Chemodynamics of Heavy Metals in Cochin Estuary and its Adjacent Coast

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Ph.D. Thesis under the Faculty of Marine Sciences

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DEPARTMENT OF CHEMICAL OCEANOGRAPHY

കൊച്ചി ശാസ്ത്ര സാങ്കേതിക സർവ്വകലാശാല

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Certificate

This is to certify that the thesis entitled ***“Chemodynamics of heavy metals in Cochin estuary and its adjacent coast”*** *is an authentic record of the research work carried out by Mrs. Bindu K.R., under my supervision and guidance at the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, Kochi-682016, in partial fulfillment of the requirements for Ph.D. degree of Cochin University of Science and Technology and no part of this has been presented before for any degree in any university. I further certify that all the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral Committee of the candidate have been incorporated in the thesis.*

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Declaration

I hereby declare that the thesis entitled **"Chemodynamics of heavy metals in Cochin estuary and its adjacent coast"** *is an authentic record of the research work carried out by me under the guidance and supervision of Dr. N. Chandramohanakumar, Professor, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, and no part of this has previously formed the basis of the award of any degree, diploma, associateship, fellowship or any other similar title or recognition.*

Kochi-16 **Bindu K.R.**
October-2015

Dedicated to ....

My Parents, Sister & Daughter...........

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Preface

Estuaries and coasts are transitional zones which transfer dissolved and particulate contaminants from land to the ocean. Estuaries and coastal areas are extremely vulnerable to pollution as they are generally heavily populated. Over emphasis on economic development and difficulties in implementing existing environmental regulations resulted in the pollution of water resources. Quality deterioration of coastal environments is a major issue around the world as they are the downstream recipients of terrestrial environment degradations. Like any other thickly populated coastal systems in the world, Cochin estuary is also under heavy anthropogenic pressures. Eloor, industrial area lying towards the north of Cochin estuary has been rated as one of the most toxic hotspots (1999 & 2003) of the world by Green Peace International. Recognizing its socioeconomic importance, Cochin estuary has been included in the list of vulnerable wetlands to be protected in the Ramsar Convention in 2002 (Name: Vembanad-Kol Wetland System, No. 1214).One of the major threats faced by Cochin estuarine and coastal systems is the heavy metal pollution. Industrial, municipal and agricultural sources were reported to contribute to the metal contamination in Kochi.

There are many reports on sedimentary heavy metal levels of Cochin estuary and its adjacent coast separately. However, an integrated study on heavy metal distribution among the different compartments in the estuarine and adjacent coast is rare. Despite the huge anthropogenic pressure in the Cochin Estuary, very few studies have been carried out so far on assessing the influence of the estuary on the heavy metal status of the nearshore environment. Understanding the processes that control the distribution, transport and fate of metal contaminants is an important aspect of protecting the environment. The thesis entitled “Chemodynamics of heavy Metals in Cochin Estuary and its Adjacent Coast” is an integrated analysis of dissolved, particulate and sedimentary heavy metals in the Cochin estuary and its adjacent coast which are vulnerable to the pollution by the industrial belt of Greater Cochin. An attempt was also done to assess the degree of pollution and sediment toxicity based on biological effects data.

The thesis has been divided into 5 chapters:

Chapter 1 gives an introduction to the topic, estuarine and coastal systems, environmental issues like pollution faced by these systems, previous research works carried out in the present study area. The limitations of previous works, the aim, scope and objective of the present study is also mentioned in this chapter.

Chapter 2 provides the description of the study region, methods adopted for sample collection and analyses of water, suspended particulate matter and sediment samples. The precision and accuracy of metal analyses, statistical methods adopted for data interpretation, indices like enrichment factor (EF), contamination factor (CF), degree of contamination (C_d), modified degree of contamination (mC_d), pollution load index (PLI) and geoaccumulation index (Igeo) for assessing pollution status and effect based sediment quality guidelines (ERL/ERM and TEL/PEL) are also mentioned in this chapter.

Chapter 3 characterises the system based on the spatiotemporal distribution of general hydrographical and sedimentological parameters. Hydrographical parameters dealt with are temperature, pH, dissolved oxygen, salinity, phosphate-P, nitrite-N, nitrate-N, ammonia-N, silicate-Si, chlorophyll 'a' and suspended sediments and sediment characteristics like Eh, pH, total carbon, total phosphorus, total nitrogen and total sulphur, Biochemical composition of the organic matter is also elaborated in this chapter.

Chapter 4 deals with the temporal and spatial distribution of dissolved and particulate heavy metals. Factor and cluster analysis were applied to find out the factors affecting heavy metal distribution and to group the sampling stations based on similarity in the analysed parameters respectively.

Chapter 5 deals with the temporal and spatial distribution of heavy metals in the sediments of Cochin estuarine and coastal systems. Statistical methods like principal component analysis to find out the factors affecting the heavy metal behaviour, Cluster analysis which groups the sampling stations based on the metals and other geochemical variables are also applied in data analysis and interpretation.

Chapter 6 deals with assessment of degree of metal contamination in the sediments by using various indices like enrichment factor, contamination factor, degree of contamination, modified degree of contamination, pollution load index and geo- accumulation index. This chapter also assesses the chronological enrichment of heavy metals in the Cochin estuary and it also compares the toxic metal levels in this system with other globally impacted coastal systems. Toxicity associated with the metals in the sediment to the aquatic organisms in the region is assessed using effect based sediment quality guidelines. Adsorption analysis has been done to find out the maximum adsorption capacity of the sediments in order to get an idea, to what extend these sediments will further adsorb heavy metals.

A summary is given at the end of the thesis followed by list of publications.

References are provided at the end of each chapter.

Contents

List of Abbreviations

Pre-M : Pre-monsoon
Mon : Monsoon
Post-M : Post-monsoon
TC : Total Carbon
TP : Total Phosphorus
TN : Total Nitrogen
TS : Total Sulfur
TOC : Total Organic Carbon
TOM : Total Organic Matter
DO : Dissolved Oxygen
CHO : Total Carbohydrates
LPD : Total Lipids
PRT : Total Proteins
BPC : Biopolymeric carbon
TAN & LIN : Tannin & Lignin
BDL : Below Detectable Limits
NS : Not Significant
PCs : Principal Components
PCA : Principal Component Analysis
CA : Cluster Analysis
ANOVA : Analysis of Variance
SPSS : Statistical Package for Social Sciences
EF : Enrichment Factor
C_d : Degree of contamination
mC_d : Modified Degree of contamination
CF : Contamination Factor

Igeo	:	Geoaccumulation Index
PLI	:	Pollution Load Index
SQGs	:	Sediment Quality Guidelines
ERL	:	Effects Range Low
ERM	:	Effects Range Medium
TEL	:	Threshold Effects Level
PEL	:	Probable Effects Level
TU	:	Toxic Units

Chapter 1

INTRODUCTION

Contents

Coastal ecosystems are the highly productive and highly threatened ecosystems in the world. Anthropogenic pressures on coastal resources compromise the delivery of many services provided by the ecosystem which are crucial to the well-being of coastal community and national economy. Over emphasis on economic development and difficulties in implementing the existing environmental regulations in the country led the water resources to severely polluted condition. In spite of the services provided by the coastal systems which contribute to the well-being of mankind, they are over exploited and are becoming increasingly vulnerable to anthropogenic pressures. Population density in coastal areas is close to 100/km^2 compared with inland densities of 38/km^2 in 2000 (Rashid *et al.,* 2005). Growth of human population accompanied by industrialization, unscientific agricultural practices, deforestation, uncontrolled and unscientific tourism activities and increased domestic sewage have resulted in contamination of the aquatic environments with organic and inorganic contaminants. The role of rivers in transporting material from continents to oceans is paramount, being 10 times that of glaciers and 100 times that of wind (Goldberg, 1976). As an estuary act as a bridge between the land and ocean, they transfer contaminants to the ocean. Usually, majority of sediment transported to the coast is suspended load (90–99 %), with relatively minor amounts as bed load (Syvitski *et al.,* 2000). Estuaries and continental shelf areas comprise 5.2 % of the earth surface, and 2 % of the oceans' volume (Koukina *et al.,* 2011). In spite of this low area, they carry disproportionate anthropogenic load. These pollutants have the potential to degrade the aesthetic and chemical quality of the water and have deleterious effects on aquatic organisms and hence human health through bioaccumulation and magnification through the food chain (Kennish, 1997).

1.1 Estuaries and Coastal Systems

Estuaries and their adjacent coastal areas are among the most productive areas in the world due to the delivery of land-derived and up-welled nutrients. Coastal waters supply about 90 % of the global fish catch (Wolanski *et al.,* 2004). They contribute ~ 20 % of the total oceanic primary production even though they comprise only 1.2 % of the total oceanic area (Smith, 1981; Charpy and Sournia, 1990). Estuaries serve as important interfaces between rivers and the coastal ocean where inputs of terrestrial materials can be significantly modified and recycled before entering the coastal zone. Except in large deltaic regions, the hydrological forcing to the coastal zone in estuaries is significantly reduced and the residence time is higher, allowing for more recycling of materials (Wollast, 1983). Estuaries represent one of the most important transport paths for the transfer of sediment between land and ocean systems. The role of the estuaries and other coastal ocean environments as global sources/sinks of key greenhouse gases, like CO_2 are reported by many researchers (Frankignoulle *et al.,* 1996; Cai and Wang, 1998; Raymond *et al.,* 1997; Raymond *et al.,* 2000; Cai, 2003; Wang and Cai, 2004; Cai *et al.,* 2004; Borges, 2005). Export of carbon from mangroves in tropical and subtropical estuaries contributes significantly to CO_2 emissions in the coastal ocean (Borges, 2005).

About 60 % of the world population lives along the coastal margin (Alongi, 1998; Lindeboom, 2002). Coastal systems especially estuaries are facing numerous pressures which include physical/chemical transformations, habitat destruction and biodiversity modifications (Halpern *et al.,* 2007; Halpern *et al.,* 2008) due to land reclamation, dredging, unmanaged tourism, introduction of alien species, climate change and pollution through increased sediment discharges, litter, oil-spills, organic and inorganic chemicals, nutrients etc. (Halpern *et al.,* 2007). Rapid increase of human population along the coastal regions and the consequent land-use changes has greatly impacted the stability of our coastal areas, the largest impact being the modification to the global flux of sediment to these coastal zones. Most of the 20×10^9 T of global suspended sediment transferred each year passes through estuarine environments generating concentrations in excess of 1,000 mg/dm^3 (Uncles *et al.,* 2001). Human interventions like construction of dams and reservoirs in the feeding rivers have modified the magnitude and temporal patterns of freshwater flow and sediment discharge to estuaries.

Quality deterioration of coastal environments due to the increased population is a major issue around the world as they are the downstream recipients of terrestrial environment degradations. Discharge to the ocean from modern rivers is reported to be strongly influenced both by paleo-conditions within the watershed and by human perturbations (Hay, 1994; Milliman and Syvitski, 1992). Nutrient enrichment (eutrophication) is reported to be the most widespread problem in estuaries (Howarth *et al.,* 2000; Howarth *et al.,* 2002; Rabalais and Turner, 2001; Rabalais and Nixon, 2002). Pollutants which have the greatest impact on aquatic environment are toxic chemicals and heavy metals. Disposal of untreated/improperly treated industrial effluents to the coastal systems is becoming a subject of great concern. Uncontrolled/unscientific use of insecticides, herbicides and organic manures in agricultural lands enter the nearest aquatic systems and finally to the coastal systems. Toxic chemicals get accumulated in bottom-dwelling animals like oysters or clams, making them a serious health risk to people who eat them. Introduction of non-native or invasive species of plants/animals drastically reduce the populations of native species and cause their extinction in some cases. Incidence of disease, emergence of new pathogens and human health consequences due to coastal degradation were reported (NRC, 2000; Rose *et al.,* 2001). Disposal of sewage, slaughterhouse and seafood-processing wastes, phosphates and nitrates from detergents and fertilizers and livestock wastes are also contributing to the degradation of coastal aquatic environments.

1.2 Heavy Metals

Heavy metals play major roles as regulators of oceanic processes including marine ecosystem dynamics and carbon cycling. Many of them have crucial roles in ecosystem functioning and so their supply controls the structure and possibly the productivity of marine ecosystems. Heavy metals like Fe, Co, Zn, Cu and Ni serve as essential micronutrients (Table 1.1) whose availability influences the physiological state and biochemical activity of aquatic organisms and some heavy metals (Cu, Zn, Co, Cd and Mn) are very significant in controlling biogeochemical processes (Morel *et al.,* 2003; Morel and Price, 2003).

Table 1.1 Classification of metals based on characteristics of health effects

Nutritionally Essential Metals	Metals with Possible Beneficial Effects	Metals with No Known Beneficial Effects
Cobalt	Nickel	Cadmium
Copper		Lead
Iron		
Manganese		
Zinc		
Chromium-III		

Non-essential metals like Cd and Pb have no known nutritional, biochemical or physiological functions in organisms. Usually the essential metals will be depleted in ocean surface waters and most of them are chelated by organic ligands. It is the unchelated metal fraction, which is usually present in small amounts, that is biologically available (Bruland and Lohan, 2003). Essential metals like Zn, Ni and Co are important components of enzymes that carry out various functions of metabolism. Zinc is the most predominant metal in the enzyme carbonic anhydrase, which catalyze the transformation of HCO_3^- to CO_2; enzyme alkaline phosphatase, which is necessary for phytoplankton to be able to use dissolved organic phosphorus during growth. Ni is a part of the enzyme urease, which is required for phytoplankton to utilize urea as a nitrogen source. Cu is labelled a ‘‘Goldilocks’’ metal because it is necessary for growth of cyanobacteria in seawater. Iron is also an integral part of enzymes that are necessary for many of the transformations among the nitrogen compounds.

However, these essential metals are highly toxic at elevated concentrations and they are non-biodegradable. It is the availability of metals, and especially of Cu, which is of more significance than its total concentration. It is the bioavailable fraction of the metals which pose threat to the aquatic inhabitants. Concentrations of the metals determine whether the metals exert beneficial or harmful effects on plant, animal and human life (Forstner and Whittman, 1981). Metals taken up by the aquatic organisms will get bioaccumulated and biomagnified and transferred through the food web. In this aspect, non-essential metals like Cd and Pb will be dangerous and even the lowest concentrations, on continuous exposure will result in bioaccumulation. Metal distribution among the different tissues of an organism depends on the mode of exposure and this can serve as a pollution indicator (Maheswari *et al.,* 2006). In humans, cadmium may cause skeletal damage, kidney dysfunction and reproductive issues (Commission of the European Communities, 2001). Zinc has significant enzymatic, regulatory and structural roles in most biological systems. However, toxicity of zinc will result in muscular stiffness and pain, irritability, loss of appetite and nausea. Although Co is an essential metal, exposure to high levels can result in heart and lung defects and dermatitis (Agency for Toxic Substances and Disease Registry, 2004). According to Commission of the European Communities (2001), Pb induces reduced cognitive development and intellectual performance in children and decreased haemoglobin synthesis, increased blood pressure and cardiovascular disease in adults. Along the west coast of India, food chain bioaccumulation of metals from the enhanced bioavailability of metals in upwelled waters has been reported (Rejomon *et al.,* 2010).

Anthropogenic activities contribute to increased addition of heavy metals and oceanic cycle of many of them has been significantly impacted. Municipal wastewater discharges, sewage sludge, industrial effluents etc. are the primary sources of these heavy metals in the environment. Mining and mineral processing, combustion of fossil fuels and fuel additives, electroplating, dyes, fertilisers, pesticides pigments etc. are other sources of these metals.

1.2.1 Metals in Aquatic Systems

Metals in the aquatic system are partitioned between the sediments, suspended particulate matter and the soluble phase and their partition coefficients vary with metals, sites and time because of the complex nature of the water chemistry that affect the partitioning of metals (James, 2002). The metal concentration depends on the redox condition, pH, ionic strengths and scavenging activity. The ecological impact of metals mainly depends on their aquatic species, complexation with dissolved organic matter, sedimentation and bioaccumulation. Several generic types of processes contribute to the removal of heavy metals from water and their burial in marine sediments. The simplest is the passage of land derived particles through the water column, without any further solid-solution reaction. Heavy metals bound within aluminosilicate minerals are included in this category. Abiological solid-solution exchange reactions like adsorption and complexation and incorporation of metals into particles by the organisms are also other transport processes. A fraction of these elements delivered to the bottom by sinking particles is preserved and buried in sediments. Dissolved metals in the bottom waters may also be removed by direct sorption to surface sediments (Nozaki, 1986). Finally, precipitation in pore waters removes some dissolved metals that diffuse into the sediments from the overlying water column. This reaction is important for redox-sensitive metals like U, Mo, V and Re that are soluble in the presence of oxygen and insoluble in anoxic conditions in the sediments (Crusius *et al.,* 1996). $Fe(OH)_3$ and MnO_2 also influence the heavy metal deposition and distribution in sediments (Jenne, 1968; Botte *et al.,* 2010; Sundaray *et al.,* 2011). The oxy-hydroxide layers restrict the flux of heavy metals from the sediment to the above oxic bottom water and so the Fe–Mn cycling in the suboxic sediment enriches many heavy metals in the surface sediments (Ingri *et al.,* 2014).

Concentrations of metals vary as a function of prevailing redox potential in anoxic conditions. Elements like Cu, Cr, Co, Zn, Ni, V and Mo, which are soluble in oxic condition, will be reduced to insoluble species under suboxic/anoxic conditions, where consumption of oxygen will be more than the supply. Thus, the behavior of the above metals can be used as indicator of sediment deposition under different environmental conditions (Calvert and Pederson, 1993).

1.2.2 Assessment of Heavy Metal Pollution

Adsorption of heavy metals on suspended particulate matter (SPM) and bottom sediments is an important process which control dissolved metal concentrations, bioavailability and toxicity to biota and both the fate and transport of heavy metals (Jannasch *et al.,* 1988; Comber *et al.,* 1996). The distribution coefficient, Kd is used normally to quantify heavy metal mobility in sediments. Batch adsorption experiments can be used to understand the partitioning of metals among the dissolved and particulate phases. Information from adsorption experiments on metal adsorption capacity can be used to estimate the maximum immobilization of heavy metals in the aquatic environment. This will be helpful in making management decisions as it give a rough idea to which extent these sediments will further adsorb toxic heavy metals.

Principal component analysis (PCA) is commonly used to find out the possible geochemical parameters which contribute to the metal distribution and their source apportionment. Cluster analysis (CA) can be used to cluster the sampling stations based on similarities (Raghunath *et al.,* 2002; Simeonov *et al.,* 2003; Singh *et al.,* 2004; Valdes *et al.,* 2005; Sundaray *et al.,* 2006; Sundaray, 2009; Deepulal *et al.,* 2012a; Hu *et al.,* 2015; Bindu *et al.,* 2015, Dang *et al.,* 2015). These multivariate statistical techniques are used for a meaningful data reduction and interpretation.

