of upwelling and the anthropogenic input, whereas the red tide off Thumba may be attributed to the succession by dinoflagellates following the exhaustion of Silicon. Because of the stratification, silicate supply was inadequate in the surface waters, which inhibited diatom growth

Table 1 Average value of chlorophyll 'a' (surface and 10 m) in the coastal and oceanic stations along the study region

Latitude (°N)	Longitude (°E)	Chl-'a'(mg/m^2)	
		Surface	10 m
Coastal			
8°30′ (Bloom infested)	76°30′	0.66	0.66
10°00′	75°30′	0.23	0.33
11°30′	75°00′	0.07	0.04
13°00′	76°00′	0.33	0.23
Oceanic			
8°30′	73°12′	0.41	0.31
10°00′	70°00′	0.11	–
11°30′	71°48′	0.24	0.27
13°00′	72°00′	0.01	0.11

prompting the dinoflagellate (causing the red tide) to occupy the space.

Phytoplankton blooms are often spontaneous and dramatic, however their development and persistence are brought by multiple interactions of physical, chemical and biological aspects in proper combination. Many red tide-forming species are prone to advection by prevailing winds and currents. Hence, it is likely that, the dinoflagellates observed off Kollam must have moved in to this region (lat.8°20'N, long. 76°29'E). These advective processes are often strong enough to transport the organisms over large distances, as observed in the study of Tester and Sleidinger (1987). It is known that diatoms and *dinoflagellates* have a similar ecological niche in coastal waters, as their nutrient requirement are similar. Hence, it is expected that competition occurs between diatoms, dinoflagellates and other small flagellates (including zooplankton) in the community. The source of the *Noctiluca miliaris* in this region (where the concentration of nitrate and silicate were low) may be the result of long shore advection of the red tide from its place of outbreak (off Kollam). While the non-availability of silicon and nitrogen seem to limit the propagation of other plant organisms, it would possibly accelerate the growth of dinoflagellates. Holmes and Lam (1985) observed an increase in red tide incidents with increased nitrogen loading in the watershed of Tolo Harbor. Ho and Hodgkiss (1991) found that a decline in N: P ratio in surface water usually resulted in domination of dinoflagellates (the main red tide causing organisms) over diatoms. The slightly high phosphate together with low levels of nitrate definitely will lower the N/P ratio in this region. As observed in Tolo Harbor, whenever there is an abrupt change in the environmental conditions, dinoflagellates take over the dominance (Holmes 1988).

Conclusion

This observation clearly indicate that the red tide bloom (*Noctiluca miliaris*) occurs during a time when the sea water is nitrogen and silicon impoverished. The variation of silicon (Si) concentration could be another cause of increased red tides in coastal waters. In addition, this study suggest the need of a regular monitoring system for such bloom, which helps to develop a forecasting or warning systems on toxic blooms and consequent fish mortality (and related stench) along the west coast of India.

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Hydrography and biogeochemistry of the north western Bay of Bengal and the north eastern Arabian Sea during winter monsoon

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Abstract

The north eastern Arabian Sea and the north western Bay of Bengal within the Indian exclusive economic zone were explored for their environmental characteristics during the winter monsoons of 2000 and 2001 respectively. The two regions were found to respond paradoxically to comparable intensities of the atmospheric forcing. There is an asymmetry in the net heat exchange of these two basins with atmosphere because of the varying thickness of barrier layer. During winter, the convective mixing in the Arabian Sea is driven by net heat loss from the ocean, whereas the Bay of Bengal does not contribute to such large heat loss to the atmosphere. It appears that the subduction of high saline Arabian Sea water mass is the mechanism behind the formation of a barrier layer in the northeast Arabian Sea; whereas that in the Bay of Bengal and the southeast Arabian Sea are already established as due to low saline water mass. The weak barrier layer in the Arabian Sea yields to the predominance of convective mixing to bring in nitrate-rich waters from the deeper layers to the surface, thereby supporting enhanced biological production. On the other hand, the river discharge into the Bay of Bengal during this period results in the formation of a thick and stable barrier layer, which insulates vertical mixing and provide oligotrophic condition in the Bay.

Keywords: Stratification; Barrier layer; Thermal inversion; North eastern Arabian Sea; North western Bay of Bengal; Winter cooling; Primary production

1. Introduction

The Northern Indian Ocean comprising of the Arabian Sea (AS) and the Bay of Bengal (BB) separated by the Indian peninsula, are tropical basins experiencing intense meteorological forcing, but differing widely in their upper ocean hydrology. The negative water balance associated with excess evaporation over precipitation and intrusion from Mediterranean Sea makes AS high saline (>36), whereas the excessive river run off into BB (1.625×10^{12} $m^3 y^{-1}$, Subramanian, 1993) leads to a positive water balance (P-E=0.8 m y^{-1}, Ramanathan and Pisharody, 1972) and low salinity (<33). A dissimilarity that is observed in the winds over the two basins is that during the summer monsoon, winds are stronger in the AS than in the BB, whereas winds are of similar intensities during the winter

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monsoon (Shenoi et al., 2002). It is well established that the AS is biologically more productive during summer monsoon, whereas the BB is traditionally considered to be a less productive system (Radhakrishna et al., 1978; Bauer et al., 1991; Brock et al., 1991; Prasannakumar et al., 2001a, 2002; Madhupratap et al., 2003). The north eastern Arabian Sea (NEAS) continues to sustain fairly high biological production during the winter monsoon also due to the nutrient entrainment into the euphotic layer by winter cooling-driven surface convection (Madhupratap et al., 1996; Prasannakumar et al., 2001a, 2001b). It is intriguing as to why in such a case, this 'biological niche' is elusive in the north western Bay of Bengal (NWBB), which also experiences a similar atmospheric forcing during winter. Although the extant of literature from the monsoon observations tends to emphasize its relation to heavy cloud cover, turbidity, low nutrient availability etc., the real mechanism that inhibits the carbon productions remains unresolved. An earlier report has attributed the difference in the biological production of these two basins during the winter monsoon to the strong thermohaline stratification in the BB (Jyothibabu et al., 2004). In this paper, we demonstrate that the significance of a thick barrier layer (BL) in the NWBB compared to a thin BL in the NEAS is the mechanism behind the contrasting biogeochemistry of the two basins during winter monsoon.