Assessment of degree of pollution using various indices like enrichment factor, contamination factor, geoaccumulation index, pollution load index etc. are in common practice nowadays (Ergin *et al.,* 1991; Crane, 2003; Adamo *et al.,* 2005; Fianko *et al.,* 2007; Paneer Selvam *et al.,* 2012; Deepulal *et al.,* 2012a; Zhuang and Gao, 2014; Bindu *et al.,* 2015). These indices will give an idea about whether the metal accumulation is from natural or anthropogenic sources.

Effect based toxicity assessment is considered as a natural and logical extension of programme dedicated to evaluating environmental quality. Many studies have been conducted to evaluate the biological effects associated with the heavy metal sediment contamination in marine and estuarine ecosystems (Carr *et al.,* 1996; Volpi Ghirardini *et al.,* 2005; Anderson *et al.,* 2007). Sediment Quality Guidelines (SQGs) have been used by many researchers as a general measure of contamination (MacDonald, 1994; MacDonald *et al.,* 2000; Thompson *et al.,* 2005; McCready *et al.,* 2006; Zhang *et al.,* 2007; Abrahim *et al.,* 2007; Zhuang and Gao, 2014). India has not formulated such a guideline to assess the contamination and so the guidelines set by US National Oceanic and Atmospheric Administration (NOAA) were used as temporary measures to assess whether the concentrations of metals in the sediments could have adverse biological impacts. These SQGs have been adopted as an informal benchmark to evaluate chemical sediment data in relation to possible adverse effects on aquatic biota. Effect Range Low (ERL) and Threshold Effects Level (TEL) are the concentrations below which adverse effects on sediment dwelling fauna would rarely be expected whereas, Effects Range Medium (ERM) and Probable Effects Level (PEL) values represent the chemical concentrations above which adverse effects are likely to occur.

1.3 Previous Studies in Cochin Estuary and Adjacent Coast

The Cochin estuary is the largest estuarine system in the southwest coast of India covering an area of 256 km^2 (Gopalan *et al.,* 1983). This highly productive wetland system is a major source of livelihood to the local community who depends on it for fishes, agriculture, coconut husk retting, sand, clay and lime shell mining, transport of passengers during the early time. This wetland system is famous for its fish and shellfish resources, Pokkali cultivation and associated prawn culture, clam shell deposits etc. Increased discharge of municipal and industrial effluents into the aquatic environments is a major issue faced by Kochi City. Also, development related loss of habitats and services are other major threats to the coastal system. Deforestation of mangroves, modification of coastal marshes and other intertidal habitats by dredging and filling operations, unscientific agricultural practices also contribute to the pollution and to the general quality deterioration of this coastal environment.

Numerous multidisciplinary studies have been undertaken in the Cochin Estuary during past several decades. The reduction in the carrying capacity of the backwaters, natural habitat destruction and disruption in the life cycle of organisms, accumulation of various pollutants, salinity intrusion, symptoms of eutrophication, over exploitation and dwindling of resources etc. stress the need for the routine monitoring and conservation of the ecosystem. Investigations carried out over the last few decades pointed to the unfavourable changes in the hydrodynamic (Madhupratap *et al.,* 1977; Joseph and Kurup, 1990; Balachandran, 2001; Revichandran *et al.,* 2012) and hydrobiological conditions (Qasim, 1980; Lakshmanan *et al.,* 1982; Menon *et al.,* 2000; Joseph and Ouseph, 2009; Martin *et al.,* 2013) of the Cochin estuary. The influx of large amount of allochthonous organic matter into the Cochin estuary has been reported in many previous studies (Saraladevi *et al.,* 1983; Thomson, 2002; Balachandran *et al.,* 2003; Babu *et al.,* 2006; Thottathil *et al.,* 2008; Martin *et al.,* 2010). Very high concentrations of dissolved organic carbon (480 µM), particulate organic carbon (320 µM) and particulate nitrogen (40 µM) have been reported in the estuary (Martin *et al.,* 2010).

Organic wastes from southern aquaculture fields (62km^2), agricultural fields (80km^2) and coconut retting yards have also been reported to contribute to the alarming pace of organic pollution (Thomson, 2002; Babu *et al.,* 2006; Martin *et al.,* 2010).

Some of the important works worth mentioning are Ramamritham and Jayaraman, 1963; Qasim and Reddy, 1967; Sankaranarayanan and Qasim, 1969; Murthy and Veerayya, 1972; Joseph, 1974; Saraladevi *et al.,* 1979; Lakshmanan *et al.,* 1982; Gopalan *et al.,* 1983; Sankaranarayanan *et al.,* 1984; Sankaranarayanan *et al.,* 1986; Saraladevi, 1986; Lakshmanan *et al.,* 1987; Joy *et al.,* 1990; Nair *et al.,* 1990; Paul and Selvaraj, 1993; Revichandran *et al.,* 1993; Balchand and Nair, 1994; Nair *et al.,* 1994; Balachandran *et al.,* 1996; Beenamma Jacob and Chandramohanakumar, 1996; Rasheed, 1997; Thresiamma *et al.,* 1998; Sheeba, 2000; Srinivas, 2000; Unnikrishnan and Nair, 2004; Laluraj *et al.,* 2005; Babu *et al.,* 2006; Geetha *et al.,* 2006; Srinivas and Dinesh Kumar, 2006; Renjith, 2006; Madhu *et al.,* 2007; Laluraj *et al.,* 2007; Narayana *et al.,* 2007; Paul and Cvetkovic, 2007; Priju and Narayana, 2007; Renjith and Chandramohanakumar, 2007; Sreedevi, 2007; Laluraj *et al.,* 2008; Balachandran *et al.,* 2008c; Miranda *et al.,* 2008; Martin *et al.,* 2008, Martin *et al.,* 2010, Martin *et al.,* 2011; Martin *et al.,* 2012; Padmalal *et al.,* 2008; Shoji *et al.,* 2008; Antony Joseph *et al.,* 2009; Gupta *et al.,* 2009; Sujatha *et al.,* 2009; Madhu *et al.,* 2010; Renjith *et al.,* 2011; Revichandran *et al.,* 2011; Deepulal *et al.,* 2012a; Deepulal *et al., 2012b*; Ammini Parvathi *et al.,* 2013; Dipu and Anju, 2013; Shivaprasad *et al.,* 2013a; Shivaprasad *et al.,* 2013b; Nair *et al.,* 2013; Bindu *et al.,* 2015.

The chemical oceanographic features of Arabian Sea have been explored by many researchers (Banse, 1959; Reddy and Sankaranarayanan, 1968; Sen Gupta *et al.,* 1980; Naqvi *et al.,* 1993; Naqvi *et al.,* 2000; Naqvi and

Jayakumar, 2000; Jyothibabu *et al.,* 2008; Thresiamma *et al.,* 2008; Balachandran *et al.,* 2008a; Balachandran *et al.,* 2008b). According to Ramaswamy (1987), along shelf transport appears to be the more dominant mechanism for sediment transport on the Western continental shelf of India rather than the cross shelf transport. 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 has been reported by Hashimi *et al.* (1981). Anthropogenically-derived pollutants, associated with clay particles discharged from the coast, tend to remain within the narrow confines of the inner continental shelf (Ramaswamy and Nair, 1989). Reddy and Rao (1992) observed differential wave activity together with static mud suspension at places in the nearshore region.

Heavy metals are the major among the pollutants posing threats to the Cochin estuary. Environmental quality degradation of Cochin estuary and coastal areas due to the heavy metal pollution have been reported by many researchers (Balachandran, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Martin *et al.,* 2012; Bindu *et al.,* 2015). Due to the weak flow and the huge inputs of effluents from the industries, higher levels of heavy metals were reported in the northern estuary (Shibu *et al*., 1990; Unnikrishnan and Nair, 2004; Balachandran *et al*., 2005). Mahesh Mohan *et al.,* (2012) reported increased bioavailability of toxic metal Cd in the estuary. Heavy metal pollution resulted in emergence of resistance strains in Cochin estuary due to reduction/adaptation of bacterial distribution, diversity and enzyme expression profile and this is proportionate to the extent of pollution (Jiya *et al.,* 2011).

Few studies were reported on partitioning of heavy metals among the dissolved and particulate phases in Cochin estuary (Nair *et al.,* 1990; Nair *et al.,* 1991; Ouseph, 1992; Suraj *et al.,* 1996; Unnikrishnan *et al.,* 2000;

Unnikrishnan and Nair, 2004; Balachandran *et al.,* 2005; Robin *et al.,* 2012; Nair *et al.,* 2013). In last two decades, studies on the heavy metal content of Cochin estuary indicated enrichment of these metals in the sediments (Sujatha *et al.,* 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Ratheesh Kumar *et al.,* 2010; Sudhanandh *et al.,* 2011; Deepulal *et al.,* 2012a; Martin *et al.,* 2012; Paneer Selvam *et al.,* 2012; Mahesh Mohan *et al.,* 2012; Dipu and Anju, 2013; Bindu *et al.,* 2015).

Metal fractionation studies of Cochin estuary and adjacent coast have been carried out by Shibu *et al.* (1990); Nair (1993); Rajamani (1994); Shibu *et al. (*1995); Joseph (2002); Mahesh Mohan *et al.* (2012); Manju and Sujatha (2013a). According to Mahesh Mohan *et al.* (2012), Cd was found to be weakly bound to sediments in comparison to other metals resulting in increased bioavailability in the Cochin estuary. Salt induced adsorption/desorption mechanism for trace and rare-earth elements in Cochin Estuary and adjacent coast has been reported by Nath *et al.,* 2000; Laluraj, 2009 and Deepulal *et al.,* 2012b. Nath *et al.* (1997) studied the trace and rare earth elemental variation in Arabian Sea across the oxygen minimum zone (OMZ).

Few studies are there on assessment of degree of pollution using pollution indices in Cochin estuary (Harikumar *et al.,* 2009; Deepulal *et al.,* 2012a; Paneer Selvam *et al.,* 2012; Mahesh Mohan *et al.* (2012); Martin *et al.,* 2012; Shaiju, 2013; Manju *et al.,* 2014; Bindu *et al.,* 2015) which reported enrichment and higher degree of pollution by heavy metals in the estuary. Effect based toxicity assessment in Cochin estuary was carried out by Harikumar *et al.* (2009); Martin *et al.* (2012), Mahesh Mohan *et al.* (2012); Shaiju (2013) and Manju and Sujatha *(*2013b) which suggested metals like Cd, Zn and Ni were in higher levels when compared to the sediment quality guidelines.

Many studies on heavy metals in water and sediments in Arabian Sea have been reported (Prakash Babu and Nath, 2005; Kaladharan *et al.,* 2005; Balakrishnan *et al.,* 2005; Laluraj and Nair, 2006; Rejomon *et al.,* 2008). Earlier studies on the geochemistry of sediments along the central southwest coast of India are limited with only very few samples to represent the environment (Murthy *et al.,* 1973; Rao *et al.,* 1974; Rajamani, 1994; Nath *et al.,* 2000; Balachandran *et al.,* 2005; Laluraj and Nair, 2006). These kinds of studies will be meaningful only when the number of sampling stations are high and cover all the seasons as these coastal regions are highly influenced by the seasonal signals. Analysis of the literature showed that the integrated analysis of dissolved, particulate and sedimentary heavy metals in the Cochin estuary and its adjacent coast are rare although these systems are vulnerable to the pollution by the industrial belt of Greater Cochin.

1.4 Aim and Scope of the Study

Heavy metals act as regulators of oceanic processes like marine ecosystem dynamics and carbon cycling (Henderson *et al.,* 2007). Several heavy metals also play vital roles in ecosystem functioning and therefore control the structure and probably the productivity of marine ecosystems. The cycle of many heavy metals has been significantly impacted by human activities. Some of these are harmful to the environment, even in low concentrations, due to their toxicity. Understanding the processes which control the transport and fate of these pollutants is an important aspect in protecting the environment. This requires precise knowledge of the natural biogeochemical cycling of the heavy metals so that changes due to anthropogenic activities can be put in context.

Many studies on sedimentary heavy metal assessment have been done so far in the Cochin estuary and southwest coast of India. Although in less numbers compared to the estuary, nearshore sedimentary metal studies were also reported. But, an integrated study of dissolved, particulate and sedimentary heavy metals in the estuarine and adjacent coast was rarely reported. Study on the influence of the estuary on the coastal metal levels is also essential in the context of heavy anthropogenic addition of metals into Cochin estuarine system.

This study is to investigate the spatio-temporal fluxes of dissolved, particulate and sedimentary heavy metals, pollution assessment using various indices, toxicity assessment using effect based sediment quality guidelines and assessment of maximum adsorption capacity of the sediments both in the estuary and its adjacent coast. Together with strengthening and supplementing existing database, the current study will also help spearhead designing of action plans for effective and sustained management of Cochin estuarine system.

1.5 Objectives of the Study

The main objectives of the study are highlighted as:

1. To characterise the study area using general hydrological and sedimentary parameters and to assess the source and quality of sedimentary organic matter, a key parameter influencing heavy metal accumulation.
2. To investigate the spatial and temporal distributions of dissolved, particulate and sedimentary concentrations of heavy metals and to compare the nature of accumulation in the estuarine and coastal environments.
3. To understand the partitioning of heavy metals between dissolved and particulate phases and hence to understand the processes of transport

and transformations of metals in different compartments of the aquatic system.

4. To assess the geochemical behaviour (processes and transport pathways) of heavy metals through principal component analysis and to cluster the sampling stations through cluster analysis based on the similarity in heavy metal distribution.
5. To assess the chronological enrichment of heavy metals in the study area and also to compare the heavy metal levels with that of other globally impacted coastal systems.
6. To assess the degree of heavy metal pollution by various pollution indices
7. To assess the toxicity of metals using effect based sediment quality guidelines.
8. To assess the adsorption capacity and intensity of the sediments through adsorption isotherms.

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Chapter 2

MATERIALS AND METHODS

Contents

2.1 Description of the Study Area

Cochin estuary was reported to be heavily polluted by the heavy metals (Balachandran, *et al.,* 2005; Martin *et al.,* 2012; Bindu *et al.,* 2015) through industrial and municipal sources. Coastal environment near this estuary will consequently be vulnerable to the changes associated with anthropogenic activities in the estuary. Pollutants carried over from the estuarine environment will get deposited along the coastal line as the dominance of along-shelf transport of sediments over cross-shelf transport restricts coastal inputs to the inner western continental shelf (Ramaswamy and Nair, 1989). In this context, the study area of the present investigation is divided in to two different environments, namely the Cochin estuarine and the adjacent coastal system which receives the anthropogenic pollutants through the estuary (Fig. 2.1).

Cochin estuary, which comes under the Ramsar site (No: 1214), Vembanad-Kol Wetland system, is the largest estuarine system in the southwest coast of India (Wetlands, 2002). It lies parallel to the coastline with several islands and small arms. The system is separated from the Arabian Sea by barrier spits which is interrupted by tidal inlets at two places, viz., Munambam (Azhikode) in the north and Cochin bar mouth in the middle. The cross-sectional area of the Cochin inlet is ~ 4,234 m^2 (Joseph, 1996) and that of Azhikode inlet is ~ 900 m^2 (Revichandran *et al.,* 1993). Cochin estuary is a bar-built micro tidal estuary, fed by 6 major rivers (Srinivas *et al.,* 2003a) viz. Pampa, Achenkovil, Manimala, Meenachil and Muvattupuzha in the south and Periyar in the north. These rivers along with their tributaries bring large volumes of fresh water in to the estuary. Nearly 33 % of these river discharges is from Periyar River. The percentage of contribution discharge are 24.2 %, 5.8 %, 19.70 %, 8.30 % from Muvattupuzha, Achenkovil, Pampa, Meenachil and Manimala respectively (Srinivas, 1999). The estuary is topographically divided into two arms; a southern one extending towards south of bar mouth from Cochin to Thanneermukkom and a northern one extending towards north from Cochin to Azhikode.

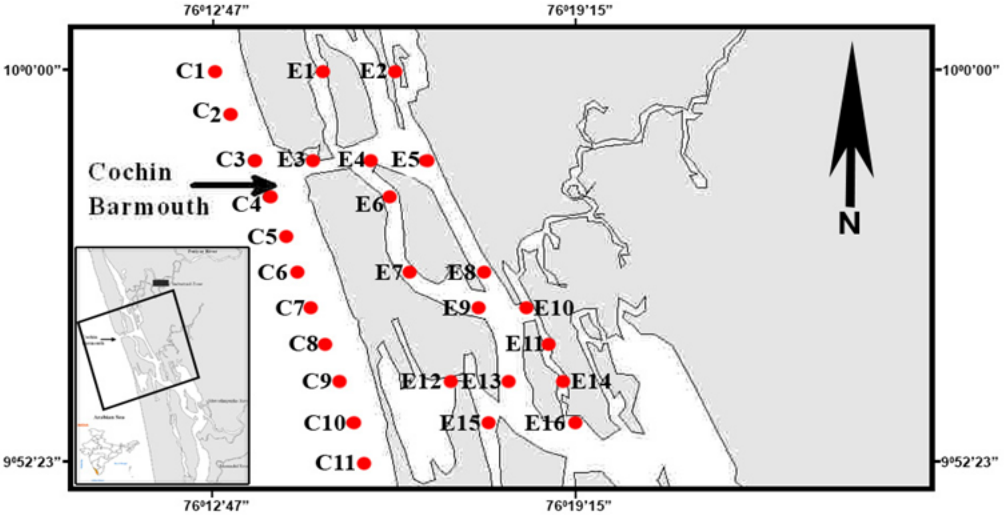

Figure 2.1 Study area showing sampling locations in the Cochin estuary and its adjacent coast

The estuary is generally wide (0.8–1.5 km) towards the south, but narrow (0.05–0.5 km) towards the northern region (Balachandran *et al.,* 2008). Depth of the estuary varies significantly from place to place and it ranges from

1 to 6 meters. However, the main channel is maintained at 10 to 12 meters for the navigational purposes. This estuary houses the second largest port in the south west coast of India and it has three dredged channel maintained at a depth of 10-13m. One approach channel having 10km length and 500m width, and two inner channels Ernakulam channel (5km length and 250-500m width) and Mattanchery channel (3km length and 170 - 250m width), situated on either side of the Willingdon Island (Menon *et al.,* 2000).

In general, the currents are dominated by semi-diurnal tides, which result in more swift currents than diurnal tides and these currents play a major role in bed-load transport (Srinivas *et al.,* 2003a). Spring tide range in the estuary is about 1meter (Srinivas, 1999). The tidal range progressively diminishes southward and northward of the Cochin bar mouth. Currents in the estuary are strongly rectilinear with a slack water at each reversal of direction which has important implications in the estuary as the settling of the finest fractions of sediments takes place at mid-tide (Srinivas *et al.,* 2003b). According to Priju and Narayana (2007) morphological history of the estuary indicated a settling environment.

The annual rain fall in the area is around 320 cm. Almost 75 % of the rainfall occurs during summer monsoon (June to September) and during the peak of this season, 40 to 50 cm rainfall in few hours was reported in this region (Qasim, 2003). During monsoon, the heavy rainfall in the area cause a drastic change in the salinity and a large part of the estuary shows a fresh water nature (Menon *et al.,* 2000). During non-monsoon, when the fresh water input is minimum, a salinity gradient develops and the lower reaches of the estuary act as a section of the Arabian Sea (Madhupratap, 1987; Menon *et al.,* 2000).