2. Sampling and analysis

The hydrographic data from the NEAS were collected during the winter monsoon of 2000 (FORV Sagar Sampada cruise no. 190 from 29th Nov–5th Jan.) and those from the NWBB (Fig. 1) were collected during the early winter monsoon of 2001 (FORV Sagar Sampada cruise no. 198 from 20th Nov–18th Dec.). The total number of stations sampled were 16 in the NEAS along 3 transects (Lat. 17°, 19° and 21° N, Long. 67–73° E) and 12 along 3 transects in the NWBB (Lat. 17°, 19° and 20.5° N, Long. 82–89° E). Surface meteorological parameters were taken at every 10 min using the ship based Automated Data Acquisition Software System. Vertical profiles of temperature (accuracy ± 0.001 °C) and salinity (accuracy ± 0.0001) were recorded at 1 m vertical intervals up to 1000 m. Seawater samples were collected from standard depths at all the stations using a Seabird CTD rosette system fitted with 12 Niskin bottles, each of 1.8 l capacity. CTD salinities were calibrated with on-deck analysis of discrete samples using a Guideline 8400 AUTOSAL (Ocean Scientific International, Pertersfield, UK). The samples were analyzed for nitrite, nitrate, phosphate and silicate with an onboard Auto Analyzer (Skalar Analytical, Breda, Netherlands) and dissolved oxygen for the corresponding depths following Winkler titration method (Grasshoff et al., 1983). Chlorophyll *a* and *in situ* primary productivity measurements were carried out from two stations in each transect representing coastal and oceanic regions respectively (Fig. 1). Primary production (PP) was measured by the radiocarbon (^{14}C) method (UNESCO, 1994; Bhattathiri et al., 1996). Water samples were taken from 7 depths (surface, 10, 20, 50, 75, 100 and 120 m) using Go-flo samplers and were transferred to 300 ml polycarbonate bottles (Nalgene, Germany). Each bottle was spiked with 1 ml of NaH^{14}CO$_3$ (5 μCi ml^{-1}, Board of Radioisotope Technology, Department of Atomic Energy, India) and the bottles were suspended at the approximate depths of sampling using a polypropylene line attached to a buoy. Three light bottles and one dark bottle were used at each depth. The incubation lasted from 1 h before sunrise to 30 min after sunset, after which the samples were retrieved and filtered through GF/F filters (pore size 0.7 μm) under gentle suction. The filters were exposed to concentrate HCl fumes to remove excess inorganic carbon and transferred to scintillation vials for subsequent estimation. A day before analysis, 5 ml of liquid scintillation cocktail (Sisco Research Laboratory, Mumbai) was added to the vials and the activity counted in a scintillation counter (Wallace 1409 DSA, Perkin-Elmer, USA). The disintegration per minute (DPM) was converted into daily production rates (mgC m^{-2} d^{-1}) taking into account the initial activity in the bottles and the initial adsorption of ^{14}C by particles in the bottles (Strickland and Parsons, 1972). Samples for chlorophyll (Chl a) analysis were also taken from the same casts as that of primary productivity (Fig. 1). One litre of water sample from each depth was filtered through GF/F filters (pore size 0.7 μm). Chl a estimation was carried out using a spectrophotometer (Perkin Elmer, USA), after extracting with 10 ml 90% acetone in the dark (Strickland and Parsons, 1972). Column PP (mgC m^{-2} d^{-1}) and column Chl a (mg m^{-2}) were calculated by integrating over 120 m depth. In the present study, since the driving force behind blooming of phytoplankton in surface waters is the availability of nutrients (especially nitrogen) and its entrainment into the euphotic zone, we examine the upper 200 m water column to understand the processes that regulate the supply of nitrogen into the surface layers of these two basins.

The mixed layer depth (MLD) discussed here is defined as the depth at which the density of the seawater changes ("$\Delta\sigma_\theta$") by 0.2 from the surface value (Sprintall and Tomczak, 1993). Note that even though this way of calculation of MLD may not hold good for the two basins, a comparison can be made only when physical properties are normalized to one format. The ILD, the

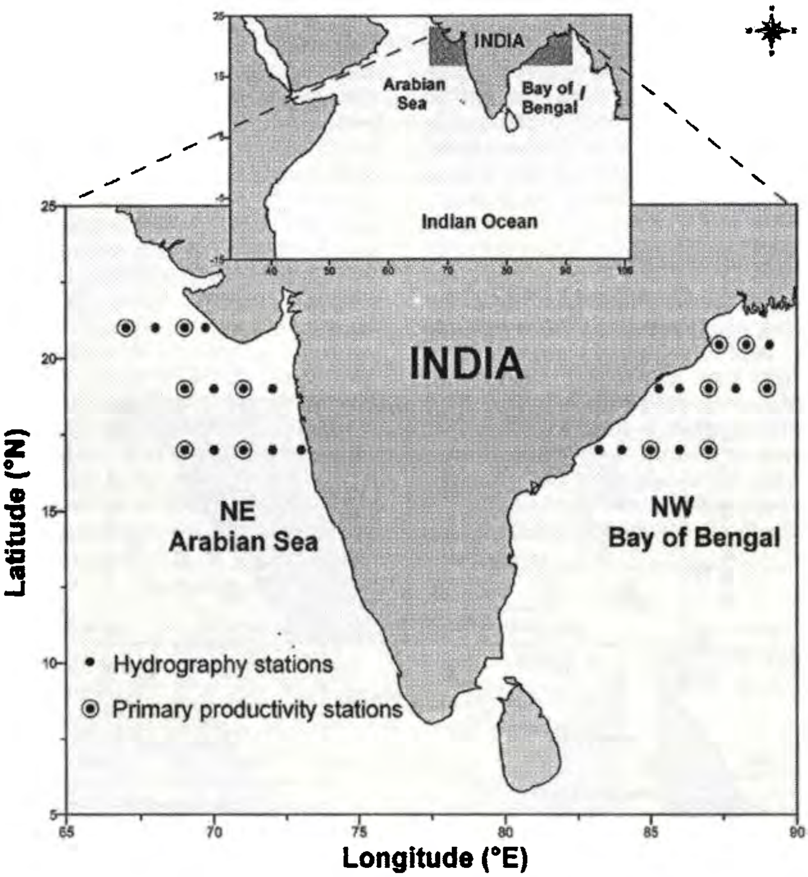

Fig. 1. Study region showing the station locations in the northeastern Arabian Sea and north western Bay of Bengal.

depth of the top of the thermocline, is defined as the depth at which surface temperature decreases by 1 °C from sea surface temperature (Kara et. al., 2000; Rao and Sivakumar, 2003). The above definition of ILD holds good only for normal temperature distribution. Therefore, for profiles with temperature inversion, ILD is defined as the depth at which the temperature at the base of the inversion layer is equal to the temperature at the top of the inversion layer. This definition is valid as the inversion layer is embedded within the barrier layer and it is sustained by the haline stratification (Pankajakshan et al., 2002, 2007a). The barrier layer (BL) in the present study is computed as the difference between ILD and MLD following the method of Lukas and Lindstrom (1991). The stability of water column represented by Brunt–Väisälä frequency (N) was computed following adiabatic leveling method (Bray and Fofonoff, 1981).

3. Results

3.1. General hydrography

The NEAS and the NWBB exhibited more or less uniform variations in the meteorology at comparable latitudes. Generally, the air temperature (AT) decreased from 30.5° to 24.5 °C along lat. 17°–21° N in the NEAS and from 29.4° to 25.5 °C along lat. 17°–20.5° N in the NWBB, whereas the atmospheric pressure ranged marginally between 1010 and 1015 mb (Jyothibabu et al., 2004). Both regions experienced moderate winds (6–9 m/s), except in the region between 19° and 20.5° N in the NWBB, where the wind was comparatively weak (~4 m/s). The sea surface temperature (SST) varied from 25.9–27.4 °C in the NEAS and from 26.1–27.8 °C in the NWBB, the cooler water being observed towards north.

3.2. Northeastern Arabian Sea

The excess evaporation over precipitation and the presence of several high density waters (Red Sea Water and Persian Gulf Water) provide AS a unique property of sustaining high saline water mass. During winter season, the evaporative cooling results in the formation of dense water mass (Arabian Sea High Salinity Water Mass), which on sinking deepens the mixed layer (ML). The heat loss by evaporation and sinking of the surface waters initiates convective mixing (Madhupratap et al., 1996). During the present study, the ML in the NEAS along lat. 17, 19 and 21° N of the NEAS was deep, but the BL, observed at some locations (maximum 35 m), though weak, is quite interesting (Fig. 2).

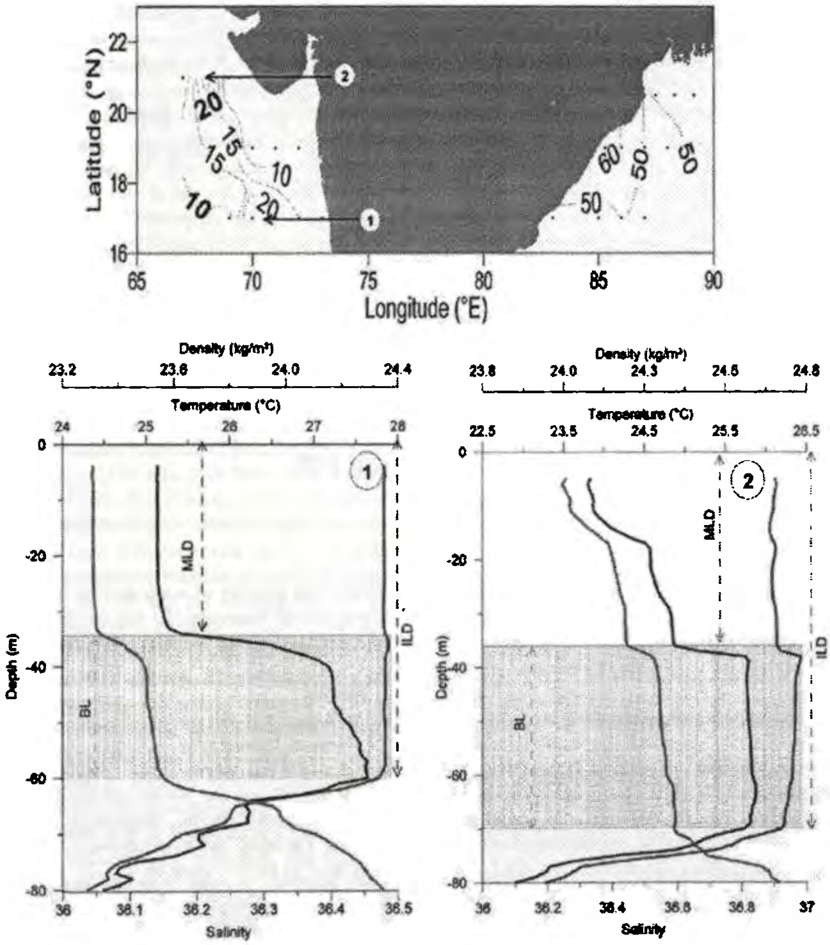

Fig. 2. Top panel — Horizontal distribution of barrier layer depth in meters in the NEAS (Dec.2000) and NWBB (November 2001). Bottom panel — Thermohaline stratification at two different locations (shown in the top panel) of the NEAS at (1) 17° N 70° E and (2) 21° N 68° E.

3.2.1. Barrier layer in the NEAS

The formation of BL in the BB and SEAS is well known (Gopalakrishna et al., 2005; Shenoi et al., 2005; Durand et al., 2007; Pankajakshan et al., 2007), but very little information is available for the occurrence of the same in the NEAS. Presence of a thick BL (20–50 m) in the NEAS is reported during January–February (Pankajakshan et al., in press). In the present study (December), we have identified a BL of more than 25 m thick at two locations (Fig. 2, top panel). The vertical profiles of the thermohaline properties at 17° N 70° E and 21° N 68° E (Fig. 2, bottom panel) indicate a shallower isohaline layer than isothermal layer. It should be mentioned here that, these locations were characterized by a thin layer containing a well developed salinity maximum (>36.2) at its base, located above the top of the thermocline and a deeper layer of lower salinity. This saline layer originates at the surface in the north AS partially in response to high evaporation, and subsequently gets subducted to 50–60 m while moving towards the NE boundary, which is known as the Arabian Sea High Salinity Water Mass (Kumar and Prasad, 1999; Pankajakshan et al., in press). It is evident that the subduction of this ASHSW along the isopycnals has initiated the BL in the NEAS (Fig. 2, lower panel). The significance of this observation is that, BL formation due to subducted high salinity waters has been so far reported only from the northwest equatorial Atlantic (Sprintall and Tomczak, 1993). A comparison of the BL from the present study in the NWBB and the NEAS with that of Pankajakshan et al. (2007a, in press) also supports a deep BL in the former and a shallow BL in the latter. Thus, the BL formation in the NEAS is due to the high salinity water mass; whereas that in the BB and SEAS is due to low saline water mass.

As a result of the thin BL and a thick ML, the convective mixing became predominant and brought the 2 μM NO_3 from the top of the thermocline at 17° N which eventually spread out along the entire surface waters of 19 and 22° N (Fig. 3). The region north of 17° N was uniformly enriched in nitrate and phosphate (0.4 μM) right up to the surface (Fig. 4) and along the

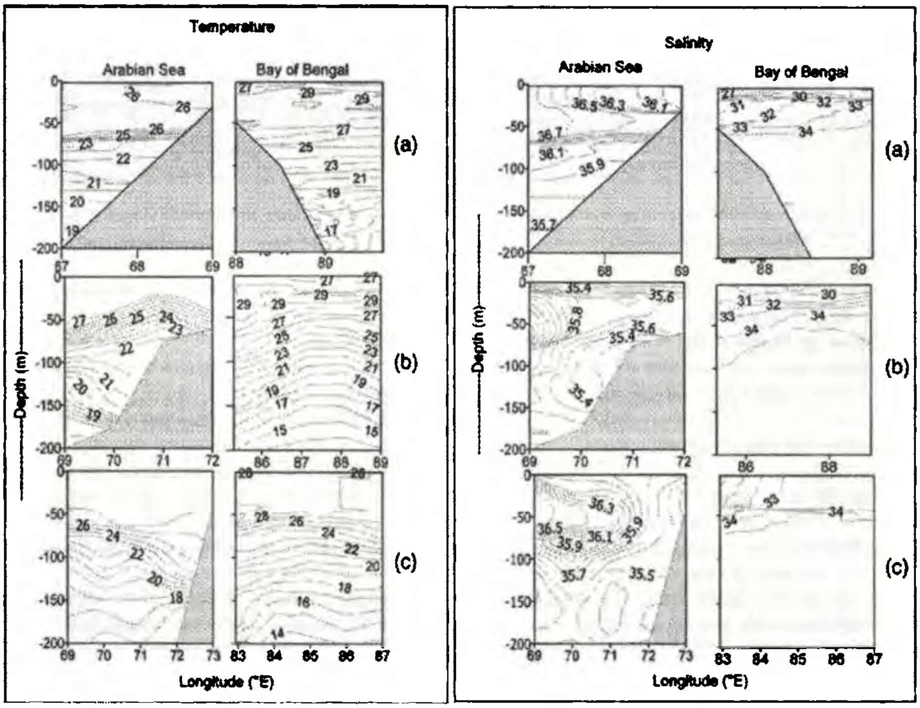

Fig. 3. Vertical sections of temperature (°C) in the left and salinity in the right panel along 17° N (a), 19° N (b) and 21° N (c) in the NEAS and 17° (a), 19° (b) and 20.5° N (c) in the NWBB.