Based on the differential responses of this system to the propagation and excursion of tides and residual currents, the Cochin estuary can be generally classified into three zones (Balachandran *et al.,* 2008):

1. Central estuary, a dynamic zone located between Cochin inlet and Vaduthala. Effective flushing of this region is maintained by strong rectilinear currents.
2. Southern estuary, the region between Vaduthala and Thanneermukkom. The southern estuary experiences weak tidal currents due to the wide area and this region exhibits a tidal amplification during the closure of the hydraulic barrier at Thanneermukkom.
3. Northern estuary, area located north of the Cochin inlet. Tidal variations in the inlet and northern estuary are analogous. The weak flow in the northern area could be attributed to the synchronous tides which enter through the two inlets creating a null zone (Ramamirtham and Muthusamy, 1986).

Cochin backwaters is unique in terms of physiographic, geologic, climatic and hydrologic conditions and land use patterns. It is used extensively for inland navigation, tourism activities, fishing and other aquaculture practices. This tropical micro tidal positive estuarine system is one of the highly productive estuarine systems (Qasim, 2003). The estuary supports diverse species of flora and fauna. Mangrove patches around the estuary are nutrient rich environments which act as breeding places for many species of fishes, molluscs and crustaceans which are economically important (Menon *et al.,* 2000). The Cochin estuarine system sustained rich bio-resources in the pristine conditions, but has undergone ecological degradation due to increased urbanisation and industrialisation (Arun, 1998; Martin *et al.,* 2010).

The unplanned and unscientific developmental and economic activities for supporting the growing needs of increasing population exert great pressure on this aquatic system. Like any other major estuarine systems of the world, the Cochin estuary has been greatly impacted by anthropogenic activities like intertidal land reclamation, domestic and industrial effluent discharges, expansion for harbour development, dredging activities and urbanisation (Gopalan *et al.,* 1983; Menon *et al.,* 2000). Of 36,500 ha of backwater that existed in the middle of 19th century, only 12,700 ha (34.8 %) remains nowadays as open waters (Gopalan *et al.,* 1983). Recently, the estuary has been reclaimed for the infrastructural developments like Vallarpadam International Container Trans-shipment Terminal (ICTT). During the last two decades, the estuary received a heavy influx of anthropogenic nutrients, heavy metals and organic matter from the increased domestic sewage inputs, industrial effluents, unscientific agricultural activities and marine fish farming (Thomson, 2002; Qasim, 2003; Balachandran *et al.,* 2005).

According to the Government of India census 2011, Cochin city has a population density of approximately 6340 people/km^2. Sky-rocketing growth in population is accompanied by huge amount of domestic sewage. The industrial belt of the Greater Cochin situated on the either banks of Periyar River drains industrial effluents into the backwaters. The branch of Periyar River feeds 30 % of its runoff into the northern parts of the estuary and the remaining 70 % discharges directly into the Arabian Sea through the Cochin bar mouth. This establishes the influence of Periyar River in contributing the pollutants from its catchment area to the estuary and to the adjacent coast. Eloor industrial area lying in the northern estuary has been rated as one of the most toxic hotspots (1999, 2003) of the world by Green Peace International. The major industries in the northern area of the Cochin city are Caprolactum

Plant, Travancore Chemicals and Manufacturing Co. Ltd., Cominco Binani Zinc Ltd., Fertilizers and Chemicals Travancore Ltd. Udyogamandal, Hindustan Insecticide, Indian Rare Earth Ltd., Indian Aluminium Co. Ltd., Travancore Rayons Ltd., Catalysts and Chemicals Ltd., Hindustan Petroleum Ltd. and Tata Oil Mills Ltd. Large quantities of industrial effluents from these factories along with the discharges from the sewage treatment plant of Cochin city resulted heavy contamination of the northern part of the estuary. In the south, effluents from the factories like Fertilizers and Chemicals Travancore Ltd., Cochin division, Cochin Refineries Ltd., Hindustan Organic Chemicals Ltd. and Carbon and Chemicals Ltd. along with the agricultural land runoff contribute to the contamination.

The surface currents along the west coast of India are south to southeasterly (April to September) and northwesterly (November to January). The coastal zone of western India experiences upwelling during southwest monsoon (Ramasastry and Myrland, 1959; Banse, 1968; Naqvi *et al.,* 2000) and during this time, the Arabian Sea surface water is displaced by the upper subsurface water, resulting in a complete overturning in the entire water over the continental shelf (Ramasastry, 1959). Although, the coastal waters are found to be less productive in zooplankton standing stock compared to Cochin backwaters (Haridas *et al.,* 1980) sudden increase of zooplankton swarms as a result of upwelling were reported in the coastal waters (Madhupratap *et al.,* 1977 & 1980).

The shoreline along Cochin has been classified under barrier beaches. Prasannakumar and Murthy (1987) reported differential wave activity together with static mud suspension at places in the nearshore region. Due to the process of flocculation, nearshore sediments were dominated by clay-sized sediments (Hashimi *et al.,* 1981) and due to this, anthropogenically derived pollutants discharged from the coast, would tend to remain within the narrow boundaries of the inner continental shelf (Ramaswamy and Nair, 1989). Unique feature of the Kerala coast is the occurrence of mudbanks - areas of sea adjoining the coast, which have a special property of diminishing the waves resulting in clearly demarcated areas of calm turbid waters during the roughest monsoon period. Along the continental shelf in this coast, the nature of bottom about 3.5 to 18 m depth is largely muddy and due to the wave actions and rip currents during monsoon, the fine mud particles get churned up into a thick suspension which consistently absorb the wave energy (Udaya Varma and Kurup, 1969). Mudbanks are well known for their fishery during the monsoon months.

Cochin estuarine system is under the profound influence of the monsoon, which contributes to about 71 % of the annual rainfall (Jayaprakash, 2002; Qasim, 2003). The Cochin estuarine and adjacent coastal area were reported to experience two distinct regimes of alluvial loading, high loading during monsoon and silting during non-monsoon months which are associated with lean flow (Balachandran *et al.,* 2005). There are three seasonal conditions prevailing namely, pre-monsoon (February-May), monsoon (June-September) and post-monsoon (October-January). Based on this, three sampling periods have been selected for the present study.

The details of the sampling stations are given in the Table 2.1. From the estuary, 16 stations have been selected for the study. Selection criteria for the stations are following. Northern stations E1 and E2 are influenced by the northern industrial belt of Greater Cochin. As E3, E4, E6 and E7 are lying in the navigational channel, they will reflect the effect of dredging. E5 is almost a null zone (accumulation zone) due to the flow from northern and southern sides and tides from the bar mouth region results in stagnation of that area.

Table 2.1 Details of sampling stations

Area	Station Name	Longitude	Latitude
Coast	C1	76^0 12’ 47”	10^0 0’00”
	C2	76^0 13’ 04”	$9^0$59’11”
	C3	76^0 13’ 18”	$9^0$58’44”
	C4	76^0 13’ 33”	$9^0$57’38”
	C5	76^0 14’ 01”	$9^0$56’52”
	C6	76^0 13’ 45”	$9^0$56’04”
	C7	76^0 14’ 15”	$9^0$55’23”
	C8	76^0 14’ 30”	$9^0$54’46”
	C9	76^0 14’ 45”	$9^0$53’50”
	C10	76^0 15’ 00”	$9^0$53’00”
	C11	76^0 15’14”	$9^0$52’23”
Estuary	E1	76^0 14’ 37”	10^0 0’00”
	E2	76^0 16’00”	10^0 0’00”
	E3	76^0 14’ 20”	$9^0$58’44”
	E4	76^0 15’ 28”	$9^0$58’44”
	E5	76^0 16’ 16”	$9^0$58’44”
	E6	76^0 15’ 43”	$9^0$57’38”
	E7	76^0 16’ 09”	$9^0$56’04”
	E8	76^0 17’ 30”	$9^0$56’04”
	E9	76^0 17’ 26”	$9^0$55’23”
	E10	76^0 18’ 28”	$9^0$55’23”
	E11	76^0 18’ 36”	$9^0$54’46”
	E12	76^0 16’ 50”	$9^0$53’50”
	E13	76^0 17’ 51”	$9^0$53’50”
	E14	76^0 19’ 02”	$9^0$53’50”
	E15	76^0 17’ 30”	$9^0$53’00”
	E16	76^0 19’ 15”	$9^0$53’00”

E8 is near the shipyard and ship building and maintenance activities will be contributing to the heavy metal pool in the estuary. Southern stations are influenced by the agricultural activities. Station E10 is influenced by a tributary. E10, E11, E14 and E16 are far from the urban sources of pollution and are assumed to be free from heavy contamination. E9, E12 and E13 are influenced by the agricultural activities, boat building / maintenance activities and numerous fish processing units are situated near these southern stations. E15 is a shallow area near fish processing units with restricted exchange.

Eleven stations from the coastal area have been selected for the study. Stations were selected assuming that the stations just north and south (C1, C2 and C4) of the bar mouth will reflect the estuarine contribution of contaminants. Moreover, areas just south and north of the bar mouth were reported as the disposal sites of dredge spoil from the estuary (Balachandran, 2001). Station C3 in the navigational channel will reflect the effect of periodic dredging. Southern stations (C5-C9) will reflect the impact of estuarine input of contaminants as the dredge spoil was reported to spread around the region near Kannamali (Balachandran, 2001) due to the along-shelf transport of sediments rather than the cross shelf transport (Ramaswamy and Nair, 1989). C10 and C11 will reflect the normal accumulation of contaminants rather than the disposal of dredge spoil.

2.2 Sample Collection and Analytical Methodology

Water, suspended particulate matter and sediment samples were collected from 16 estuarine and 11 coastal stations covering the pre-monsoon (Pre-M), monsoon (Mon) and Post-monsoon (Post-M) seasons of 2009. All the samples were used for the assessment of dissolved, particulate and sedimentary heavy metal analyses, while 3 representative sediment samples each from the Cochin estuary and the adjacent coast were selected for the adsorption study.

Surface water samples were collected using a clean plastic bucket and bottom water samples were collected using a Niskin sampler (Hydrobios 5L). Temperature and pH were recorded in situ. Water samples for dissolved oxygen was collected and fixed by adding the reagents. Sample for Chlorophyll-a was collected separately and kept in iceboxes till analysis on the same day. Water samples for the analysis of salinity and nutrients were collected in pre-cleaned polythene bottles which were rinsed with the samples at the time of collection and kept in iceboxes until analysis at the shore laboratory, within hours of collection. Water samples were filtered using a pre-weighed 0.45µm membrane filter. The suspended particulate matter (SPM) loaded filters were dried (80 ^{0}C) to constant weight in an air oven. The filtrate obtained was collected in a plastic container which was previously cleaned by soaking in 5 % $HN0_3$, washed several times with deionised water and finally rinsed with Milli-Q water. Filtered water samples were preserved by acidifying to pH below 2 using Conc. HNO_3 in order to prevent precipitation of the metals.

Surface sediment (0-5 cm) samples were collected using a Van Veen grab (0.042 m^2) and placed in previously rinsed clean plastic bottles. Temperature and pH were recorded in situ. Samples kept frozen under -20^{0}C and whenever necessary, sub-samples were taken from each sediment sample for different physical and chemical analyses. The sediments were freeze-dried (1.030 mbar, –20 °C), disaggregated by Agate mortar, quartered and stored at 4°C for preliminary laboratory handling. All the analyses were carried out in triplicates and the average value was reported.

2.2.1 General Water and Sediment Characteristics

General hydrographical and sedimentary parameters were analysed following standard methods. pH of the water column was measured in situ using a portable pH meter. Temperature was measured using a sensitive thermometer. Salinity of the water samples was estimated by Mohr- Knudsen method (Muller, 1999). Modified Winkler method was used for the estimation of dissolved oxygen (Hansen, 1999). Nutrients (nitrite, nitrate, ammonia, phosphate and silicate) were estimated spectrophotometrically using Genesys 10UV

Thermospectronic. Nitrite was converted to an azo dye with sulphanilamide and N- (1-naphthyl) ethylene diamine dihydrochloride (Grasshoff *et al.,* 1999). Nitrate was reduced to nitrite using copper-coated cadmium column and estimated as nitrite (Grasshoff *et al.,* 1999). Ammonia was determined by indophenol blue method using citrate buffer (Koroleff, 1983). Formation of heteropoly acids of phosphomolybdate complex by ammonium heptamolybdate, acidified potassium antimonyl tartrate and ascorbic acid used for phosphate determination (Grasshoff *et al.,* 1999). Silicate measurement was based on the reduction of silicomolybdate in acidic solution to molybdenum blue by ascorbic acid. Oxalic acid was introduced to the sample before the addition of ascorbic acid to minimize interference from phosphates (Grasshoff *et al.,* 1999). Chlorophyll-a was measured as per the standard procedure in APHA (1998). A known volume of water sample is filtered through a pre-washed 47mm glass fiber filter (Whatman GF/C). $MgCO_3$ suspension has been added just prior to the end of filtration to buffer the sample preventing premature phaeophytinization. Pigments were extracted with 90 % acetone (24 hrs in the dark at 4 ^{0}C), centrifuged for 10 minutes at 3000-4000 rpm. The extinction of the supernatant solution is measured using spectrophotometer against a reference cell containing 90 % acetone at 630, 647, 665 nm and again at 750 nm which is a correction made for the 665 nm wavelength (for phaeophytin). The concentration is calculated using standard equations.

Suspended particulate matter (SPM) was determined gravimetrically by filtering the water samples through pre-weighed Whatman membrane filters (0.45 μm), immediately after collection. The filter papers were previously soaked in 5M HNO_3 for 24 hours and washed thoroughly with Milli-Q water to avoid any metal contamination as the suspended solids along with the filter paper will be digested later to find particulate metals. The filter paper carrying the particulates was washed with 5 ml of Milli-Q water (Owens *et al.,* 1997) to remove sea salts and dried (80 ^{0}C) to constant weight in an air oven. The filter paper together with the suspended particulate matter was weighed, and the difference in weights gave the suspended loads (mg/L) in water. Each filter paper was then separately stored in acid washed polythene petri dishes for particulate heavy metal analyses.

Redox potential of the wet sediment was measured using Zobell's solution for the calibration of the electrodes (Brassard, 1997). The textural characteristics of the sediments were determined by pipette analysis (Krumbein and Pettijohn, 1938) after removing the inorganic carbonates using 10 % HCl and organic matter using 15 % H_2O_2. Pipette analysis is based on Stoke's law. Sediment was dispersed in sodium hexametaphoshate overnight and then wet sieved through a 63 µm sieve to collect the sand fraction. The mud fraction was divided into silt and clay fractions by the timed gravimetric extraction of dispersed sediments (Folk, 1980). Total organic carbon of the sediments was analysed in triplicate with Elementar TOC analyser. The amount of total organic matter (TOM) was obtained by multiplying the organic carbon values with 1.724 (Nelson and Sommers, 1996). Total carbon (TC), Total sulphur (TS) and Total nitrogen (TN) were determined using Vario EL III CHN-S Analyser. The analyses were preceded by treatment of samples with 1M HCl to remove carbonates. The process was repeated 2-3 times to ensure the complete removal of carbonates, washed with Milli-Q water to remove salts and finally freeze dried. Samples were run with blank cups in order to correct the carbon and nitrogen associated with tin/silver cups. Elemental analyser was calibrated using acetanilide standards. The detection limits for TC and TN are 0.07 and 0.01 respectively.

2.2.2 Biochemical Composition

Spectrophotometric methods were employed for the determination of biochemical compounds in sediments. Total protein (PRT) analysis was conducted following extraction with NaOH (1M, 2hrs at 80 ^{0}C) and determined according to Hartree (1972) modified by Rice (1982) to compensate for phenol interference using bovine serum albumin (BSA) as the standard. The amount of protein nitrogen was obtained by multiplying protein with a factor of 0.16 (Mayer *et al.,* 1986). Total carbohydrates (CHO) were extracted with H_2SO_4 (2M, 2hrs at 100 ^{0}C), analysed according to Gerchacov and Hatcher (1972) and expressed in glucose equivalents. Total lipids (LPD) were extracted from 1 g of freeze-dried homogenised sediment samples at 60 ^{0}C in a water bath for 30 min, using 30 ml chloroform: methanol (2:1 v/v) (Bligh and Dyer, 1959) and analysed by the method of Barnes and Blackstock (1973). Lipid concentrations were expressed as cholesterol equivalents. Blanks for each analysis were performed with pre-combusted sediments at 450-480 ^{0}C for 4 hrs. All analyses were carried out in triplicate and the average value was reported. The sum of all PRT, CHO and LPD was defined as the labile or easily assimilable organic fraction (Danovaro *et al.,* 1993; Cividanes *et al.,* 2002). The PRT, CHO and LPD concentrations were converted to carbon equivalents assuming a conversion factor of 0.49, 0.40 and 0.75 mg, respectively (Fabiano and Danovaro, 1994). The sum of PRT, LPD and CHO carbon equivalents was reported as the biopolymeric carbon (BPC) and used as a reliable estimate of the labile fraction of organic matter (Fabiano *et al.,* 1995). Tannin and lignin in sediments were extracted using 0.05M NaOH at 60 ^{o}C for 90 minutes and the estimated spectrophotometrically by the sodium tungstate-phosphomolybdic acid method (Nair *et al.,* 1989; APHA, 1998), using tannic acid as the standard. The principle involved is the development of a blue colour on reduction of Folin phenol reagent by the aromatic hydroxyl groups present in tannins and lignins. The effects of Mg and Ca hydroxides and/or bicarbonates present in the seawater were suppressed by the addition of trisodium citrate solution (Nair *et al.,* 1989).

2.2.3 Heavy Metal Analysis

Filter papers loaded with SPM were digested using 1:3 mixture of concentrated $HClO_4$ and HNO_3 which is then evaporated to dryness. The residue was dissolved in 0.1N HNO_3 and made up to a definite volume (APHA, 1998).

Acid preserved water samples were pre-concentrated using 1 % solution (1 ml) of chelating agents APDC (ammonium-1-pyrrolidine dithiocarbamate), DDDC (diethylammonium diethyl dithiocarbamate) and 30 ml chloroform in several steps (APHA, 1998). Solvent extraction by the above mixture was done after adjusting the pH of the acidified sample to 4.5 by the addition of ammonium hydroxide. The chloroform layer was acidified with sub-boiling distilled Conc. HNO_3 (2ml) and the metals were brought into the aqueous phase by equilibration with Milli-Q water. This aqueous layer was then transferred to a standard flask, boiled off the excess chloroform and made up to a definite volume.

1 g of the dried and finely powered sediment sample was repeatedly digested using a mixture of $HClO_4$ and HNO_3 (Loring and Rantala, 1992) and brought into solution by 0.5 M HNO_3 (25 ml) in Milli-Q water.

Dissolved, particulate and sedimentary heavy metals were analysed using flame AAS (Perkin Elmer 3110) after calibration with suitable E-Merck elemental standards. Precisions of the analytical procedure were checked using a triplicate analysis of a certified reference material (BCSS-1) from the National Research Council of Canada. Precisions were typically 4 % for Cu, Zn, Cd, and Pb; 9 % for Cr, Co, and Mn; and 11 % for Ni (Table 2.2). The results were mostly comprised within the uncertainty associated to certified concentration. Also the analysis of the elements using blanks was reproducible with an analytical precision better than 10 %.