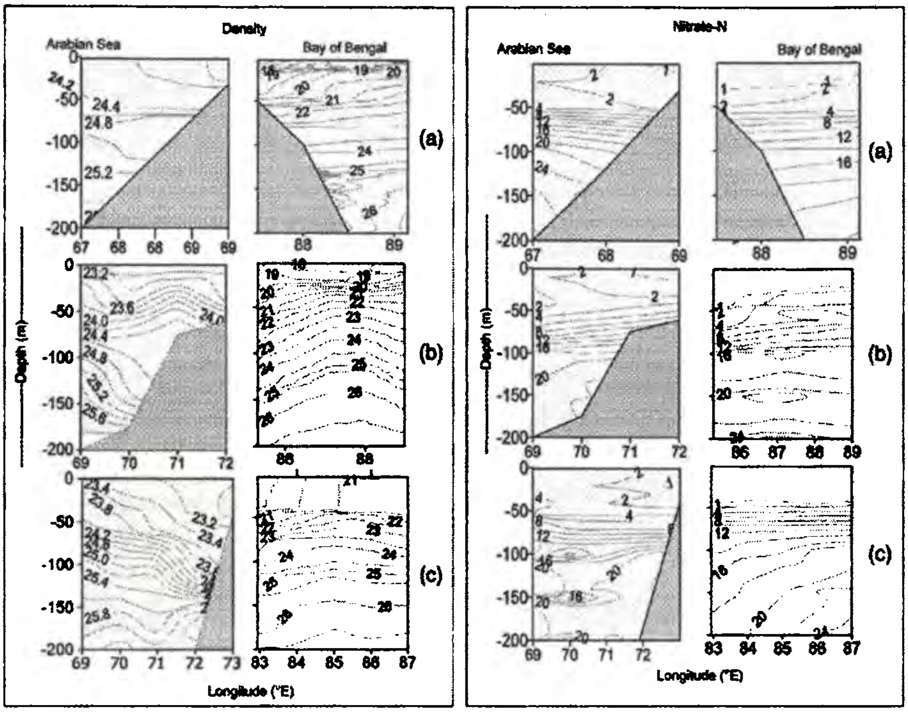

Fig. 4. Vertical sections of density (kg/m³) in the left and nitrate (μM) in the right panel along 17° N (a), 19° N (b) and 21° N (c) in the NEAS and 17° N (a), 19° N (b) and 20.5° N (c) in the NWBB.

coast up to 72° E (17° N).It was spreading out further offshore along 21° N and 68° E, whereas silicate (1 μM) did not show any repletion (Fig. 5) The impoverishment of the surface waters with nutrients at locations where the BL thickness was >25 m is noticeable.

3.3. Northwestern Bay of Bengal

It can be seen from the vertical sections of temperature and density of the northern bay that instead of a well-defined thermocline, the subsurface layers (30–50 m) were increasingly getting warmer (>3 °C) towards the northern latitudes (Fig. 3). As the fresh water discharge spreads over the sea surface, the winter cooling further modifies to trap the warm BB waters just below a thin lid (<30 m) of cool surface waters The distribution of salinity in the NWBB indicates the influence of fresh water run off from the land. The low salinity (~25) observed towards the coasts between 17 and 20.5° N may be due to the fresh water discharges from Godavari, Mahanadi and Ganges rivers. This fresh water flow imposes stratification with a salinity gradient of 1.8 in the upper 30 m at 17° N (31.6–33.4), increasing to 5.5 (26.5–31) at 20.5° N (Fig. 3). Salinity increased gradually from 30 to 75 m, and below this depth, it remained homogeneous.

The subsurface layer was also impoverished in nutrients, as the 1 μM nitracline was suppressed to below MLD (30–50 m) along all the latitudes (Fig. 4). Dissolved inorganic phosphate was also low (DIP<0.2 μM), but silicate was fairly distributed (>2 μM) in surface and increased towards the northern latitudes (20.5° N), indicating its river source (Fig. 5). The salinity gradient was found to intensify towards west in all transects, due to the increased fresh water discharge. It is evident from Fig. 6 that in the NWBB, the 20–60 m thick subsurface layer has more stability (120 cycles/h). It is therefore assumed that the fresh water flow stabilizes the euphotic zone by forming a deep BL with a shallow ML embedded in it, which insulates the entrainment of nutrient-rich deep waters into the mixed layer.

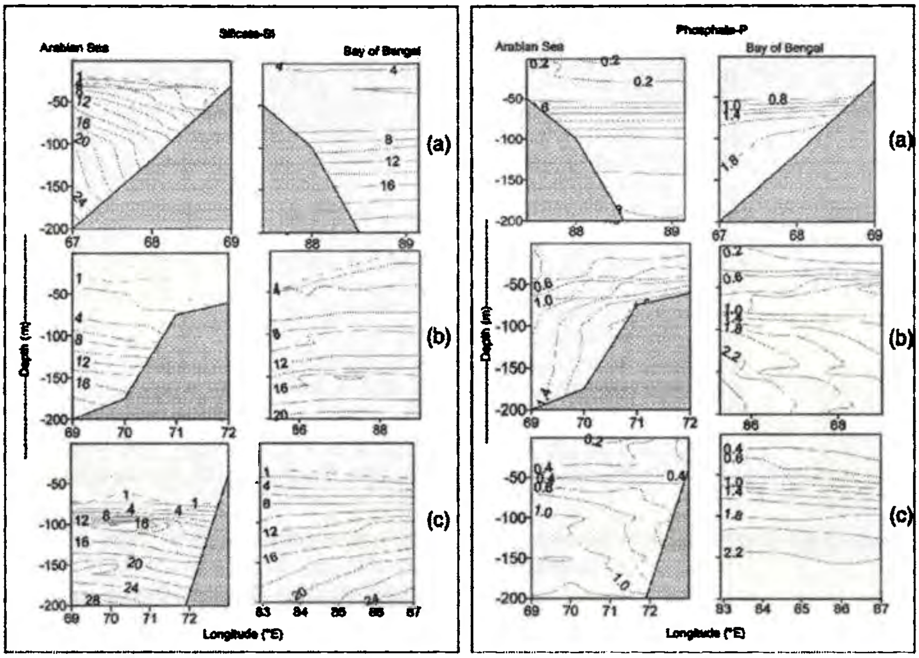

Fig. 5. Vertical sections of silicate (µM) in the left and phosphate (µM) in the right panel along 17° N (a), 19° N (b) and 21° N (c) in the NEAS and 17° (a), 19° (b) and 20.5° N (c) in the NWBB.

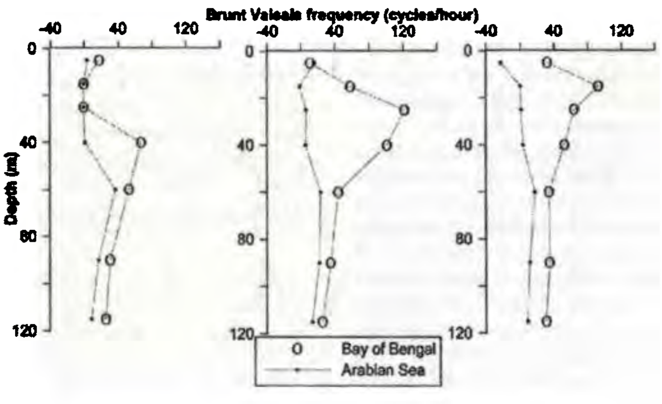

Fig. 6. Vertical profiles of Brunt–Vaisala stability frequency (cycles per hour) along 17° N (a), 19° N (b) and 21° N (20.5° for NWBB). Solid circle represents the AS and open circle represents the BB.

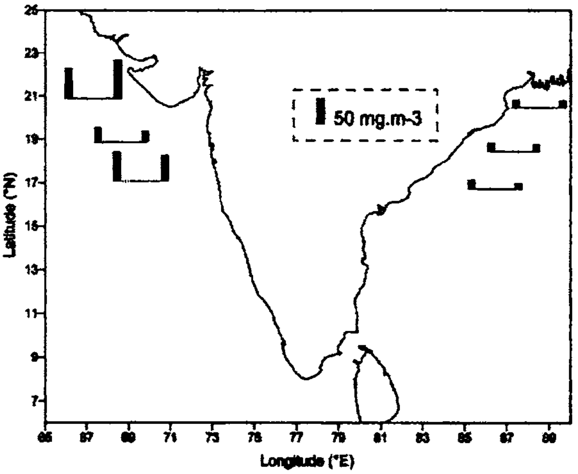

Fig. 7. Integrated column chlorophyll a (mg m^{-3}) during Dec. 2000 (in NEAS) and Nov.–Dec. 2001 (in NWBB).

3.4. Winter cooling and environmental responses — a comparison

It is interesting to note that while the intensities of atmospheric forcing were almost similar in both regions, the NEAS showed enhanced biological activity, whereas the NWBB remained low in the primary production. This suggests that, whereas the NEAS is vulnerable to atmospheric forcing, the NWBB remains stable due to the formation of a thick BL. In the NEAS, the convective mixing is strong enough to erode the BL and bring the nutrient-rich waters into the ML. This is a preconditioning for biological production evidenced by an increased column chlorophyll a biomass along 17°, 19° and 21° N (45–58 mg m^{-3}, 19–25 mg m^{-3} and 82–56 mg m^{-3}) respectively (Fig. 7). The corresponding

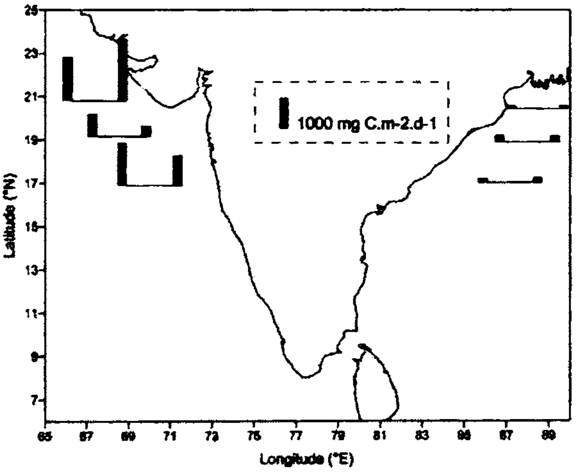

Fig. 8. Integrated column primary productivity (mgC m^{-2} d^{-1}) during Dec. 2000 (in NEAS) and Nov.–Dec. 2001 (in NWBB).

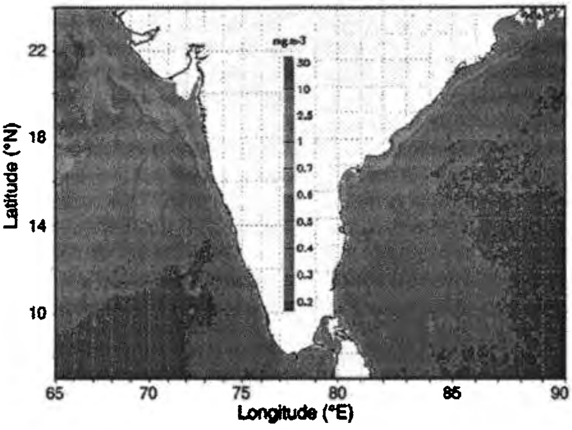

Fig. 9. Surface chlorophyll *a* distribution (monthly average compiled from Sea WiFS) in the AS (Dec. 2000) and the BB (Nov–Dec 2001).

primary production (PP) ranged from 1016–1348 mgCm^{-2}d^{-1}, 373–731 mgCm^{-2}d^{-1} and 1363–1854 mgCm^{-2}d^{-1}, respectively (Fig. 8). In contrast, the thick BL in the NWBB prevented the nitrogen entrainment from deeper waters. Hence, the biological activity was kept low along 17, 19 and 20.5° N (column chlorophyll *a* 14–9, 15–13 and 9–9 mg m^{-3}, respectively). The PP along these latitudes (Fig. 8) also remained low (101–145, 164–187 and 87–115 mgCm^{-2}d^{-1}, respectively). Surface chlorophyll *a* derived from satellite imageries (SeaWiFS, Fig. 9) during the respective periods also indicated an increase in the biomass in the NEAS compared to NWBB, corroborating our studies. It is estimated that the average column chlorophyll biomass sustained in the NEAS was 10 times higher than that in the NWBB (Table 1).

Table 1

Average values of column chlorophyll *a* (mg m^{-3}) and column primary production (mgC m^{-2} d^{-1}) in the coastal and oceanic stations of NEAS and NWBB

Latitude ° N	NEAS coastal	NEAS oceanic	NWBB coastal	NWBB oceanic
Chlorophyll a (mg m^{-3})				
17	45	58	14	9
19	19	25	15	13
20.5	–	–	9	9
21	82	56	–	–
Primary production (mgC m^{-2} d^{-1})				
17	1016	1348	145	101
19	373	731	187	164
20.5	–	–	115	87
21	1854	1363	–	–

4. Discussion

The mixed-layer dynamics have a strong influence on both water mass formation and hence, nutrient availability in the surface layers, which modulate biological productivity. The formation and spreading of BL has a significant role in maintaining the warm SST (>28 °C) in the NWBB. During winter monsoon, the northern bay experiences strong temperature inversions (up to 3 °C) in the subsurface layer, following which, a thick BL (~50 m) is spatially organized along the entire area. Since the inversion layer is embedded within the BL and exhibits large salinity stratification, the BL in the bay is a more stable and sustained feature (Pankajakshan et al., 2002). The thick BL acts as a barrier for the transfer of momentum, heat and nutrients, as observed in the present study. During winter monsoon, the ML in the NEAS is deeper (60–70 m) and cooler than that of the NWBB (8–30 m). The main reason for this difference is the asymmetry in the net heat exchanged between the ocean and atmosphere of these two basins (Prasad, 2004). The latent heat flux is dependant on humidity; the drier air over the AS facilitates enhanced cooling. The evaporative cooling leads to buoyancy of the surface waters owing to net heat loss from the ocean. The buoyancy flux due to salt has an influence on the deepening of ML (>80 m) in the AS, but is limited to shallow depths (8–30 m) in the BB (Prasad, 1997; Prasad, 2004). Thus, a comparatively weaker winter cooling (loss of net heat flux) in the NWBB had resulted in less nutrient supply to the surface leading to low biological production. However, cyclonic storms are found to disrupt the BL bringing nutrient-rich waters from the deep to enhance phytoplankton production in the BB (Rao et al., 1994; Madhu et al., 2000).

The situation is different in the AS, as there is no fresh water input during the period and the BL is very weak over the entire northeast AS (Fig. 2). This is further evidenced by the low stability of the NEAS surface waters compared to the NWBB (Fig. 6). The maximum stability of the upper 120 m water column in the NWBB was 70–120 cycles/h (between 17 and 21° N) during winter, while that in the NEAS for corresponding latitudes was <20 cycles/h.

It is evident that the enrichment of the euphotic layer with silica was not favoring primary production in the NWBB, because according to the Redfield ratio, the available phosphorus should have a minimum nitrate (> 1 μM) to support phytoplankton production (Redfield et al., 1963). In contrast, the NEAS was uniformly enriched in nitrate and phosphate (0.4 μM) in the euphotic zone from 17° to 21° N, whereas the silicate (1 μM) remained comparatively low (Figs. 4 and 5). The rising of the nitracline triggered enhanced biological activity in the region because, there was a net increase in the ratio of N: Si to ~2/1, vs. ~1 assumed to be the approximate ratio of uptake by diatoms (Morrison et al., 1998). Thus, there appears to be silica limiting for the diatom growth in the NEAS, as observed in the open ocean upwelling regions. This is an anomaly since it has been observed that Si concentrations of the AS are higher than minimum N concentration in surface waters and a net removal of Si may not be possible below 0.6–0.8 μM in warm waters (David et al., 1994; Brezinski and Nelson, 1995). Because of the insignificant contribution of fresh water flow into the AS during winter monsoon, it is possible that silica may be more limiting to diatom blooms in the continental shelf than nitrogen, a situation that has been described only for open-ocean upwelling regions (Dugdale et al., 1995; Dugdale and Wilkerson, 1998).