Table 2.2 Analysis of standard reference material (BCSS-1) for heavy metals

Metal	Certified Value	Observed Concentration (n=3)
Pb (mg/L)	22.7 ± 3.4	24.9 ± 0.08
Cr (mg/L)	123 ± 1.4	112 ± 0.65
Ni (mg/L)	55.3 ± 3.6	49.16 ± 2.01
Co (mg/L)	11.4 ± 2.1	10.67 ± 2.68
Cu (mg/L)	18.5 ± 2.7	18.2 ± 0.25
Zn (mg/L)	119 ± 12	123.64 ± 2.51
Mn (mg/L)	229 ± 15	189.47 ± 10.75
Fe (%)	4.7± 0.14	4.64± 0.41

2.2.4 Adsorption Analysis

Batch adsorption experiments were conducted to assess the adsorption characteristics of the sediment for the heavy metals Cd, Zn, Pb, Cu and Co (Seo *et al.,* 2008). 20 ml solution containing specific concentrations of each metal was added to the sediment sample (0.025 g) taken in glass Erlenmeyer flasks. For each metal, concentration levels of 0, 50, 100, 150, 200, 250 and 300 mg/L were evaluated. All samples were equilibrated for 24 hrs (providing sufficient time for the system to reach equilibrium, as determined by the pilot test) on a 25 mm sway gyratory shaker at constant room temperature (25 ^{0}C). After settling, a 30 mL aliquot of the supernatant was filtered through a Whatman GF/C filter (0.45 µm) and then analysed for the equilibrium metal concentrations. The amount of metal adsorbed by the sediment was calculated from the concentration decrease in solution.

Adsorption behaviours of the metals by the sediment were evaluated using both the Freundlich and Langmuir adsorption isotherms. The Freundlich equation (Bohn *et al.,* 1979), in its original form, can be written as $q = KC_e^{1/n}$ where q is the metal concentration in the sorbent material (adsorption capacity), K is a constant related to the sorption capacity, C_e (mg/L) is the concentration in solution, and n is an empirical parameter related to the intensity of sorption, which varies with the heterogeneity of the material. The Langmuir equation (Bohn *et al.,* 1979), in its original form, can be written as $q = (abC_e) / (1 + bC_e)$, where C_e (mg/L) is the concentration of metal in solution at equilibrium, q (mg/kg) is the mass of metal adsorbed to the sediment, a (mg/kg) is the maximum adsorption capacity of metal, and b is a constant related to the binding strength of metal, which represents the inverse of the equilibrium concentration of adsorption at one half saturation.

When measured under the same experimental conditions, distribution coefficients (Kd) can be used for comparing the sorptive capacities of different soils or materials for any particular metal ion (Alloway, 1995). The Kd was calculated using the equation

$$\mathrm{Kd} = \frac{\text{Equilibrium metal concentration adsorbed}}{\text{Equilibrium metal concentration insolution}}$$

where the equilibrium metal concentration adsorbed is given per unit weight of soil and the equilibrium metal concentration in solution per unit volume of liquid.

2.3 Data Analysis

2.3.1 Enrichment Factor (EF)

For assessing the impact of heavy metal pollution and status of contamination in an area we use a baseline sample of known metal composition or a reference background such as average shale values (Turekian and Wedepohl, 1961) or average crustal values (Taylor, 1964). The extent of heavy metal contamination compared to the background area can be assessed by enrichment factor (Salomons and Förstner, 1984). Metal concentrations were normalized to the textural characteristic of sediments with respect to Fe. The EF was calculated according to the following equation:

$$\text{EnrichmentFactor}\ (\text{EF}) = \frac{M_x \ / \ Fe_x}{M_b \ / \ Fe_b}$$

Where, M_x and Fe_x are the sediment sample concentrations of the heavy metal and Fe, while M_b and Fe_b are their concentrations in shale (Salomons and Forstner, 1984). Fe was used as normaliser in this study because it is a major sorbent phase for heavy metals, and is a quasi-conservative tracer of the natural metal-bearing phases in fluvial and coastal sediments (Schiff and Weisberg, 1999; Turner and Millward, 2000) and is not expected to be substantially enriched from anthropogenic sources in estuarine sediments due to its relatively high natural concentration (Niencheski *et al.,* 1994). The ranking system used to denote the degree of anthropogenic influence on the metal concentration levels in the estuarine sediments (Kartal *et al.,* 2006; Sutherland, 2000) is given in Table 2.3

Table 2.3 Ranking system based on enrichment factor

EF Value	Enrichment Level
EF < 2	deficiency to minimum enrichment
EF 2–5	moderate enrichment
EF 5–20	significant enrichment
EF 20–40	very high enrichment
EF >40	extremely high enrichment

2.3.2 Contamination Factor (CF), Degree of Contamination (C_d) and Modified Degree of Contamination (mC_d)

The assessment of sediment contamination was carried out using the contamination factor and the degree of contamination, based on four classification categories (Table 2.4) recognised by Hakanson (1980). Contamination factor express the level of contamination of sediment by a metal, and it can be calculated using the equation,

$$\text{ContaminationFactor}\left(\text{CF}\right) = \frac{\text{Metalconcentration in sediment}}{\text{Background value of metal}}$$

Degree of contamination (C_d) was calculated using the equation proposed by Håkanson (1980),

$$Cd = \sum_{i=1}^{n} CF_i$$

where n is the number of elements analysed and *CF* is the contamination factor.

Table 2.4 Contamination factors and degree of contamination categories and terminologies

CF classes	CF and C_d terminologies	Cd classes
$CF < 1$	Low *CF* indicating low contamination / low C_d	$C_d < 8$
$1 \leq CF < 3$	Moderate CF / C_d	$8 \leq C_d < 16$
$3 \leq CF < 6$	Considerable CF / C_d	$16 \leq C_d < 32$
$CF \geq 6$	Very high CF / C_d	$C_d \geq 32$

Modified degree of contamination was calculated based on the method proposed by Abrahim (2005), which is a modified and generalized version of the formula suggested by Hakanson (1980).

$$mC_d = \frac{1}{n} \sum_{i=1}^{n} CF$$

where n = number of analysed elements and i = i^{th} element (or pollutant) and CF = Contamination factor.

For the classification and description of the modified degree of contamination (mC_d) in estuarine sediments the following gradations are proposed (Table 2.5).

Table 2.5 Modified degree of contamination classification and description

mC_d classes	Modified degree of contamination level
$mC_d < 1.5$	Nil to very low degree of contamination
$1.5 \leq mC_d < 2$	Low degree of contamination
$2 \leq mC_d < 4$	Moderate degree of contamination
$4 \leq mC_d < 8$	High degree of contamination
$8 \leq mC_d < 16$	Very high degree of contamination
$16 \leq mC_d < 32$	Extremely high degree of contamination
$mC_d \geq 32$	Ultra high degree of contamination

2.3.3 Pollution Load Index (PLI)

Tomlinson *et al.* (1980), had employed a simple method based on pollution load index (PLI), to assess the extent of pollution by metals in sediments. Sediment pollution load index (PLI) was calculated using the equation

$$PLI = (CF_1 \times CF_2 \times \dots\dots\dots\dots CF_n)^{1/n}$$

Where, CF is the contamination factor and n is the number of metals. World average concentration of metals reported for shale was taken as their background values (Turekian and Wedepohl, 1961). The *PLI* gives an estimate of the metal contamination status. $PLI \leq 1$ denote no pollution or only baseline levels of pollutants are present and $PLI > 1$ indicate pollution (Tomlinson *et al.,* 1980).

2.3.4 Geoaccumulation Index (Igeo)

The index of geoaccumulation can be used to estimate the enrichment of metal concentration above background or baseline concentrations (Muller, 1969).The geoaccumulation index assesses the degree of metal pollution in terms of seven enrichment classes, based on the increasing numerical values of the index calculated using the equation,

$$Igeo = \log_2 (C_n/1.5B_n)$$

where C_n is the concentration of the element in the enriched samples, and the B_n is the background in average shale value (Wedephol, 1995) of the element. The factor 1.5 is introduced to minimise the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Stoffers *et al.,* 1986). Muller (1969) proposed the following descriptive classes for increasing numerical Igeo values (Table 2.6).

Table 2.6 Descriptive classes for increasing numerical Igeo values

Igeo value	Igeo class	Designation of sediment quality
>5	6	extremely contaminated
4 – 5	5	strongly to extremely contaminated
3 – 4	4	strongly contaminated
2 – 3	3	moderately to strongly contaminated
1 – 2	2	moderately contaminated
0 – 1	1	free to moderately contaminated
0	0	free

2.3.5 Sediment Quality Guidelines (SQG) of USEPA

In order to estimate the possible environmental consequences of the metal analysed, the concentrations of heavy metals in the study area were compared to SQuiRT (Screening Quick Reference Table) developed by NOAA

(National Oceanic and Atmospheric Administration, USA). The Effects Range Low (ERL) and Effects Range Median (ERM), Threshold Effects Levels (TEL) and Probable Effects Levels (PEL) concentrations (Table 2.7) are considered in the present study (Bakan and Ozkoc, 2007; Buchman, 2008). ERL and TEL represent concentrations below which adverse effects upon sediment dwelling fauna would infrequently be expected whereas, ERM and PEL represent chemical concentration above which adverse effects are more frequently observed. Generally, adverse effects occurred in less than 10 % of studies in which concentrations were below the respective ERL values, and adverse effects were observed in more than 75 % of studies in which concentrations exceeded ERM values (Long *et al.,* 1995 & 1997). Classification proposed by Perin *et al.* (1997) based on Sediment Quality Guidelines are given in Table 2.8. The potential acute toxicity of contaminants in sediment sample can be estimated as the sum of the toxic units (TU) defined as the ratio of the determined concentration to PEL value (Pederson *et al.,* 1998).

Table 2.7 Screening Quick Reference Table (SQuiRT) for heavy metals in marine sediments

Element, (mg/ kg)	Cd	Pb	Cr	Ni	Cu	Zn
ERL	1.20	46.70	81.00	20.90	34.00	150.00
ERM	9.60	218.00	370.00	51.60	270.00	410.00
TEL	0.68	30.20	52.30	15.90	18.70	124.00
PEL	4.20	112.00	160.00	42.80	108.00	271.00

Table 2.8 Classification based on Sediment Quality Guidelines

Element, mg/kg	Elemental Background Concentration	SQG non-polluted	SQG moderately polluted	SQG heavily polluted
Cd	0.2	_	_	_
Pb	12.5	<40	40-60	>60
Cr	100.0	<25	25-75	>75
Ni	75.0	<20	20-50	>50
Cu	55.0	<25	25-50	>50
Zn	70.0	<90	90-200	>200

2.3.6 Statistical Analysis

Statistical analyses were performed using Statistical Package for Social Sciences (SPSS) version 16.0. Pearson correlation analysis was performed to identify the relationship of various hydrographical and sedimentary parameters, relationship of metals with the hydrographical / geochemical parameters and inter-metallic relationship. Spatial and temporal variations of general hydrographical, geochemical parameters and heavy metals (Cd, Pb, Cr, Ni, Co, Cu, Zn, Mn & Fe) were assessed by two-way analysis of variance (ANOVA) without replication with season and space (stations) as sources of variation. The log (x+1) transformation were used to obtain normal distribution of the data set and normality was checked using criteria of Webster (2001).

Factor analysis were used to extract information from the most meaningful parameters which better described the whole data affording data reduction with minimal loss of information (Vega *et al.,* 1998; Helena *et al.,* 2000; Katsaounos *et al.,* 2007). In factor analysis, principal component analysis and varimax rotation methods were used for extraction and deriving principal components (PCs) respectively and the factor loading were considered significant if they were greater than 0.50. Principal component analysis (PCA) was used to identify the significant parameters for the characterization of the system and the source identification of micro pollutants (Bartolomeo *et al.,* 2004; Glasby *et al.,* 2004; Ghrefat and Yusuf, 2006).

Cluster analysis (CA) is a multivariate technique, used to classify the object of the system into categories or clusters based on their similarities. The result of a hierarchical clustering procedure can be displayed graphically using a dendrogram, which shows all the steps in the hierarchical procedure (Richard and Dean, 2002; Alvin, 2002). CA is used to integrate geochemical data and identify clusters of sampling stations based on their similarities (Singh *et al.,* 2004; Shrestha and Kazama, 2007).

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Chapter 3

SYSTEM CHARACTERISTICS

Contents

3.1 Introduction

Hydrography of an estuary depends on the intrusion of sea water, incursion of fresh water from rivers, precipitation, evaporation, estuarine mixing, bottom topography and geographical conditions. Seasonal hydrographic changes play a major role in regulating the metal concentration in the sediment also; terrestrial transport appears to occur mostly during the monsoon periods, due to the high riverine discharge and bed-load movements (Nair *et al.,* 1993) and the post-monsoon periods are associated with enrichment of metals in the accumulative phases in the sedimentary environment. Hydrographical conditions have major role in modifying the biogeochemical cycles of metals as they account for the accretion and remobilization of toxic metals in the sedimentary environment and hence they are very much significant in assessing heavy metal pollution (Forstner and Wittmann, 1979; Sinex and Wrigt, 1988; Hoshika *et al.,* 1991). Natural environmental changes like a fall in pH can cause the release of previously complexed toxicants. Majority of aquatic animals prefer a pH range of 6.5-8.0. Low pH favours toxic metals to be mobile and bioavailable for uptake by aquatic organisms.

Sediment characteristics such as pH, redox conditions, organic matter content and salinity determine the metal sorption and precipitation processes which in turn are related to the metal's mobility, bioavailability and potential toxicity (Du Laing *et al.,* 2009). The chemical form of sulphur is reported to be important in determining the availability of metal ions in marine environments. Heavy metal accumulation is reported to be tightly coupled with organic matter content in the sediments (Mahony *et al.,* 1996; Jones and Turki, 1997; Maria Jesus Belzunce *et al.,* 2001; Dell Anno *et al.,* 2003; Zhangdong *et al.,* 2010; Bindu *et al.,* 2015) and its texture (Rubio *et al.,* 2000; Deepthi *et al.,* 2008; Bindu *et al.,* 2015). Humic and fulvic acids play important role in the complexation (or chelation) and release of metals. For example, lowering the pH to around 2 can release most of the humic-bound iron. The concentration of humic material and metal ions are important factors as there may be competition between metals for active sites on humic materials. Fine grain size, high organic matter and anoxic conditions of subtidal and intertidal estuarine sediments provide a suitable background for intense diagenetic processes which favour the formation of pyrites along with the incorporation of heavy metals in these minerals (Berner, 1970 & 1983; Williams *et al.,* 1994).

In aquatic systems, dissolved organic matter (DOM) exerts control on the transport, speciation, toxicity of trace metals like mercury, the depth of light penetration and the formation and stability of particles. Dissolved organic matter components have many functional groups including fluorophores or chromophores which have strong capacity to bind the dissolved metals (Saar and Webber, 1980; Malcolm, 1985; Senesi, 1990; Morel and Hering, 1993; Morra *et al.,* 1997; Leenheer *et al.,* 1998; Xia *et al.,* 1998; Bloom *et al.,* 2001; Steelink, 2002; Stenson *et al.,* 2003; Leenheer and Croue, 2003; Mostofa *et al.,* 2009). Rapidly sinking particles accumulate organic matter which have undergone continuous degradation of its labile fractions while passing through the water column. The organic detritus contains planktonic materials, animal faecal pellets and vascular plant materials which show differential reactivity to the leaching and remineralisation processes in the aquatic environment. Continuous degradation and mixing processes of the organic materials are active even after the sedimentation process (Colombo, 1996; Cotano and Villate, 2006). Organic detritus is known as an important food source for the benthic organisms and it has significant role in the biogeochemical cycles of water column and sediments (Mann and Lazier, 1991; Bianchi and Bauer, 2011).

Both the composition of the organic matter and the chemical/ biological/physical processes that occur after its deposition control the biogeochemistry of the sediments. Diagenesis is directly linked to the redox conditions and organic compounds resistant to degradation and those survive diagenesis are stored in the sedimentary environments depending on the redox status. The remineralisation of organic constituents of sediments significantly control the diagenetic behaviour of a number of heavy metals, their cycling and subsequent release to the overlying waters. Biochemical composition of sedimentary organic matter has been used to gather information on the source of organic matter and also the parameters controlling its diagenetic fate (Colombo *et al.,* 1996).

Assessment of the quantity and quality of organic matter, which provide a clear picture of the biogeochemical characterization of the sedimentary environment, is a prerequisite for explaining the organic matter dynamics in the estuarine and coastal systems. The concentrations of labile organic biopolymers (carbohydrates, proteins and lipids) are considered as the best tool for the evaluation of nature and quality of organic matter (Colombo, 1996; Dell Anno *et al.,* 2002; Pusceddu *et al.,* 2009; Pusceddu *et al.,* 2011; Venturini *et al.,* 2012). Apart from the characterisation and quantification, source identification is also important in understanding the relative importance of biogeochemical processes. Due to the complexity of origin and nature of organic matter in the estuarine and coastal sediments, chemical biomarker approach is often used to characterise the organic matter sources. This molecular information is more specific and sensitive than bulk elemental and isotopic techniques and it allows for identification of multiple sources (Meyers, 1997 & 2003). The terrigenous sediments contain some signatures of vascular plants like phenolic compounds that can be considered as a biomarker. These phenolic compounds are nitrogen-free polymers intended to give structural support (e.g. lignin) and protection (e.g. tannin) to the higher plants. The vascular plants require such molecules, as they are confined almost exclusively to land (with the exception of sea grasses), as an adaptation.

Deposition and preservation of organic matter is greater in coastal sediments compared to any other sedimentary reservoir (Romankevich, 1984; Hedges and Kiel, 1995). The influx of large amount of allochthonous organic matter into the Cochin estuary was reported in many previous studies (Saraladevi *et al.,* 1983; Thomson, 2002; Balachandran *et al.,* 2003; Babu *et al.,* 2006; Thottathil *et al.,* 2008; Martin *et al.,* 2010). Very high concentrations of dissolved and particulate organic carbon were reported from central estuary (Martin *et al.,* 2010) and organic wastes from southern aquaculture fields ($62km^2$), agricultural fields ($80km^2$) and coconut retting yards have also been reported to contribute to the alarming pace of organic pollution (Thomson, 2002; Babu *et al.,* 2006; Martin *et al.,* 2010).

This chapter is aimed to discuss the general hydrographical and sedimentary parameters which have profound influence on the distribution of heavy metals, the quality and quantity of organic matter in terms of its biochemical composition to identify the major biogeochemical pathways and the relative contribution of different sources of sedimentary organic matter by the application of bulk geochemical proxies like C : N ratio.

3.2 Results & Discussions

3.2.1 General Hydrography

Results of the general hydrographic parameters of the estuary and its adjacent coast are given in Appendix 1 to 6. Two-way ANOVA without replication was performed to examine the spatial and temporal variations in the distribution of these parameters in the study area (Table 3.1). Correlation matrices obtained from the Pearson correlation analysis of the estuary are represented in Tables 3.2 to 3.7 and that of adjacent coast are represented in Tables 3.8 to 3.13.

3.2.1.1 Temperature

Temperature plays a major role in regulating estuarine physiological processes (Glibert *et al.,* 1982; Boynton *et al.,* 1990; Smith and Kemp, 1995; Lomas *et al.,* 2002) like oxygen and carbonate solubility, viral pestilence, pH, conductivity, and photosynthesis and respiration rates of estuarine macrophytes (Marschner, 1995; Rooney and Kalff, 2000) and it shows very regular and reasonable impacts on the quality of lake water (Imteaz *et al.,* 2003). Seasonal variation of water temperature has no direct effect on the metal solubility in water (Zumdahl, 1992). Concentrations of metals in the interstitial water of the sediments was reported to decrease with decreasing temperature (Forstner and Wittmann, 1979; Fritioff *et al.,* 2005).

Annual average of water temperature in the estuary was 29.81 ± 0.96 ºC (average ± standard deviation) in the surface and 28.85 ± 1.07 ºC in the bottom (Fig.3.1). In the surface waters, highest temperature (32 ºC) was observed in E15 during Mon season. Highest and lowest temperature in the bottom waters was observed in E15 (32 ºC) and E3 (26 ºC) respectively during Mon season. Seasonal variation in the temperature distribution was prominent only in the surface water. In the estuary, Post-M season showed higher temperature followed by Mon and Pre-M seasons. The annual variation in temperature is found to be less in tropical estuaries like Cochin Estuary when compared to other temperate estuaries (Ammini Parvathi *et al.,* 2013). Lack of vertical thermal stratification in Cochin Estuary was also reported by Qasim and Gopinathan (1969), which can be attributed to the shallow nature of the estuary (Shivaprasad *et al.,* 2013b).

In the coast, annual average of temperature was 29.45 ± 0.79 ºC and 28.72 ± 0.63 ºC in the surface and bottom waters respectively (Fig.3.1). Bottom water temperature showed seasonal variations significant at 95 % confidence levels. Post-M season showed higher temperature followed by Pre-M and Mon seasons. Nutrient rich, low oxygenated cold water due to upwelling phenomena is fairly widespread along the Western Indian coast during monsoon months (Sharma, 1968; Guptha *et al.,* 1990; Madhu Joshi and Rao, 2012). Relatively lower temperature observed in the coastal waters during Mon season can be attributed to the influx of upwelled water (Premchand *et al.,* 1987; Shivaprasad *et al.,* 2013a).

3.2.1.2 pH

pH affects almost all the processes in an aquatic system either directly or indirectly and thus it is considered as a master variable for the chemical state of that aquatic ecosystem (Morel and Hering, 1993; Stumm and Morgan, 1996; Hofmann *et al.,* 2009). pH is an important hydrographical parameter which indicate the level of dissolved carbon dioxide, which in turn reflect the activity of the phytoplankton and the level of dissolved oxygen in an aquatic system (Skirrow, 1975; Regnier *et al.,* 1997; Vanderborght *et al.,* 2002; Soetaert *et al.,* 2007). pH influences the speciation of metals in the aquatic environments and decides their partitioning between dissolved and particulate phases (Shiva Kumar and Srikantaswamy, 2012). At lower pH, water dissolves more metals (Charlson and Rodhe 1982; Gonzalez *et al.,* 1990; Sundaray, 2006), as metals face strong competition from H^+ ions for aquatic ligands at low pH values metals tend to exist in free ionic forms, which are increasingly available to biota (Rensing and Maier, 2003; Sagi Magrisso *et al.,* 2009). Metals get precipitated as their insoluble oxides and hydroxides resulting in lower concentration of metals in water at higher pH (Stumm and Morgan, 1970; Sundaray *et al.,* 2011).

In the estuary, annual average in pH was 7.59 ± 0.43 in the surface and 7.62 ± 0.44 in the bottom waters. Highest pH was detected in E1 during Pre-M both in the surface (8.82) and bottom (8.87). Lowest pH was observed in E15 in the surface (6.9) and E12 in the bottom (6.75) during Mon season (Fig.3.1). pH showed spatial (p value = 0.025) and temporal variations (p value = 9.77×10^{-7}) in its distribution in the surface water; whereas only temporal variations were significant in the bottom waters (p value = 2.29×10^{-7}). Pre-M season showed higher pH values followed by Post-M season. However, estuarine stations E5 - E8 in the surface and E5 - E9 in the bottom showed lower pH values during Pre-M compared to Post-M season. These were the stations around Wellingdon Island. In comparison with Pre-M and Post-M seasons, pH was lower during Mon season. In Cochin estuary, higher pH values during non-monsoon months due to the excessive photosynthetic activity was reported by earlier workers (Nair *et al.,* 1975; Silas and Pillai, 1975, Balachandran *et al.,* 2003 & 2005; Madhu *et al.,* 2010).

Annual average in pH was 8.16 ± 0.18 in the surface and 7.97 ± 0.33 in the bottom coastal waters. Station C10 was detected with highest pH; 8.75 in the surface during Mon and 8.3 in the bottom during Post-M (Fig.3.1). Lowest pH values were detected during Mon season; C1 (7.8) in the surface and C11 (7.32) in the bottom. pH showed significant seasonal variations both in the surface (p value = 0.008) and bottom (p value = 1.71×10^{-13}) waters. pH was found to be higher during Post-M season followed by Pre-M and lowest values were observed during Mon season. Compared to rest of the surface coastal stations, lower pH values were observed in stations C1 and C3-C7 which are nearer to the bar mouth. This can be due to the mixing by the heavy estuarine runoff during Mon.

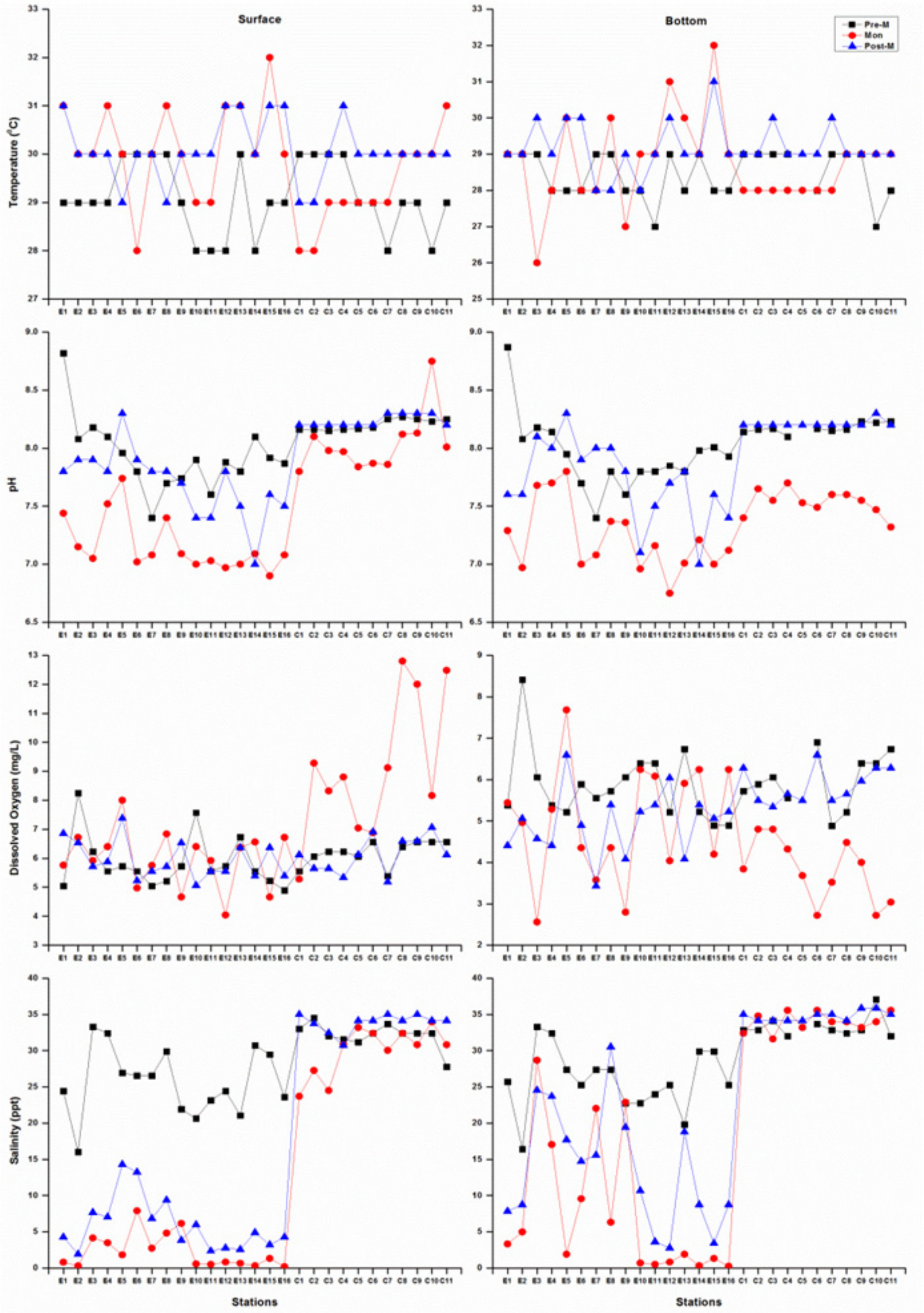

Figure 3.1 Spatial and temporal variations of temperature, pH, dissolved oxygen and salinity in Cochin estuarine and coastal system

3.2.1.3 Dissolved Oxygen (DO)

Dissolved oxygen plays a vital role in the aquatic environment as the survival of aquatic life is based on the availability of dissolved oxygen. Various physical, chemical and biological processes taking place in the natural waters can be explained using DO data (De Sousa and Sen Gupta, 1986; Maya *et al.,* 2011). Variation in dissolved oxygen affects the presence of heavy metals in various phases in an aquatic system. Remobilisation of sorbed metals depends on the changes in redox potential which in turn depends on the presence of oxygen (Dekov *et al.,* 1997; Facetti *et al.,* 1998; Soares *et al.,* 1999; Reible *et al.,* 2002). Oxidation of the anoxic sediments through activities like dredging, flooding etc. results in positive change in the redox potential and a decrease in sediment pH, which might cause increased release of the heavy metals in the sediment (Meyer *et al.,* 1994; Ohimain *et al.,* 2008). Bioavailability of heavy metals increase under low oxygen conditions (Whitehead *et al.,* 2009). Metals like Fe may undergo reductive dissolution under lower dissolved oxygen (Hatje *et al.,* 2001; Hatje *et al.,* 2003; Lee *et al.,* 2003).

Dissolved oxygen showed an annual average of 5.92 ± 0.86 mg/L in the surface and 5.26 ± 1.11 mg/L in the bottom estuarine waters. Highest value was found in E2 both in the surface (8.25 mg/L) and bottom (8.42 mg/L) during Pre-M (Fig.3.1). Lowest DO was observed in E12 (4.04 mg/L) in the surface and E3 (2.56 mg/L) in the bottom during Mon season. Temporal variation in the distribution of DO was significant only in the bottom water (p value = 0.028). Although spatial variations in DO were not significant in the estuarine area, stations which have the influence of fresh water input (E2, E5 and E10) were associated with highly oxygenated waters. Comparatively higher DO during non-monsoon months due to higher photosynthetic activities were reported (Kunjukrishnapillai *et al.,* 1975; Wetzel, 2001; Balachandran *et* *al.,* 2003; Balachandran *et al.,* 2005; Madhu *et al.,* 2010; Abhilash *et al.,* 2012). Strong positive correlations observed between DO and chlorophyll-a substantiated the above observation (Tables 3.2, 3.3 & 3.7).

In the coastal area, annual average in DO was 7.14 ± 2 mg/L in the surface and 5.19 ± 1.18 mg/L in the bottom. In the surface waters, highest DO (12.81 mg/L) was detected in C8 during Mon and lowest (5.18 mg/L) was in C7 during Post-M. Station C6 was detected with lowest (2.72 mg/L during Mon) and highest (6.90 mg/L during Pre-M) DO in the bottom water (Fig.3.1). Highly significant temporal variations were observed for DO in the coastal area; p value being 0.00005 in the surface and 3.12×10^{-6} in the bottom. Surface waters were highly oxygenated during Mon season which can be attributed to the increased rainfall and runoff. However, bottom waters were associated with very low dissolved oxygen during this season. Subsurface decrease in DO due to the upwelling phenomena along the western Indian coast during monsoon months have been reported by many authors (Sharma, 1968; Guptha *et al.,* 1990; Madhu Joshi and Rao, 2012). Subsurface oxygen demand arising out of the oxidation of organic matter at subsurface levels also reported to contribute to low dissolved oxygen (Naqvi *et al.,* 2000).

3.2.1.4 Salinity

Salinity has been considered as an index of estuarine mixing processes and tidal effects (Regnier and O'Kane *et al.,* 2004). Phytoplankton dynamics, zooplankton biomass, dissolved inorganic nutrients, suspended particulate matter, residual currents etc are influenced by salinity stratification (Cloern, 1984; Sebastian diehl, 2002). Salinity plays major role in the distribution of contaminants (Chapman and Wang, 2001) like heavy metals in the sediment and overlying or interstitial waters (Gambrell *et al.,* 1991; Gambrell, 1994; Padmalal *et al.,* 1997; Guieu *et al.,* 1998; Jeong-ju Oh *et al.,* 2012) and can be used to explain the adsorption/desorption mechanisms and chemical reactions occurring in estuarine environments (Schubel and Kennedy, 1984; Millero *et al.,* 1987; Byrd *et al.,* 1990; Zhang *et al.,* 2008). At elevated salinity, competition by the cations for the binding ligands results in desorption of the metals from the particulate to dissolved phase (Adebowale *et al.,* 2009) which is more bioavailable.

Cochin estuary is highly influenced by the influx of fresh water from the feeding rivers and by the intrusion of seawater from the adjacent coast through the bar mouth (Ratheesh Kumar *et al.,* 2010; Martin *et al.,* 2010; Robin *et al.,* 2012). Saraladevi (1986) and Nair *et al.,* (1988) observed wide range of salinity variation (0.24 to 31 psu) in Cochin estuary which can be attributed to its shallow nature, monsoonal flow and the tidal forcing. Salinity intrusion beyond 21 km in the Periyar river estuary during pre-monsoon and up to 5 km during the monsoon has been observed by Sankaranarayanan *et al.,* (1986). Salinity distribution in the Cochin estuary is influenced mostly by tide-induced circulation (Narayana Pillai *et al.,* 1973) and the salinity intrusion in the estuary has a major role in metal adsorption/desorption mechanism (Balachandran *et al.,* 2005; Laluraj *et al.,* 2007; Martin *et al.,* 2012). Cochin estuary is reported to vary from a well-mixed type to partially mixed type even during the lean discharge period (Balachandran, 2001).

Salinity of the estuarine waters showed an annual average of 11.30 ± 11.02 ppt in the surface and 15.78 ± 10.76 ppt in the bottom. Highest salinity (33.29 ppt) was recorded in E3 during Pre-M both in the surface and bottom waters (Fig.3.1). Lowest values were found in E16 during Mon season; 0.20 ppt in the surface and 0.26 ppt in the bottom waters. Salinity distribution in both the surface and bottom waters showed significant variations among the seasons (p values 1.08×10^{-20} and 3.98×10^{-9}) and stations (p value = 0.004).

Pre-M season was associated with highest salinity, followed by Post-M. Almost a fresh water condition prevailed in the estuary during Mon season. Revichandran *et al.* (2012) reported the complete freshening of the Cochin estuary during the peak monsoon period. In the surface, highest salinity was observed in station E6 during this season, while in the bottom, highest value was recorded in E3. Surface layers in the bar mouth was mixed by the heavy monsoonal influx of fresh water, whereas in the bottom, denser seawater predominated. During Mon season, the estuary is virtually converted into a freshwater basin even in areas around the bar mouth where salt water penetration were reported to occur at depths below 5 m depth only (Menon *et al.,* 2000; Renjith *et al.,* 2011). The extend of salinity intrusion in Cochin estuary was found to depend on the strength of the tidal influx and strength of fresh water flux which varies with season (Joseph and Kurup, 1989).

Annual average of salinity in the coastal waters was 32.01 ± 2.77 ppt in the surface and 34.04 ± 1.31 ppt in the bottom. In the surface, stations C1, C7 and C9 were found with highest salinity (35.01 ppt) during Post-M and in the bottom, C10 (37.08 ppt) showed highest salinity during Pre-M season (Fig.3.1). Lowest salinity was recorded during Mon season both in the surface (C1, 23.72 ppt) and in the bottom in (C3, 31.63 ppt). Salinity showed significant temporal variations both in the surface (p value = 0.004) and bottom (p value = 3.13×10^{-6}). During Mon season, salinity stratification was observed in the coast as surface coastal waters were mixed by the heavy influx from the estuary. Unlike the estuary, coastal waters exhibited less salinity during Pre-M compared to the Post-M season. According to Balachandran (2001), northerly coastal currents along the west coast of India bring low saline waters from Bay of Bengal during pre-monsoon period. Salinity of the bottom waters during Pre-M was even less than that in the Mon season.