5. Summary and conclusions

The observations show that during the winter monsoon, the atmospheric forcing and continental drainage influence the biogeochemistry of the NEAS and the NWBB, respectively. Although the winter evolutions of oceanographic features resulted in convective mixing and enhanced biological production in the NEAS, the same intensity of winter cooling resulted in low biological production in the NWBB. This is primarily due to the increased stability of the water column in the NWBB, by the formation of a thick BL having an inversion layer embedded in it, which restricted the entrainment of nutrients from subsurface waters. It should be noted that an increased nitrogen loading (4.5 mg $Nm^{-2}d^{-1}$) by freshwater did not contribute repletion of nitrate concentration in the surface waters of the BB, and the resultant low biological activity inferred from the low pCO_2 concentrations in this region (Kumar et al., 1996). In conclusion, this study shows that the biological activity in the northern Indian Ocean is controlled by Air↔Sea↔Land interactions on varying geographic scale. The Air–Sea interactions in the NWBB are insignificant, where the hydrography is mainly controlled by Land–Sea interactions. In contrast, the negative water balance and the Arabian Sea High Salinity Waters make the NEAS highly vibrant to Air–Sea interactions, where atmospheric forcing dictates the upper ocean hydrography. This communication shows that high saline waters are the principal cause of the formation of BL in the NEAS, whereas those in the BB and SEAS are due to low saline water mass.

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Origin and characterisation of microparticles in an ice core from the Central Dronning Maud Land, East Antarctica

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Abstract The scanning electron microscopy–energy dispersive spectroscopic (SEM–EDS) study of selected samples from an ice core collected from Central Dronning Maud Land (CDML), East Antarctica, revealed several microparticles. They are mainly siliceous and carbonaceous particles and have distinct variations in their shape and composition. The morphology and major element chemistry of the particles suggest their origin from either volcanic eruptions or continental dust. The EDS analysis revealed that the volcanic particles are enriched in silica (average SiO_2 62%), compared to the continental dust particle (average SiO_2 56%). We found that the tephra relating to Agung (1963) and Karkatau (1883) volcanic eruptions, as recorded, in the ice core harbored microbial cells (both coocoid and rods). The occurrence of organic and inorganic particles which bear relation to volcanic eruption and continental dust implies significant environmental changes in the recent past.

Keywords Tephra · Dust · Microbe · Nanobe · Ice core · East Antarctica

Introduction

Polar ice cores are important natural archives of paleoclimatic changes, as they indicate large variations in atmospheric dust load in association with the past climatic changes. The changing wind pattern accompanied by seasonality in circulation and biogeochemistry leads to varied depositions in the polar snow. This deposition acts as fingerprints of significant geological events such as glacial weathering, volcanic eruptions, cyclones and tsunamis (Petit et al. 1999; Laluraj et al. 2006). Some of these dust particles are exclusively of aeolian origin, where wind blows across long distance from the continents. Among them, the Vostok ice core revealed that the dust input to Antarctica was high during pleniglacial periods and low during stadials and interstadials (Petit et al. 1999). Large volcanic eruptions may also be detected in polar ice cores by the associated ash and cryptotephra particles (de Angelis et al. 1985; Palais et al. 1990; Silva and Zielinski 1998; Zielinski et al. 1997; Davis et al. 2004). Records of several past volcanic eruptions in the tropical, temperate and polar regions have been deduced from acidity and ionic measurements in ice cores from the polar regions (Zielinski et al. 1996; Clausen et al. 1997). However, the biogenic components of the aeolian particles have

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received little attention, despite its known role in microbial transport (Griffin et al. 2003). The occurrence of biological material in the ice cores are of special interest because the biosphere interacts more vigorously with variations in the temperature and other environmental parameters.

Several studies using Antarctic ice cores have demonstrated the ability of ice cores as an archive of random historical volcanic eruption records (Robock 2000; Zielinski et al. 1997; Zielinski 2000; Narcisi et al. 2001). Volcanic emissions lead to fallout of both gaseous aerosols and solid (tephra) components, which can travel great distances. For example, the tephra from the 1259 AD eruption of El Chichòn, Mexico was found preserved in the Greenland and Antarctic ice caps (Palais et al. 1992). Studies on tephra layers in ice cores have significantly improved our understanding of the volcanic impact on climate and their effective usage as a chronological tool. There are no detailed studies regarding the nature and chemistry of dust particles from the Central Dronning Maud Land (CDML) region of the East Antarctica. Therefore, the present attempt is to classify the different microparticles accreted in an ice core from CDML region based on their elemental composition and morphology. This information would benefit studies undertaken to resolve the origin of microparticles and their transport mechanisms involved for their distribution in the Southern Hemisphere and subsequent burial in Antarctic region.

Material and methodology

A 62.2 m long core (IND-22/B4) was collected from the continental ice sheet at 70°51.3'S and 11°32.2' E, near the Tallaksenvarden nunatak of CDML region during the 22nd Indian Antarctic Expedition (Fig. 1). The drilling was carried out using an electromechanical drill system (core diameter ~10 cm) during the austral summer (February–March), 2003. The cores were sealed in frozen conditions (−20°C) to avoid physical changes as well as chemical and biological contamination. The cores were then transported to the ice core laboratory at the National Centre for Antartic and Ocean Research, Goa, India. Subsequently the cores were processed and sub-sampled at −15°C facility. As a precaution to avoid contamination, we collected only the inner part of ice core samples, which were melted in a class 100 clean room before chemical and biological analysis. Major soluble ions such as sulphate (SO_4^{2-}) and sodium (Na^+) were measured from the thawed samples using ion chromatographic techniques. The chromatographic analysis was carried out in Dionex™ ICS-2500 system equipped with automated EG50 Eluent Generator Module and a CD25 conductivity detector. Detailed analytical setup, procedures and the analytical precision are provided in Thamban et al. (2006). Chronology of the core was obtained by volcanic stratigraphy using the non-sea-salt sulphate records (Thamban et al. 2006).

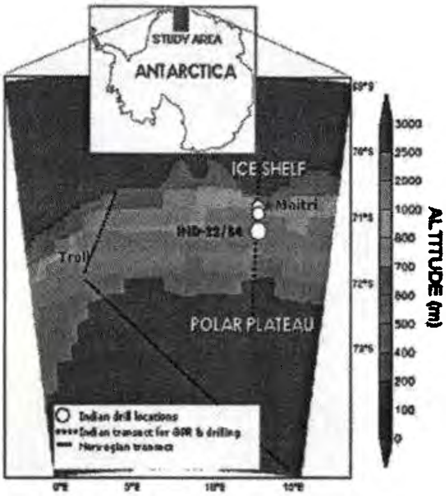

Fig. 1 Study region and location of the ice core (*IND-22/B4*) within the Central Dronning Maud Land

Based on the chronology constructed for the core, samples were selected from five discrete depth intervals, representing volcanic events. The selected samples from 0.5, 2.5, 9.4, 19.5 and 41.7 m revealed signatures of major volcanic events during 1991, 1963, 1883, 1815 and 1600 A.D (Thamban et al. 2006). Among these, two intervals of recent and well known volcanic eruptions of Agung (1963) and Karkatau (1883) were studied in detail to decipher the microbial cells attached to volcanic particles. About 50 ml of the melted samples were filtered in a Class 100 clean room at room temperature using 0.22 µm track-etched membrane filter paper, following the clean procedures. Thereafter, a small portion of the filter was dried and platinum-coated for 30–40 s in a

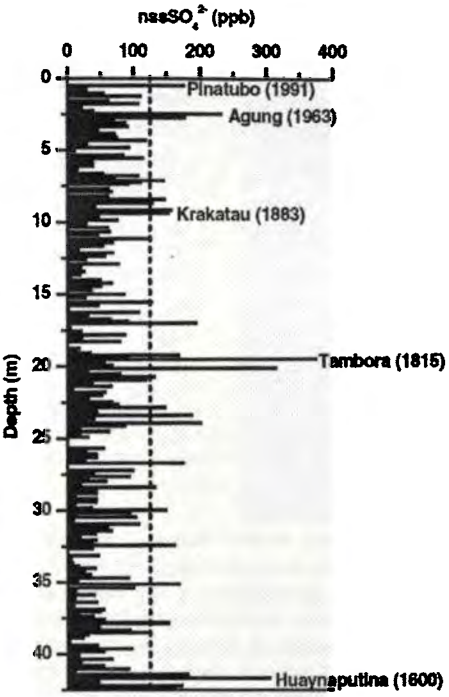

Fig. 2 The estimated non-sea salt sulphate concentration with references to depth. The major volcanic events marked with chronology (years in A.D.), represents the samples used for the study. The vertical dashed line of record is the upper limit defined for the biogenic sulphate (125 ppb)

JEOL JFC-100 auto fine sputter coater. The shorter periods were selected to minimize the induction of 'bacteria-looking' artifacts (Folk and Lynch 1997). The SEM was tuned to get optimal resolution as high as 43000X. The JEOL JSM -6360LV microscope was used at a closer working distance (~10 mm) with voltage range between 10–25 kV. The preliminary semi-quantitative major elemental analysis (area average) was carried out using energy dispersive spectroscopy (OXFORD INCA 200), attached to the JEOL 6360 LV SEM.

Results and discussion

The sulphate concentration in the ice core depends on the deposition from sea spray or crustal sources (Maupetit and Delmas 1992; Cole-Dai et al. 2000), atmospheric oxidation of dimethyl-sulphide (DMS) emitted by the marine phytoplanktons (Saltzman 1995; Prospero et al. 1991) and volcanic eruptions emitting millions of tons of sulphur compounds into the atmosphere (Legrand and Mayewski 1997). The non-sea-salt sulphate in the ice core was estimated using the formula $(nssSO_4^{2-}) = (SO_4^{2-}) - 0.252(Na^+)$. The maximum biogenic sulphate background for the core was estimated at 125 ppb, considering all the possible sources (Thamban et al. 2006; Fig. 2). The present study has focused on the evaluation of different particles that were deposited at the selected volcanic horizons identified within the ice core and their possible provenance. These microparticles which included siliceous, carbonaceous and certain biological forms are either attached or dropped on the surface of siliceous particles. The detailed study of the particles present on the ice core is given below.

Siliceous particles

The silica-rich particles (>50% SiO_2) are grouped in this category. The SEM observations indicate that samples are composed of morphologically distinct particles that have either smooth or rough surfaces (Fig. 3). The smooth particles resembled glass shards with sharp features, whereas the rough particles

Fig. 3 SEM images of smooth (**a**) and rough (**b**) surface particles present in the Ice core samples

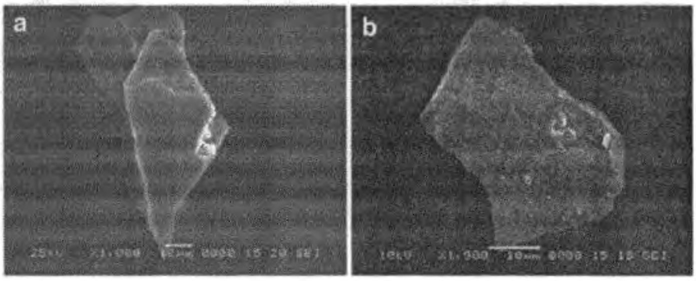

Table 1 Average major elemental composition of smooth and rough particles from different depths of IND-22/B4 ice core (values are in percentage and '*n*' is the number of particle analysed)

Depth	Year (A.D.)	SiO_2	Al_2O_3	FeO	Na_2O	K_2O	CaO
Smooth glass shard Siliceous particles							
0.5 (*n*=6)	1991	60.1±2.0	18.9±1.2	2.4±1.2	6.8±0.8	0.24±0.2	3.6±1.5
2.5 (*n*=15)	1963	62.4±2.5	16.6±1.8	2.2±1.0	7.1±1.2	0.31±0.3	3.1±1.8
9.4 (*n*=17)	1883	62.3±2.2	17.1±2.3	2.1±1.4	7.7±1.7	0.14±0.1	4.1±2.1
19.5 (*n*=9)	1815	61.8±3.5	19.1±1.1	2.5±1.5	7.5±2.1	0.27±0.2	3.2±2.5
41.7 (*n*=4)	1600	62.1±3.2	18.6±1.5	2.3±1.7	7.8±2.3	0.28±0.2	3.7±1.3
Mean	–	61.7	18.1	2.3	7.4	0.25	3.5
Rough surface Siliceous particles							
0.5 (*n*=3)	1991	57.4±10.2	22.2±7.5	0.5±0.3	5.8±3.5	0.9±0.7	8.7±5.1
2.5 (*n*=12)	1963	60.1±11.5	18.7±6.4	0.6±0.5	3.1±2.8	0.4±0.2	6.7±4.2
9.4 (*n*=12)	1883	51.4±5.8	20.4±8.5	1.3±1.1	4.1±3.3	0.5±0.3	7.7±3.1
19.5 (*n*=7)	1815	53.4±8.5	21.8±10.2	0.9± 0.8	5.4±4.5	0.1±0.1	8.3±3.5
41.7 (*n*=3)	1600	59.2±12.5	17.6±8.7	1.4±1.0	2.5±2.2	0.3±0.2	8.1±2.8
Mean	–	56.3	20.1	0.9	4.2	0.4	7.9

appear to have undergone weathering during their transport. The major elemental chemistry by EDS is given at Table 1. The mean percentage composition (major elements) of smooth particle (SiO_2 61.7, Al_2O_3 18.1, FeO 2.3, Na_2O 7.4, K_2O 0.25 and CaO 3.5) is different from the one with that of rough surface (SiO_2 56.3, Al_2O_3 20.1, FeO 0.9, Na_2O 4.2, K_2O 0.4 and CaO 7.9). This variability could be due to an intrinsic feature derived from their provenance or reworking during transport. The chemical composition and morphology revealed that the smooth-surfaced particles are homogeneous as compared to the rough-surfaced particles and their formation may be attributed to fragmentation of quenched magma as a result of quick chilling during hydration (Heiken 1972). The particles containing high silica and resembling glass shards could be the primary fallout of volcanic eruptions (Bjorck et al. 1991; Narcisi et al. 2005; Pattan et al. 2002), where as the particles having rough surface indicates signatures of weathering and transport from the continental dust. This is further substantiated by a ternary plot of smooth and rough particles with CaO, FeO and K_2O as end members showing a distinct difference in composition, thereby suggesting its difference in provenance through volcanic and continental dust (Fig. 4). The volcanic particles (tephra) at the site are stratospherically transported, whereas the crustal dust particles could be wind transported. The dust records in an ice core from the Antarctic Peninsula revealed that the crustal dust had doubled during in 20th century compared to the previous century and related it to the enhanced desertification of the Patagonia and northern Argentina (McConnell et al. 2007). Considering, the proximity of Antarctic Peninsula and the prevailing wind pattern, it is practical to arrive at such conclusion. However, no such increased input of the dust material was found at the ice core site during the past few hundred years. It is therefore opined that the micro dust particles observed here might have a local source in the ice-free areas of Schumacher Oasis and the Tallaksenvarden nunatak.