Table 3.1 ANOVA results of the hydrographic parameters in the Cochin estuary and its adjacent coast

Estuary	**Spatial ($df=15$)**				**Temporal ($df=2$)**			
	Surface		**Bottom**		**Surface**		**Bottom**	
	F	**P-value**	**F**	**P-value**	**F**	**P-value**	**F**	**P-value**
Temperature	1.22	NS	1.19	NS	10.95	0.000**	2.88	NS
pH	2.30	0.025*	1.92	NS	44.81	0.000**	26.56	0.000**
DO	1.59	NS	1.38	NS	0.12	NS	4.04	0.028*
Salinity	3.04	0.005**	3.07	0.004**	306.45	0.000**	39.46	0.000**
Phosphate	1.33	NS	2.96	0.006**	0.64	NS	0.79	NS
TP	1.19	NS	0.78	NS	8.70	0.001**	5.49	0.009**
Ammonia	1.15	NS	1.62	NS	33.04	0.000**	40.79	0.000**
Nitrite	1.32	NS	3.23	0.003**	17.74	0.000**	11.12	0.000**
Nitrate	1.77	NS	1.10	NS	30.16	0.000**	8.76	0.001**
TN	1.59	NS	1.69	NS	194.21	0.000**	200.46	0.000**
Silicate	1.04	NS	1.04	NS	22.06	0.000**	28.46	0.000**
SPM	0.77	NS	1.56	NS	4.80	0.016*	9.59	0.001**
Chlorophyll-a	0.90	NS	0.84	NS	0.70	NS	0.33	NS
Coast	**Spatial ($df=10$)**				**Temporal ($df=2$)**			
Temperature	0.67	NS	0.57	NS	2.75	NS	4.78	0.022*
pH	1.66	NS	0.52	NS	6.07	0.009**	226.89	0.000**
DO	1.38	NS	0.33	NS	16.70	0.000**	27.80	0.000**
Salinity	0.84	NS	0.94	NS	7.24	0.004**	3.91	0.039*
Phosphate	1.12	NS	0.74	NS	8.54	0.002**	2.29	NS
TP	0.85	NS	0.58	NS	11.24	0.001**	3.27	NS
Ammonia	1.04	NS	1.39	NS	3.46	NS	10.00	0.001**
Nitrite	2.19	NS	0.95	NS	3.94	0.036*	0.48	NS
Nitrate	1.50	NS	0.93	NS	14.58	0.000**	16.60	0.000**
TN	0.81	NS	2.60	0.040*	61.19	0.000**	64.89	0.000**
Silicate	1.02	NS	0.98	NS	28.66	0.000**	31.11	0.000**
SPM	1.23	NS	1.11	NS	6.67	0.006**	3.27	NS
Chlorophyll-a	0.94	NS	1.01	NS	12.30	0.000**	9.00	0.002**

** Significant at the 0.01 level, * Significant at the 0.05 level, NS Not Significant

3.2.1.5 Nutrients

Macronutrients are fundamental to organic matter production in aquatic environments. However, higher rates of nutrient loading into the aquatic environments enhance phytoplankton growth and biomass, thus increasing the rate of organic matter loading which ultimately results in eutrophication (Nixon, 1995; Smith *et al.,* 1999; Lim *et al.,* 2012). Heavy metals are reported to have high affinity for organic matter (Singer, 1977; Langston, 1982; Forstner and Wittman, 1983; Coquery and Welbourn, 1995; Lim *et al.,* 2012; Bindu *et al.,* 2015). Hence, nutrient enrichment which induces the organic carbon production would enhance the possibility of heavy metal enrichment in an aquatic system.

a) Phosphate-Phosphorus

Phosphorus is one of the key elements essential for the growth of planktons and thus the higher plants and animals in an ecosystem. However, its enrichment leads to eutrophication of the system and this can be greatly accelerated by human activities that increase the rate at which nutrients are released into the aquatic system. Sources of phosphate include agricultural fertilizers, domestic wastewater, detergents, industrial effluents and geological formations. Phosphate has a significant role in the dynamics of heavy metal like Cd (Kudo *et al.,* 1996; Hinojosa *et al.,* 2001; Garcia *et al.,* 2010) and in highly acidic soils of the tropics, fixation of phosphate is as iron phosphates (Le Mare, 1981). In spite of receiving 42.4 x10^3 Md^{-1} of inorganic phosphate from Periyar River, the export to the coastal waters was only 28.2 x 10^3 Md^{-1} (Hema Naik, 2000). Hence, the estuary acts as a sink for the nutrients and flushes out only a portion of the total load it receives.

Phosphate-P showed annual average of 3 ± 1.52 µmol/L and 3.58 ± 2.47 µmol/L in the surface and bottom waters respectively. In the surface, lowest value was detected in E7 (0.78 µmol/L) during Mon and highest value detected in E1 (9.49 µmol/L) during Pre-M season (Fig.3.2). E5 and E3 were associated with highest (12.92 µmol/L) and lowest (0.73 µmol/L) values in the bottom during Pre-M season. High concentrations of phosphate found in the estuary during all seasons could be attributed to the high load of phosphate dumped into the system. Although temporal variations were not significant in the estuary, bottom waters showed significant spatial variation in the distribution of phosphate (p value = 0.005). Highest values during Pre-M and Post-M seasons were reported in bottom waters of station E5, which is exposed to anthropogenic sources of phosphate like industrial and municipal wastes. Because of the weak flow in this null zone, accumulation of these elevates the level of phosphate in the bottom waters. Higher concentrations of phosphate were also observed in the southern stations like E12 and E15 which also have lower depth and restricted flows facilitating accumulation of fine particles. Fine particles with greater surface area were reported to have more adsorption sites for phosphate ions (Andrieux-Loyer and Aminot, 2001; Liu *et al.,* 2002; Zhou *et al.,* 2005). Regeneration from the sediments also results in enrichment of phosphate in the overlying waters (Seshappa and Jayaraman, 1956; Reddy and Sankaranarayanan, 1972; Jacob and Qasim, 1974; Nambisan *et al.,* 1987).

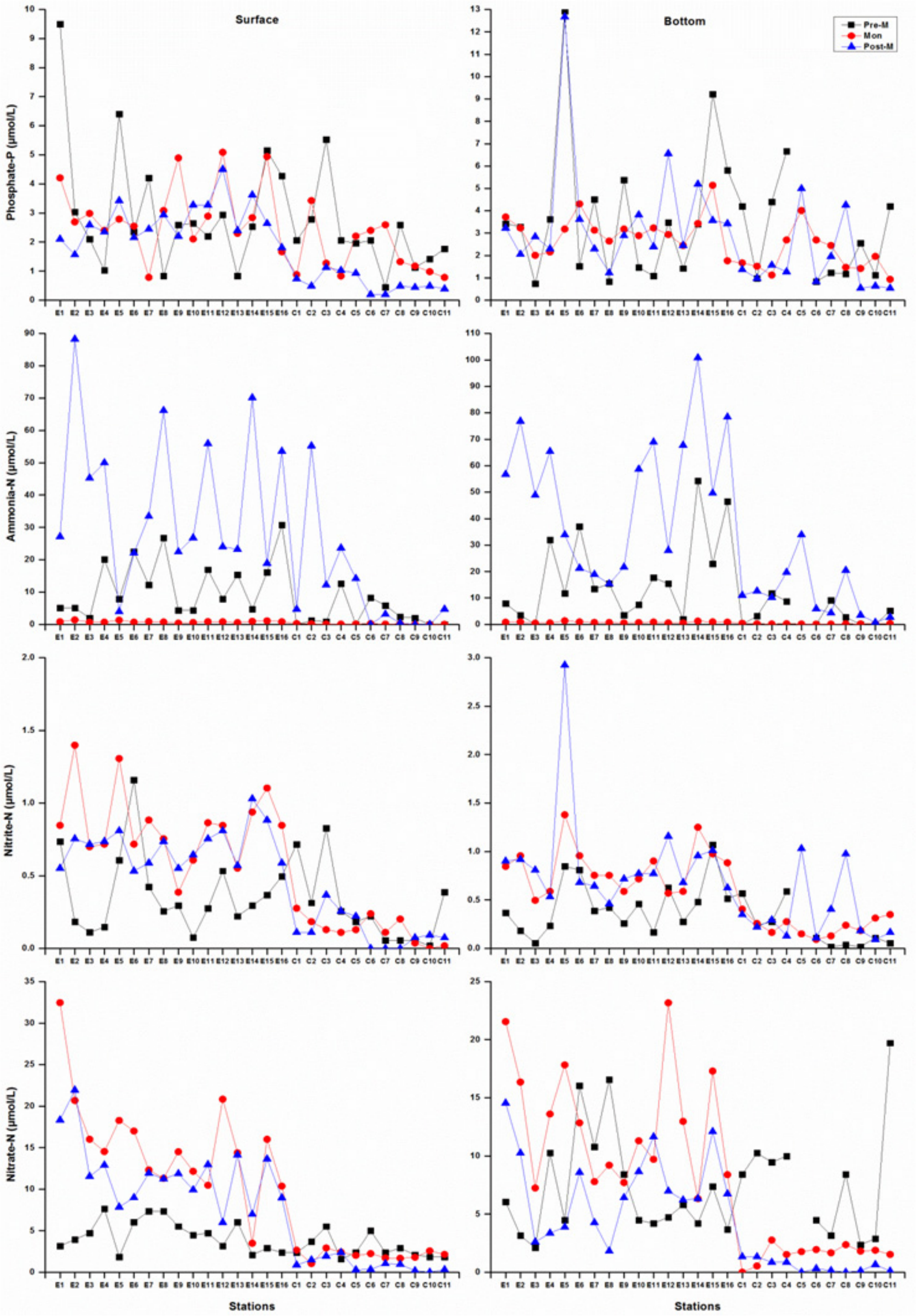

Figure 3.2 Spatial and temporal variations of phosphate-P, ammonia-N, nitrite-N and nitrate-N in Cochin estuarine and coastal system

Phosphate-P content in the coastal waters showed an annual average of 1.46 ± 1.11 μmol/L in the surface and 2.13 ± 1.54 μmol/L in the bottom. Highest values were observed during Pre-M season both in the surface (C3, 5.53 μmol/L) and bottom (C4, 6.66 μmol/L). Post-M season was associated with lowest values; C6 & C7 (0.2 μmol/L) in the surface and C9 & C11 (0.54 μmol/L) in the bottom (Fig.3.2). Phosphate showed highly significant temporal variation in the surface waters (p value = 0.002) only. Post-M season was observed to be with low phosphate content. Although significant spatial variations lacked in the distribution of phosphate in the coastal area, stations around the bar mouth were found to be associated with higher phosphate concentrations pointing to the estuarine input of this nutrient. Coastal stations away from the bar mouth also showed higher levels of phosphate, suggesting along with the discharges from the Cochin estuary which bring in substantial amount of phosphorus to the coastal waters, the sediments of the shallow coastal region including the mud bank sediments were also reported to regulate the adsorption-desorption of phosphate to the overlying waters (Balachandran, 2001).

Table 3.2 Pearson correlation matrix of hydrographic parameters in the surface waters of Cochin estuary during pre-monsoon (n=16)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	-0.207										
DO	-0.182	0.063	1								
Salinity	0.116	0.105	-.583*								
Phosphate	0.040	.546*	-0.298	-0.09	1						
Ammonia	0.370	-0.38	-0.464	0.165	-0.253	1					
Nitrite	0.344	0.111	-0.447	0.012	0.460	0.247	1				
Nitrate	0.430	-0.422	-0.011	0.138	-.572*	0.312	-0.171	1			
Silicate	0.298	0.242	0.462	-0.475	0.316	-0.431	0.174	-0.237	1		
SPM	0.200	0.050	-0.461	.677**	-0.327	0.496	0.018	.599*	-.590*	1	
Chlorophyll-a	-0.375	-0.011	.748**	-.602*	-0.255	-0.477	-0.428	0.071	0.230	-0.486	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.3 Pearson correlation matrix of hydrographic parameters in the bottom waters of Cochin estuary during pre-monsoon (n=16)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	0.261	1									
DO	0.016	-0.076	1								
Salinity	0.141	0.183	-.718**	1							
Phosphate	-0.155	0.024	-0.427	0.156	1						
Ammonia	-0.111	-0.055	-.521*	0.365	0.098	1					
Nitrite	-0.128	-0.106	-.541*	0.169	.628**	0.363	1				
Nitrate	0.032	-0.331	-0.175	0.146	-0.172	0.170	0.240	1			
Silicate	0.201	0.354	0.368	-.498*	0.360	-0.452	-0.020	-0.245	1		
SPM	0.271	-0.201	-.498*	.549*	-0.150	0.365	0.352	.588*	-.537*	1	
Chlorophyll-a	0.305	0.192	.556*	-0.337	-0.209	-0.206	-0.417	-0.355	0.256	-0.089	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

b) Ammonia-Nitrogen

In most coastal environments, the majority of recycled nitrogen is released from sediments to water in the form of ammonium ion (Kemp *et al.,* 1990). Sources of ammonia include domestic, industrial or agricultural, primarily fertilizers. Occurrence of ammonia in the waters can be accepted as the chemical evidence of organic pollution (Trivedi and Goel, 1984). The toxicity of ammonia is critically dependent on pH and temperature. Primary production in a coastal system to a certain extent is controlled by the supply of NH_4^+ excreted by zooplankton and other organisms at the higher trophic levels, when the interaction of NO_2^- and NO_3^- was found to be one of the limiting factors during summer (Balachandran *et al.,* 2008). Among the nitrogen compounds, ammonia is reported to be the preferred form for assimilation by the phytoplankton (Strickland *et al.,* 1969; Goldman, 1976; Conway, 1977). Presence of higher levels of ammonia in waters is indicative of the balance between the production and utilization, and these reserves might play a vital role for the propagation and growth of phytoplankton at a higher rate (Balachandran, 2001).

Ammonia-N in the estuary showed annual average of 17.65 ± 21.39 µmol/L and 23.23 ± 26.97 µmol/L in the surface and bottom waters respectively. Highest values were recorded during Post-M in E2 (88.24 µmol/L) and E14 (100.80 µmol/L) in the surface and bottom waters respectively (Fig.3.2). Mon season was associated with lowest values in the surface in E9 (0.39 µmol/L) and in the bottom in E3 (0.5 µmol/L). Highly significant temporal variations were observed in the case of ammonia (p value 2.61×10^{-8} and 2.77×10^{-9} in the surface and bottom waters respectively) and spatial variations were not significant in its distribution in the estuary. Post-M season was recorded with highest ammonia levels followed by Pre-M season and this can be attributed to the death and subsequent decomposition of phytoplankton; active regeneration from the sediment and the excretion of ammonia by the planktonic organisms (Segar and Hariharan, 1989). Ammonia-N was below the detectable limits in E3 during Pre-M season. Mon season was characterised with very low ammonia content. Increased fresh water inputs during Mon season is capable of diluting the inputs of nutrients. During Mon season, only few of the stations (E2, E5 & E15 in the surface and E5 & E14 in the bottom) showed ammonia levels greater than 1 µmol/L. High ammonia concentrations were observed in the northern and southern estuarine stations in comparison to the central stations. Northern stations may be receiving ammonia from the industries north off the Cochin estuary (Sarala Devi *et al.,* 1979; Maya, 2005) and southern stations might be having influence of agricultural practices and fish processing units situated on the banks of the wetland system.

Annual average of ammonia-N in the coast was 4.63 ± 10.58 µmol/L and 5.26 ± 7.77 µmol/L in the surface and bottom waters respectively. Highest concentrations were detected in C2 (55.25 µmol/L) in the surface and C5 (33.88 µmol/L) in the bottom during Post-M. Lowest levels of ammonia was found in C11 (0.02 µmol/L) in the surface and in C6 (0.09 µmol/L) in the bottom during Mon season (Fig.3.2). Significant spatial variations were not observed in the case of ammonia. Ammonia showed significant temporal variations in the bottom waters only. Post-M season recorded with highest ammonia levels followed by Pre-M. Active regeneration of ammonia from the sediments which are high in organic matter was reported (Ketchum, 1962; Nair, 1990). During Mon season, coastal waters were detected with very low ammonia levels. During this season, the coastal environment experiences the upwelling resulting in high population of phytoplankton which consume ammonia in the waters. Although active regeneration from the sediments might have raised the ammonia levels in the waters, the utilization might have outweighed the production (ammonification process).

Table 3.4 Pearson correlation matrix of hydrographic parameters in the surface waters of Cochin estuary during monsoon (n=16)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	0.168	1									
DO	-0.100	.624**	1								
Salinity	-0.300	0.081	-0.285	1							
Phosphate	0.441	-0.089	-.602*	0.074	1						
Ammonia	0.126	0.294	0.368	-0.435	-0.037	1					
Nitrite	0.129	0.291	0.368	-0.436	-0.039	1.000**	1				
Nitrate	0.249	0.293	-0.224	-0.008	0.425	0.199	0.195	1			
Silicate	-0.117	0.120	0.247	-0.113	-.705**	0.269	0.271	-0.18	1		
SPM	-0.043	-0.299	-.585*	0.054	.665**	-0.367	-0.372	0.056	-.584*	1	
Chlorophyll-a	0.009	0.396	0.457	-0.241	0.085	0.297	0.298	0.138	-0.308	-0.11	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.5 Pearson correlation matrix of hydrographic parameters in the bottom waters of Cochin estuary during monsoon (n=16)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	-0.435	1									
DO	0.396	0.073	1								
Salinity	-.789**	0.457	-.744**	1							
Phosphate	0.409	-0.338	-0.072	-0.255	1						
Ammonia	0.336	0.101	.629**	-.516*	0.459	1					
Nitrite	0.337	0.101	.630**	-.516*	0.453	1.000**	1				
Nitrate	.583*	-0.208	0.178	-0.425	0.358	0.098	0.093	1			
Silicate	0.078	-0.127	0.108	-0.180	-0.173	-0.010	-0.009	0.066	1		
SPM	-0.127	0.414	.534*	-0.115	-0.218	0.494	0.495	-0.407	-0.160	1	
Chlorophyll-a	-0.095	0.059	0.351	-0.169	0.122	0.493	0.497	-0.403	0.364	0.339	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

c) Nitrite-Nitrogen

Annual average of nitrite-N in the estuarine surface water was 0.64 ± 0.30 and that of bottom water was 0.73 ± 0.43 µmol/L. Highest nitrite content was found in the surface (E2, 1.40) during Mon and in the bottom (E5, 2.92) during Post-M (Fig.3.2). Lowest concentrations were detected in E10 (0.07) in the surface and E3 (0.06) in the bottom during Pre-M season. In general bottom stations were associated with higher nitrite concentrations compared to the surface waters. The nitrification-denitrification processes may probably account for the observed high concentrations of nitrite in the bottom waters. Nitrite exhibited highly significant temporal variations in the estuary (p value 8.22×10^{-6} and 0.0002 in the surface and bottom waters respectively), but spatial variation was significant only in the bottom waters (p value = 0.003). Mon season was associated with highest nitrite levels, which then followed by Post-M season and this may be due to the input of urban/industrial effluents and the monsoon floodwater into the estuary (Robin *et al.,* 2003). Lowest nitrite concentrations were detected during Pre-M season except in E1 and E6 in the surface and E6, E12 and E15 in the bottom waters. This observation is in agreement with the previous reports which stated that during Pre-M season lowest nitrite levels were observed in Cochin backwaters (Sankaranarayanan and Qasim, 1969; Balchandran, 2001).

Nitrite-N in the coastal waters showed annual averages of 0.18 ± 0.19 µmol/L in the surface and 0.27 ± 0.24 µmol/L in the bottom. Highest values were detected in C3 in the surface (0.83 µmol/L) during Pre-M and in C5 in the bottom (1.03 µmol/L) during Post-M (Fig.3.2). Lowest concentration (0.02 µmol/L) was detected in C10 (Pre-M) & C11 (Mon) in the surface and C7 & C9 in the bottom (Pre-M). Nitrite in the surface coastal waters showed significant temporal variations only (p value = 0.03); whereas in the bottom, it lacked spatial and temporal variations during the study period. During Mon and Post-M seasons, bottom stations were associated with high nitrite; whereas during Pre-M, surface waters were found to be associated with higher nitrite levels. Higher nitrite level in the bottom during Mon can be attributed to the retrieval from the sediments as a result of the disturbances during this season and upwelling phenomena. Higher nitrite levels during Post-M can be attributed to the decay of dead organism resulting in partial denitrification and the resultant high values of nitrite-nitrogen. Whereas, during Pre-M, the main source of nitrite might be the estuarine surface inflow.

Stations near the bar mouth were associated with higher nitrite levels during Pre-M; but during Mon season, stations just south of the bar mouth (C6-C8) took over this position. In the bottom waters also, stations C1 and C4 were associated with highest nitrite during Pre-M and the southern coastal stations were found to be with lower nitrite. In general, the higher amount of nitrite detected near the bar mouth indicated the influence of estuarine input of nutrients into the costal environment.