The SEM images of the siliceous particles from at 2.5 and 9.4 m depth of the ice core showed the presence of certain microbial cells (clusters as well as isolated) of different shapes (cocci and rods) and sizes

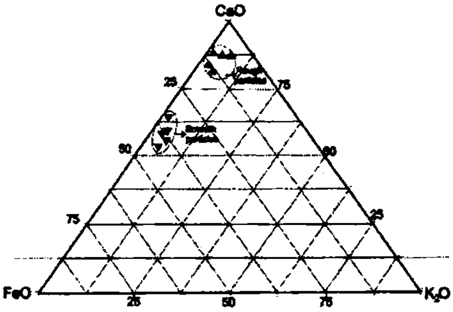

Fig. 4 Ternary plot of CaO vs. FeO vs. K_2O of smooth and rough particles

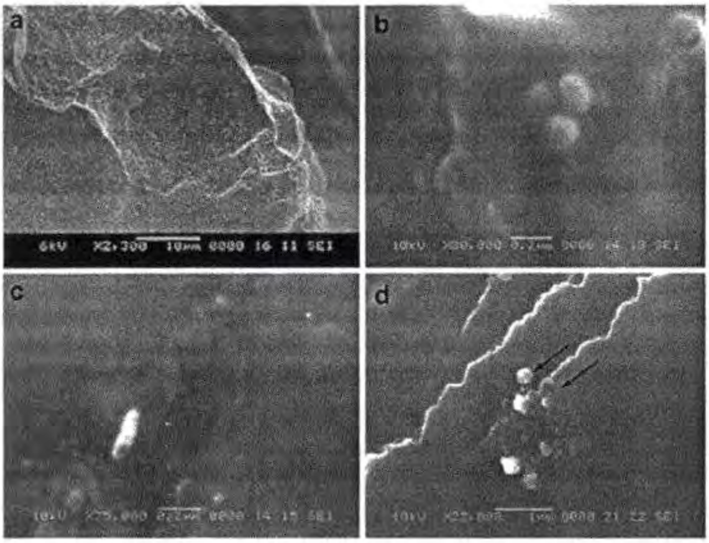

Fig. 5 SEM of a siliceous particle with cells adhered on to it. The surface of the particle appears to be completely coated with a mat of tiny spherical cells (**a**). Extremely small cocci cells of size ~180 nm diameter clubbed to each other (**b**). Magnified image of a short-rod shaped cell (~70× 250 nm) adhered on to a particle with silica enrichment (**c**). Two types of cocci cells can be seen on the surface of a particle with sharp edges. The diameter of these cells ranged from 50–300 nm (**d**)

(micron and sub micron) adhered onto the volcanic particles (Fig. 5a). The chronological constraints obtained from this core revealed that the depths of 2.5 and 9.4 m represent periods of eruptions from the Agung Volcano in 1963 and the Karkatau Volcano in 1883, respectively (Fig. 2). Extremely small size of coocoid cells (~180 nm) and rods of microbial cells (~70 × 250 nm) were also seen adhered to the volcanic

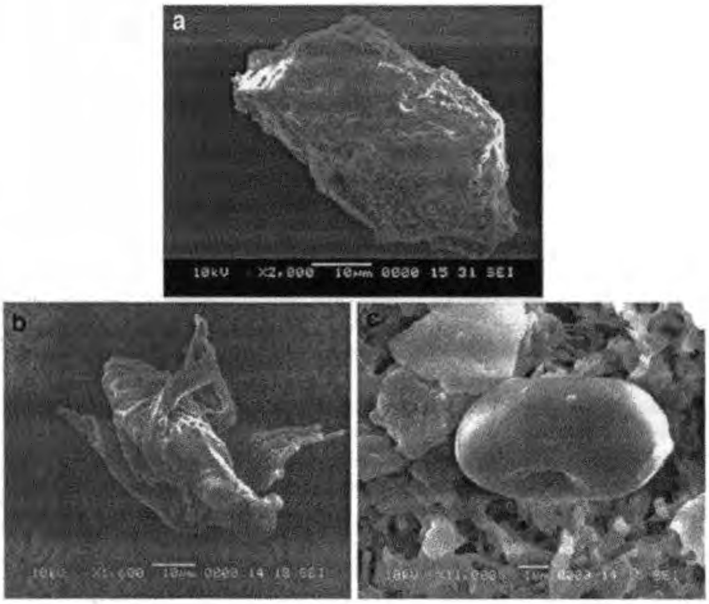

Fig. 6 SEM images of calcium containing carbonaceous particle (**a**) and unusually shaped organic debris found in ice (**b**). Spherical object with a depression at the center; probably a radiolarian with an organic coat (**c**)

dust (tephra) trapped in accreted ice (Fig. 5b and c). Microbial attachments to surface of substratum is a well-established mechanism for survival and sustainability of life in the frozen environments since these dusts have an important role in changing ecosystems by feeding, sheltering and limiting biological activities (Fung et al. 2000; Deming and Baross 2000; Carpenter et al. 2000; Rothchild and Mancinelli 2001). Nano-scale objects are hypothesized as fossilized microbes, both in terrestrial and extra-terrestrial rocks, including Martian meteorite ALH84001 (McKay et al. 1996) and Tataouine meteorite (Benzerara et al. 2003). The occurrence of nano bacteria (Fig. 5b) in conjunction with microbes (Fig. 5d) in our samples suggests that the former may not be a fossilized form; rather it is a unique group with their morphologies bearing relationship to the extreme environments. It is also possible that these nanobes and microbes got adhered to the volcanic dust during their transport within the atmosphere or while deposition of particles. Nanobes are documented for their role in altering the geochemistry of volcanic particles (Folk and Rasbury 2002). These tiny living entities together with the particles on which they are adhered, could provide a significant micro-niche in accreted ice, hitherto thought.

Carbonaceous particles

The EDS analysis showing particles rich in carbon are represented as carbonaceous particles. These particles are further classified into two groups; one enriched in both carbon and calcium (Fig. 6a) and the other containing 100% carbon (purely organic; Fig. 6b and c). Several of these forms found in this study clearly resembled the anomalous form reported by NASA scientists from Vostok ice cores (http://science.msfc.nasa.gov), although a detailed analysis is required to identify their origin and implications. These bodies do not represent any individual microbes, but might have been derived from organic detritus or pieces of larger multi-cellular organisms. Some of the strange forms resembling cotton balls or coiled coir do not represent a new organism, instead their age and habit might have resulted in their unusual shapes. The ice core may represent biological forms such as fungi, Bacteria, algae or diatoms. More detailed investigations could throw light into the importance of environmental changes in the distribution of these particles.

Conclusion

The SEM–EDS studies of micro-particles and presence of anomalous sulphate in the ice core supports their origin from volcanic eruptions and could be useful as a stratigraphic marker horizons. The continental dust particles observed in the ice core at certain intervals could suggest local inputs from ice-free areas and nunatak related to the prevailing wind pattern. The characterisation of the accreted particles in the ice by morphological and chemical means provide preliminary information on the origin and mechanism by which these particles are transported to Antarctica. We report here that tephra related to Agung (1963) and Karkatau (1883) volcanic eruptions harbor microbial cells (both cocci and rods). It appears that a plethora of microscopic and sub microscopic living entities with peculiar adaptive strategies are often entrapped in the ice. The geochemical signature revealed by volcanic and continental dust particles could be extended to minor and major elements, thereby allowing more accurate evaluation of their provenance.

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