Table 3.6 Pearson correlation matrix of hydrographic parameters in the surface waters of Cochin estuary during post-monsoon (n=16)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	-0.341	1									
DO	-0.060	.530*	1								
Salinity	-.663**	.557*	0.042	1							
Phosphate	-0.138	-0.176	-0.214	0.063	1						
Ammonia	-0.186	-0.336	-0.297	-0.322	-0.217	1					
Nitrite	-0.185	-0.264	0.002	-0.080	.581*	0.313	1				
Nitrate	0.162	0.150	0.447	-0.419	-.666**	0.335	-0.245	1			
Silicate	0.386	0.213	0.334	-0.338	0.169	0.068	0.431	0.301	1		
SPM	0.288	-0.278	-0.112	-0.374	.727**	-0.200	0.319	-0.450	0.120	1	
Chlorophyll-a	0.258	0.167	0.155	-0.155	.608*	-0.272	0.425	-0.301	.540*	.648**	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.7 Pearson correlation matrix of hydrographic parameters in the bottom waters of Cochin estuary during post-monsoon (n=16)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	0.219	1									
DO	0.339	-0.108	1								
Salinity	-0.303	.632**	-0.279	1							
Phosphate	0.420	0.188	.693**	-0.165	1						
Ammonia	-0.043	-.661**	0.082	-0.383	-0.097	1					
Nitrite	0.421	0.303	.642**	-0.115	.946**	-0.098	1				
Nitrate	0.221	-.517*	0.011	-.787**	-0.120	0.301	-0.059	1			
Silicate	.605*	-0.277	.512*	-.756**	0.488	0.182	0.447	.572*	1		
SPM	0.309	-0.381	.559*	-.548*	0.396	0.016	0.197	0.167	.578*	1	
Chlorophyll-a	.720**	-0.011	.654**	-.579*	0.489	-0.07	0.454	0.277	.834**	.664**	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

d) Nitrate-Nitrogen

In the estuary, nitrate-N showed annual averages of 10.57 ± 6.28 µmol/L and 8.96 ± 5.12 µmol/L in the surface and bottom waters respectively. Highest nitrate levels were found in E1 (32.46 µmol/L) in the surface and E12 (23.17 µmol/L) in the bottom during Mon season (Fig.3.2). E5 (1.84 µmol/L during Pre-M) and E8 (1.82 µmol/L during Post-M) were recorded with lowest values in the surface and bottom waters respectively. During Pre-M, nitrate in the bottom waters predominated than that in the surface waters (exceptions were E2, E3, E11 and E13). But majority of the estuarine stations showed surface predominance on nitrate concentrations (exceptions were E12, E14 and E15 during Mon; E12 during Post-M). In the estuary, nitrate exhibited highly significant temporal variations (p value 6.61×10^{-8} and 0.001 in the surface and bottom waters respectively) and spatial variations were not significant in the case of nitrate. In the surface waters, nitrate levels decreased from Mon to Post-M and lowest concentrations were detected during Pre-M season. Whereas in the bottom waters, this much variability was not found. Mon season was associated with higher nitrate levels in majority of the estuarine stations (exceptions E2, E11 and E14 in the surface; E6-E9, E11 and E14 in the bottom). This suggested that riverine input and land drainage were the major source of nutrients into the Cochin estuarine system during Mon season (Sankaranarayanan and Qasim, 1969; Shaiju, 2013).

Nitrate-N in the coastal surface waters showed an annual average of 1.96 ± 1.23 µmol/L and that of bottom waters was 3.21 ± 4.32 µmol/L (Fig.3.2). In the bottom, C11 was registered with the highest (19.72 µmol/L) and lowest (0.01 µmol/L) values during Pre-M and Post-M seasons respectively. Whereas in the bottom, C9 showed lowest value (0.189 µmol/L) during Post-M and C3 showed highest value (5.52 µmol/L) during Pre-M season. Nitrate exhibited highly significant temporal variations (p value 0.0001 and 0.00008 in the surface and bottom waters respectively) and spatial variations were not significant in the case of nitrate. Pre-M season was found to be detected with highest nitrate content followed by Mon and Post-M seasons. During Pre-M, bottom waters were found to be associated with higher nitrate levels. However, the situation reversed during Mon and Post-M seasons and the surface waters were associated with high nitrate content. Monsoonal runoff might be the reason for the higher nitrate content and this high amount of nitrates is indicative of pollution of an aquatic system. During Pre-M, when the surface estuarine runoff is low, bottom regeneration/nitrification is more resulting in higher nitrate level in the bottom waters. Nitrification rates in non-monsoon months were reported to be about 2 orders of magnitude greater than in monsoon (Miranda *et al.,* 2008).

Strong negative correlation observed between salinity and ammonia (r^2 = - 0.516 in the bottom waters during Mon), salinity and nitrite (r^2 = - 0.516 in the bottom waters during Mon), salinity and nitrate (r^2 = - 0.787 in the bottom waters during Post-M), silicate and salinity (r^2 = - 0.498 & - 0.756 in the bottom waters during Pre-M and Post-M respectively) showed the nutrient levels are controlled by the fresh water discharges. Nitrogen fractions were found to have strong negative correlations compared to other nutrients and this may be attributed to the disproportionate increase in nitrogen inputs where there is greater fresh water flow (Korner, 1987).

Table 3.8 Pearson correlation matrix of hydrographic parameters in the surface waters of Cochin coast during pre-monsoon (n=11)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	-.728*	1									
DO	-0.089	0.242	1								
Salinity	0.058	-0.218	-0.462	1							
Phosphate	.644*	-0.542	0.144	-0.006	1						
Ammonia	0.085	-0.147	-0.016	0.121	-0.185	1					
Nitrite	.726*	-.647*	-0.252	-0.115	.718*	-0.233	1				
Nitrate	0.324	-0.431	0.089	0.272	.724*	0.000	0.462	1			
Silicate	.672*	-0.468	-0.083	-0.174	0.203	-0.293	.614*	-0.176	1		
SPM	0.532	-.607*	-0.343	0.431	.713*	-0.267	.711*	.737**	0.295	1	
Chlorophyll-a	-0.061	0.054	0.166	-0.391	0.110	0.337	-0.196	0.122	-0.469	-0.178	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.9 Pearson correlation matrix of hydrographic parameters in the bottom waters of Cochin coast during pre-monsoon (n=10)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	-0.385	1									
DO	-0.535	.675*	1								
Salinity	-0.597	-0.171	-0.013	1							
Phosphate	0.252	-0.365	-0.068	-0.126	1						
Ammonia	0.327	-0.468	-0.472	0.055	0.488	1					
Nitrite	0.341	-0.453	-0.105	-0.306	.637*	0.084	1				
Nitrate	-0.015	-0.162	0.052	-0.033	0.514	0.370	0.092	1			
Silicate	0.189	0.400	0.304	-0.508	0.187	-0.517	0.511	-0.035	1		
SPM	0.208	-0.423	-0.188	0.118	0.403	0.563	0.254	.675*	-0.109	1	
Chlorophyll-a	0.252	-0.103	-0.007	-0.429	-0.270	-0.223	0.140	-0.179	0.161	0.204	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

e) Silicate-Silicon

Large amount of silica get into the marine environments mainly by the rivers (Livingstone, 1963; Ganjian-Khenari, 2010; Mahmoudi *et al.,* 2013). General trend for decreasing levels of silica in rivers, lakes and coastal marine areas during the last half of the twentieth century has been reported (Canfield *et al.,* 2005) and this has been related to high discharges of nitrogen and phosphorus, and to the regulation of rivers by damming (Mahmoudi *et al.,* 2014). Silicon is a biologically essential nutrient to many marine organisms for the growth and formation of their skeletal materials. Conservative and non-conservative mixing of silicate in estuarine environments have been reported and in Cochin estuarine system silicon behaves non-conservatively in the salinity range 4 to 22 psu where substantial removal of this element is observed (Sankaranarayanan *et al.,* 1984; Balachandran *et al.,* 1996).

Average annual silicate-Si content in the estuarine surface water was 10.82 ± 17.65 µmol/L and that in the bottom waters was 12.27 ± 20.07 µmol/L. E2 during Pre-M was registered with highest silicate content both in the surface (78.33 µmol/L) and bottom (81.22 µmol/L) waters (Fig.3.3). Lowest values were detected in E9 (0.32 µmol/L) and E12 (0.40 µmol/L) during Mon season. In the estuary, nitrate exhibited highly significant temporal variations (p value 1.27×10^{-6} and 1.17×10^{-7} in the surface and bottom waters respectively) and spatial variations were not significant in the case of silicate. Pre-M season was found to be with highest silicate concentrations followed by Post-M season.

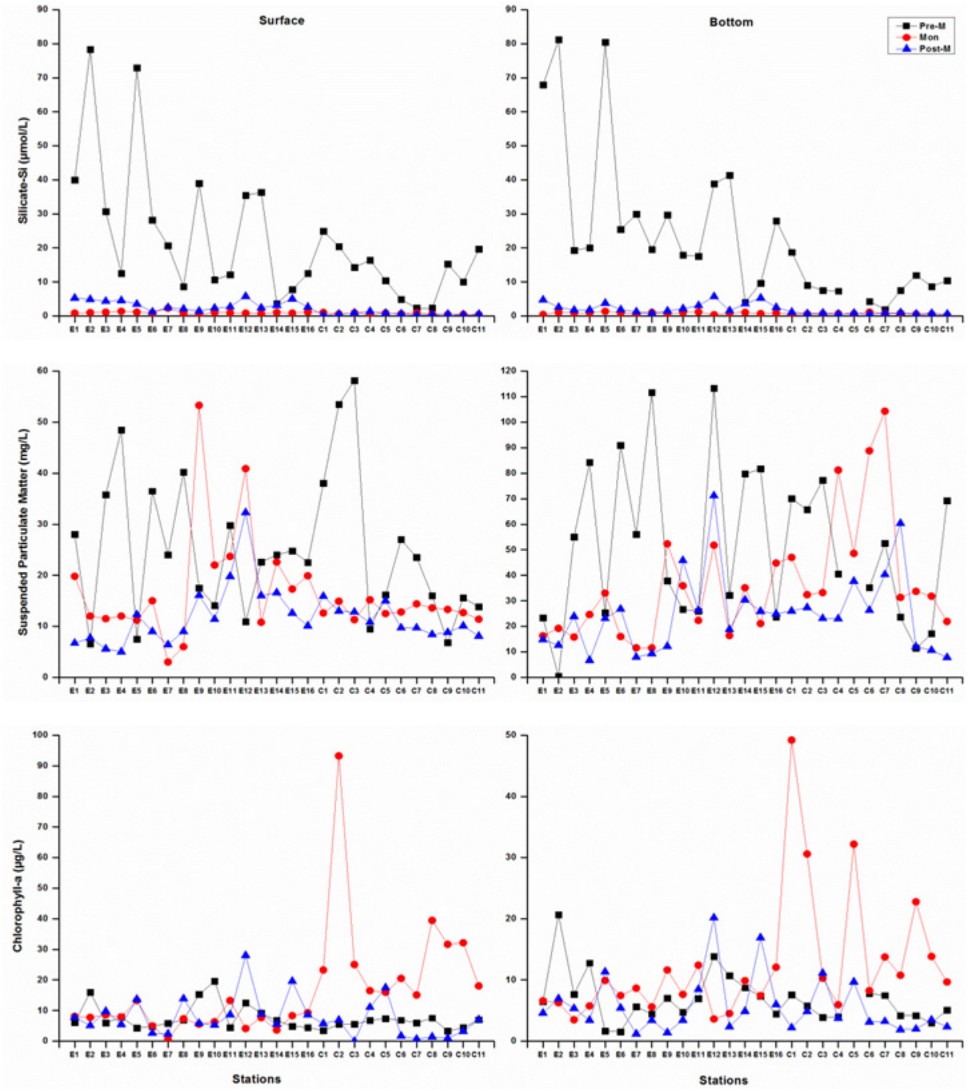

Figure 3.3 Spatial and temporal variations of silicate-Si, suspended particulate matter and chlorophyll-a in Cochin estuarine and coastal system

Silicate showed annual average of 4.69 ± 7.20 µmol/L in the surface and 3.22 ± 4.50 µmol/L in the bottom coastal waters. Highest silicate content was found in C1 both in the surface (24.89 µmol/L) and bottom (18.71 µmol/L) during Pre-M (Fig.3.3). Lowest levels was detected in the surface in C1 (0.25 µmol/L) during Post-M and in the bottom in C11 (0.23 µmol/L) during Mon. Silicate exhibited highly significant temporal variations (p value 1.34×10^{-6} and

1.44×10^{-6} in the surface and bottom waters respectively) and spatial variations were not significant in the case of silicate. Highest values were reported during active mud bank periods (Rao *et al.,* 1984) and the subsequent Post-M season and lowest silicate was reported during the pre-monsoon months (Nair, 1990). In contrast to the previous reports, Pre-M season was associated with highest silicate distributions. Higher values were found in stations near the bar mouth and in the southern coastal stations when compared to the central stations. This might be pointing to the riverine influence or the diffusion from the bottom sediments.

Re-suspension of fine silicates due to salinity intrusion during Pre-M might be causing higher silicate-Si in the estuary. Possibility of the localized circulation near small islands in the res-suspension of sediments can contribute to the higher silicate-Si during Pre-M season. Evidences of such localised circulation in the Cochin estuary has been reported earlier (Anto *et al.,* 1977; Sundaresan Pillai, 1989). High rate of bioturbation and bioirrigation by benthic organisms like polychaetes, oligochaetes, copepods and tuberllarians, which were usually highly populated during pre-monsoon periods in response to the increased salinity, has been reported to cause increase in benthic fluxes of silicate to the overlying waters (Callender and Hammond, 1982; Ansari *et al.,* 1986; Ansari and Parulekar, 1993; Mortimer *et al.,* 1999; Anil *et al.,* 2009). Physical reworking of the sediments by waves and tidal actions (Hammond et al., 1977), transport through abiogenic bubble tube structures (Martens *et al.,* 1980) and advective flows arising from bottom unevenness (Huettel *et al.,* 2003) have also been reported to increase the exchange of silicate from the sediment and pore water to the overlying waters (Santschi *et al.,* 1990). Physical disturbances caused during the sampling also release silicates to the water column.

Table 3.10 Pearson correlation matrix of hydrographic parameters in the surface waters of Cochin coast during monsoon (n=11)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	0.422	1									
DO	.731*	0.246	1								
Salinity	0.579	0.405	0.313	1							
Phosphate	-0.517	-0.238	-0.181	0.013	1						
Ammonia	-.708*	-0.588	-0.485	-0.441	0.324	1					
Nitrite	-.711*	-0.581	-0.478	-0.435	0.338	1.000**	1				
Nitrate	0.061	0.041	-0.461	-0.226	-.680*	-0.043	-0.059	1			
Silicate	-.674*	-.615*	-.662*	-0.581	0.23	0.577	0.569	0.259	1		
SPM	-0.392	-0.014	0.064	0.128	0.413	0.147	0.161	-0.585	-0.117	1	
Chlorophyll-a	-0.333	0.282	0.170	-0.208	0.539	0.161	0.178	-.651*	-0.241	0.396	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.11 Pearson correlation matrix of hydrographic parameters in the bottom waters of Cochin coast during monsoon (n=11)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	-0.345	1									
DO	-0.262	.627*	1								
Salinity	0.118	0.076	-0.377	1							
Phosphate	-0.484	0.273	-0.255	0.133	1						
Ammonia	0.290	-0.407	0.014	0.024	-0.447	1					
Nitrite	0.313	-0.416	-0.004	0.033	-0.453	1.000**	1				
Nitrate	0.290	0.160	-0.021	-0.105	0.02	-0.591	-0.587	1			
Silicate	-0.435	0.376	-0.047	0.036	0.452	-.661*	-.663*	0.259	1		
SPM	-0.589	0.355	-0.237	0.301	0.576	-0.487	-0.491	-0.012	.627*	1	
Chlorophyll-a	-0.270	-0.210	0.163	-0.471	0.098	0.362	0.355	-.753**	-0.159	-0.221	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

3.2.1.6 Suspended Particulate Matter (SPM)

Particulate material comprises both living and non-living organic matter and these suspended solids play significant role in geochemical processes at the sedimentogenesis stage due to their high activity. Thus, in effect it is an indicator of a basin's productivity, its nutrient supply and of the intensity of biochemical processes. Suspended particulate matter has a significant role in transportation of pollutants like heavy metals. These metals carried by the particles may be mobilized to an extent during estuarine mixing. Metals can be transferred to the next trophic levels through the ingestion of these metal adsorbed particles by the detrital feeders.

Annual average of SPM in the estuary was 18.56 ± 11.71 mg/L in the surface waters and 34.92 ± 26.96 mg/L in the bottom waters. Highest levels of SPM was found in the surface in E9 (53 mg/L) during Mon and in the bottom in E12 (113.30 mg/L) during Pre-M seasons (Fig.3.3). Station, E7 (3 mg/L) in the surface during Mon and E2 (0.4 mg/L) in the bottom during Pre-M was associated with lowest particulate matter contents. Bottom waters were associated with higher SPM compared to the surface waters. SPM showed significant temporal variations both in the surface (p value = 0.015) and bottom (p value = 0.0006). Pre-M season was found to be with higher SPM followed by Mon and Post-M seasons.

Suspended particulate matter showed annual averages of 16.52 ± 11.74 mg/L in the surface coastal water and 40.98 ± 24.59 mg/L in the bottom water. In the surface waters, C9 was recorded with lowest (6.80 mg/L) and C3 (58.20 mg/L) with the highest SPM during Pre-M (Fig.3.3). While in the bottom, C11 detected with lowest SPM (7.80 mg/L) during Post-M and C7 with the highest SPM (104.30 mg/L) during Mon season. SPM showed significant temporal variations in the surface waters only (p value = 0.006) and spatial variation was not significant in the coastal waters. Higher SPM was detected in the surface waters during Pre-M season, followed by Mon and Post-M seasons. In the coastal environment also, the bottom waters were associated with more SPM than the surface waters.

Table 3.12 Pearson correlation matrix of hydrographic parameters in the surface waters of Cochin coast during post-monsoon (n=11)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	0.134	1									
DO	-0.092	0.298	1								
Salinity	-0.600	0.436	0.414	1							
Phosphate	0.230	-0.467	-0.352	-.667*	1						
Ammonia	-0.286	-0.472	-0.514	-0.411	0.273	1					
Nitrite	0.245	-0.520	-0.415	-.696*	.937**	0.338	1				
Nitrate	0.218	-0.357	-.754**	-.777**	0.574	0.545	0.576	1			
Silicate	.669*	-0.499	-0.404	-.906**	.678*	0.362	.721*	.629*	1		
SPM	-0.485	-0.555	-0.273	-0.050	0.589	0.395	0.521	0.228	0.103	1	
Chlorophyll-a	0.121	-0.523	-0.213	-0.280	0.460	0.392	0.365	0.036	0.460	0.495	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.13 Pearson correlation matrix of hydrographic parameters in the bottom waters of Cochin coast during post-monsoon (n=11)

	Temperature	pH	DO	Salinity	Phosphate	Ammonia	Nitrite	Nitrate	Silicate	SPM	Chlorophyll-a
Temperature	1										
pH	-0.149	1									
DO	-0.518	0.320	1								
Salinity	-0.143	0.537	.656*	1							
Phosphate	0.013	-0.238	-0.500	-0.566	1						
Ammonia	-0.204	-0.354	-0.521	-.747**	.841**	1					
Nitrite	-0.015	-0.266	-0.460	-0.494	.980**	.773**	1				
Nitrate	-0.019	0.088	-0.038	-0.179	-0.412	-0.08	-0.433	1			
Silicate	0.262	-0.033	-0.234	-0.225	0.477	0.272	0.528	0.250	1		
SPM	0.160	-0.354	-0.468	-0.576	.803**	0.586	.799**	-0.245	0.558	1	
Chlorophyll-a	0.448	-0.092	-0.584	-0.521	0.373	0.467	0.286	0.101	0.097	0.058	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

3.2.1.7 Chlorophyll-a

Phytoplanktonic biomass in terms of chlorophyll-a concentration is a generally accepted method of assessing the biological production (Luo *et al.*,

2009) and is often used to assess the eutrophic status of an aquatic environment (Jayaweera and Asaeda, 1995; Yung *et al.,* 1997; Zhou *et al.,* 2004). Chlorophyll pigments are documented as markers of various processes acting in the sea water and sediments (Szymczak-Zyła and Kowalewska, 2007). In the northern part of the Cochin Estuary, high biomass of chlorophyll-a due to the enrichment of nutrients by industrial and domestic activities have been reported by Jyothibabu *et al.(* 2006) and Madhu *et al.*(2007). Weak flushing resulted from the anthropogenic activities might have led to an increased production of chlorophyll-a in the northern and central estuary (Shaiju, 2013).

Chlorophyll-a of the estuarine surface waters showed an annual average of 8.40 ± 5.07 µg/L and that of bottom waters was 7.36 ± 4.43 µg/L. Highest concentration in the surface waters was recorded in E12 (28.04 µg/L) during Post-M and in E2 (20.70 µg/L) during Pre-M in the bottom water. Lowest values were detected in the surface in E7 (0.58 µg/L) during Mon and in the bottom in E7 (1.20 µg/L) during Post-M (Fig.3.3). Significant spatial and temporal variability was lacking in the case of chlorophyll-a distribution during the study period. Still, Mon season was found to be with lower chlorophyll-a levels in many of the stations, which can be attributed to the high riverine discharge which leads to reduced residence time, leading to increased flushing of phytoplankton biomass out of the estuary (Boynton *et al.,* 1982; Bianchi *et al.,* 1997; Jyothibabu *et al.,* 2006; Lane *et al.,* 2007).

Annual average of chlorophyll-a in the coast was 13.67 ± 17.47 µg/L in the surface and 9.62 ± 10.42 µg/L in the bottom waters. Highest concentration in the surface waters was recorded in C2 (93.25 µg/L) during Post-M and in C1 (49.21 µg/L) during Mon in the bottom water. Lowest values were detected in the surface in C7 (0.71 µg/L) during Post-M and in the bottom in C8 (1.90 µg/L) during Post-M (Fig.3.3). Spatial variation was lacking in the case of chlorophyll-a distribution in the coastal waters. Chlorophyll-a showed significant temporal variability in its distribution (p value = 0.0003 in the surface and 0.001 in the bottom waters). Mon season was characterised with high chlorophyll a levels. This can be attributed to the upwelling widespread along the western Indian coast during Mon season (Sharma, 1968; Guptha *et al.,* 1990; Madhu Joshi and Rao, 2012) as the phytoplankton biomass is stimulated by nutrient availability in the upwelled waters (Muller-Karger *et al.,* 2004). The upwelling of cold, nutrient-rich water into the euphotic zone was reported to stimulate high phytoplankton production near the coast (Pauly & Christensen, 1995; Garcia-Reyes *et al.,* 2014). This is substantiated by the low dissolved oxygen observed in the subsurface waters during this season. Another reason for the monsoonal peak of chlorophyll-a may be the high flushing of Cochin estuary which facilitates the faster removal of primary producers to the coastal area during monsoon season (Jyothibabu *et al.,* 2006).

3.2.2 General Sedimentary Characteristics

Results of the general sedimentary parameters of the estuary and its adjacent coast are given in Appendix 7 to 9. Two-way ANOVA without replication was performed to examine the spatial and temporal variations in the distribution of these parameters in the study area (Table 3.14). Correlation matrices obtained from the Pearson correlation analysis of the estuary are represented in Tables 3.15 to 3.17 and that of adjacent coast are represented in Tables 3.18 to 3.20.

3.2.2.1 Temperature

The average annual temperature of the Cochin estuarine sediments was 28.48 ± 0.71 ºC, with a minimum of 27 ºC during Mon and maximum of 30 ºC during Post-M (Fig.3.4). Temporal variation was highly significant in the case of temperature (p value = 0.0002). However, it lacked spatial variability in the estuary. Coastal sediments showed an annual average temperature 28.13 ± 1.06 ºC. Temperature exhibited highly significant spatial (p value = 0.02) and temporal (p value = 1×10^{-8}) variations in the coast. Post-M season was characterised with high temperature followed by Pre-M and Mon seasons.

Seasonal variation of water temperature has no direct effect on the metal solubility (Zumdahl, 1992). But, dissolution of oxygen is higher in cold water than the warm water. Hence, metal concentrations in the interstitial waters of the sediment may decrease with decrease in temperature as more metals are bound to the sediment colloids at higher redox potential (Forstner and Wittmann, 1979; Fritioff *et al.,* 2005).

3.2.2.2 pH

The bioavailability of the sedimentary trace metals is influenced by pH (Luoma, 1983; Chapman and Wang, 2001; Zunkel and Krueger, 2009); weakly adsorbed metals are more bioavailable than the organic-bound metals and structurally complex minerals (Chapman *et al.,* 2003). Lower pH increases metal solubility and reduces the adsorption of metals to the particles that constitute the upper sediment layer. With decrease in the pH of surface sediments, metal mobility in sediment pore water and the overlying water column was reported to be enhanced (Coz *et al.,* 2007). Sediment pH was reported to be an important factor in governing the rate of hydrocarbon mineralisation and the highest mineralisation rates were measured at pH 8.0 (Gordon *et al.,* 1980).

pH showed an annual average of 7.05 ± 0.38 in the sediments of estuary. Highest pH was observed in E3 (7.80) during Post-M and the minimum was in E7 (6.06) during Pre-M season (Fig.3.4). pH of the estuarine sediments varied seasonally (p value = 2.98×10^{-7}). Post-M season recorded highest pH value followed by Pre-M and Mon seasons. Annual average of pH of the coastal sediments was 7.07 ± 0.37. Highest pH was observed in C3 (7.80) during Post-M and the lowest pH was detected in stations C5, C6 & C7 (6.50) during Mon season (Fig.3.4). pH of the coastal sediments varied seasonally (p value = 7.6×10^{-5}). The results showed that the sediment pH was always circumneutral (pH = 6-7). Intense reduction in submerged sediments tends to buffer sediments close to pH 7.0 (Ponnamperuma, 1972).

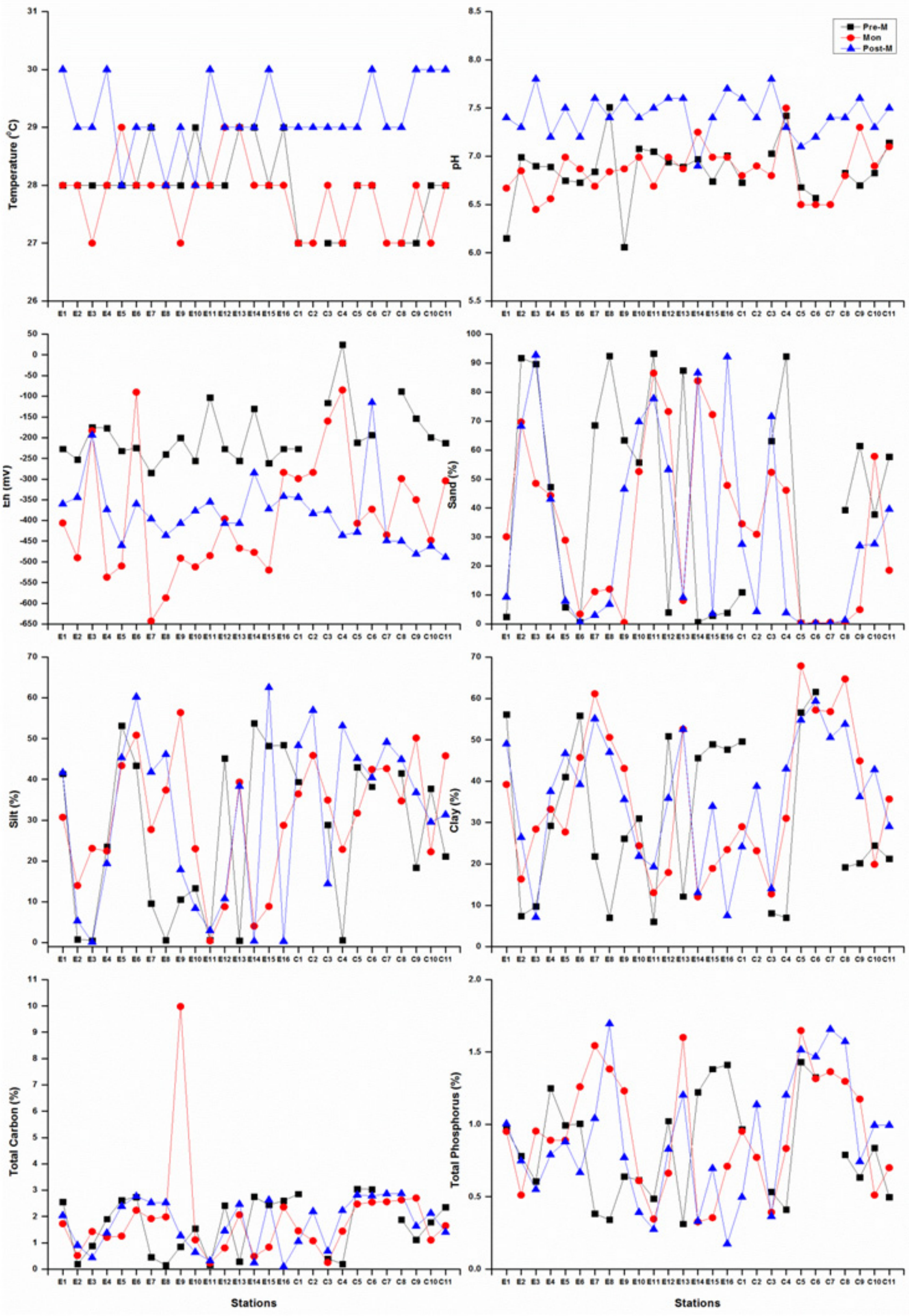

Figure 3.4 Spatial and temporal variations of temperature, pH, Eh, texture, total carbon and total phosphorus in the sediments of Cochin estuarine and coastal system

3.2.2.3 Eh

Oxidation-reduction reactions regulate many of the biogeochemical reactions in surface environments and therefore, sediment redox potential (Eh) can be used to characterise oxidation/reduction status of the surface environments. Eh measurements allow for rapid characterisation of the degree of reduction and for predicting stability of various compounds that regulate nutrients and metal availability in sediments. Iron oxides play a key role in determining the spatial distribution patterns of many of the heavy metals as a result of both the Eh-pH controlled sorption-desorption reactions and some reductive dissolution process (Pauline and Mike, 2002).

The oxidation-reduction (redox) conditions in the surface sediments depend on the degree of organic matter enrichment, combined effects of the biological and chemical processes (reversible/irreversible nature) taking place in the aquatic environment. Negative Eh values are associated with anoxic/reducing conditions, where the anaerobic bacteria perform the degradation of the organic matter. In marine environments, anaerobic bacteria mainly use sulphate as the electron acceptor, which is reduced to hydrogen sulphide (Chamberlain, 2002; Danovaro *et al.,* 2004; Porrello *et al.,* 2005). Anoxic conditions in the sediments cause significant changes in metal speciation and their solubility across the redox interface (Balistrieri *et al.,* 1994). Sediment redox potential was found to be an important factor in governing the rate of hydrocarbon mineralisation, it decreased with decreasing sediment redox potential (Gordon *et al.,* 1980).

Eh showed an annual average of -342.27 ± 132.73 mV in the estuary. Highest and lowest values were recorded in E7 (-643 mV) and E6 (-90 mV) during Mon season (Fig.3.4). Eh of the estuarine sediments showed highly significant temporal variations (p value = 3.44×10^{-8}). Mon season was associated with lowest redox potential followed by Post-M and Pre-M seasons. Annual average of Eh of coastal sediments was -297.90 ± 140.99 mV. Highest Eh was observed in C11 (-489 mV) during Post-M and the lowest value was recorded in C4 (25 mV) during Pre-M (Fig.3.4). Redox potential of the coastal sediments also exhibited highly significant temporal variations (p value = 0.0003). Post-M season was associated with highly reducing sedimentary environment followed by Mon. Pre-M season was associated with comparatively lower reducing conditions. C4 was the only station with a positive redox potential (25 mV) in the entire study area. This station is near the bar mouth with a high sandy sediment texture. This can be attributed partly to the active discharge through the bar mouth which sweep away the fine grained sediments and partly to the continuous dredging in the shipping channel which prevent accumulation of the fine grained sediments along with organic matter.

Submerged sediments display a range of redox potentials from +700 mV, which indicates highly oxidised sediment, to -300 mV, which indicates highly reduced sediment (De Laune *et al.,* 1976). From the high negative Eh values observed, it can be said that the sedimentary environment in the study area is highly reducing (the average Eh is below the redoxcline, i.e. 230 mV). Positive Eh value (25 mV) was observed in only one station, C4 during Pre-M, which is also a moderately reducing condition (De Laune and Reddy, 2005).

3.2.2.4 Texture

Sediment texture is considered to be an important prerequisite for explaining sedimentary metal distribution (Burton and Liss, 1976; Forstner and Wittmann, 1983). Sediment texture is one of the main factor influencing organic matter accumulation which can be ascribed to the close hydraulic equivalence of both organic and mud particles and/or to the relatively high absorptive capacity of fine particles for the organic molecules (Cotano and Villate, 2006). Silt and clay fractions reported to be enriched with organic carbon, nutrients and metals than the sand fraction (Krishna Prasad and Ramanathan, 2008; Wen *et al.,* 2008; Renjith *et al.,* 2011) and this may be due to the greater surface area of these fine particles which result in more adsorption sites for these ions (Andrieux-Loyer and Aminot, 2001; Liu *et al.,* 2002; Zhou *et al.,* 2005). The larger surface area provided by finer sediments preferably adsorb metal scavenging phases like Fe/Mn hydroxides (Thuy *et al.,* 2000; Bradl, 2004; Magesh *et al.,* 2011).

Annual averages of sand, silt and clay in the estuary were 42.80 ± 34.65, 25.29 ± 20.06 and 31.91 ± 16.27 % respectively. Highest sand content was detected in E11 (93.36 %) during Pre-M and lowest was in E9 (0.51 %) during Mon season (Fig.3.4). Lowest and highest silt content was observed during Post-M season in E3 (0.10 %) and E15 (62.52 %) respectively. Highest clay content was observed in E7 (61.14 %) during Mon and lowest in E11 (6.02 %) during Pre-M. Textural features lacked significant spatial and temporal variability in their distribution in the estuary. Estuarine stations E2-E4, E10 and E11 retained high sand content throughout the study period. E2 may be getting sand from the riverine input; E3 and E4 which are the bar mouth stations retain their sandy nature due to estuarine bed-load movements associated with tides (Nair *et al.,* 1993; Srinivas *et al.,* 2003) and the usual dredging activities in this channel also prevent the accumulation of finer sediments. E10 lies in the mouth of a tributary. Stations E1 and E5 were clayey in nature during Pre-M and Post-M seasons, however these station moved to a fine coarse nature due to the monsoonal inflow of sand. Stations E2-E4, E10 and E11 retained high sand content and E6 remained clayey in nature during the entire study period. Stations E7, E8 and E13 changed from sandy texture during Pre-M to clayey nature during Mon and retained its clayey character during Post-M season also. Estuarine station E9, which was sandy during Pre-M undergone a drastic change to silty nature during Mon, which then changed to clayey nature during Post-M season. E12 and E14-E16 changed from clayey nature (Pre-M) to sandy (Mon) season. E12, E14 and E16 retained their sandy character during Post-M, whereas, E15 went back to clayey nature during this season.

Sand, silt and clay in the coastal sediments showed annual averages of 26.26 ± 26.50, 36.41 ± 12.33 and 37.33 ± 18.03 % respectively. Highest sand (92.40 %) and lowest silt (0.59 %) and clay (7.01 %) contents were observed in C4 during Pre-M (Fig.3.4). Lowest sand content was recorded in C5 during Post-M. Highest silt and clay contents were observed in C2 (56.95 %) during Post-M and in C5 (67.87 %) respectively during Mon season. Although significant spatial variation was observed for clay and sand fractions, temporal variations were not prominent in the coastal area. Significant temporal and spatial variations were not observed in the case of silt. Central coastal stations were associated with finer sediments during the entire study period which can be attributed to the dumping of dredge spoil (Balachandran, 2001). Station C3 remained sandy during the entire study period and this can be attributed to the strong discharge through the bar mouth which does not allow the settling of finer materials and the continuous dredging activities in the navigational channel. C4 was very sandy during Pre-M, which then became less sandy during Mon. C4 showed a drastic change in its texture during Post-M season as it became silty in nature. As Post-M season was characterised with a settling environment, siltation is more during this season. Clay fraction dominated in the stations south of the bar mouth during Mon and Post-M seasons, whereas silt dominated in stations just north of the bar mouth (C1 & C2).

3.2.2.5 Nutrient Elements

a) Total Carbon (TC)

Total Carbon showed annual averages of 1.64 ± 1.53 % in the estuary and 1.91 ± 0.87 % in the coast. Highest and lowest values in the estuary were detected in E9 (9.98 %) during Mon and E16 (0.09 %) during Post-M (Fig.3.4). In the coast, highest and lowest values were recorded in C5 (3.05 %) and C4 (0.20 %) during Pre-M season. Spatial and temporal variations were not significant in the case of TC in the estuarine sediments. TC showed significant spatial variability (p value = 0.01) in the coastal sediments. However, temporal variations were not significant in the case of TC.

b) Total Phosphorus (TP)

Total phosphorus in the estuary showed an annual average of 0.83 ± 0.39 % and that of the coast was 0.99 ± 0.40 %. In the estuary, lowest and highest values were reported in E16 (0.18 %) and E8 (1.70 %) during Post-M (Fig.3.4). In the coast also, lowest (0.36 % in C3) and highest (1.66 % in C7) values were detected during Post-M season. Spatial and temporal variations were not significant in the case of TP in the estuarine sediments. Although spatial variation was highly significant in the case of TP (p value = 0.001) in the coast, it lacked temporal variability in the distribution.

c) Total Nitrogen (TN)

Total nitrogen in the estuarine sediments showed an annual average of 0.17 ± 0.11 % and that of the coastal sediments was 0.20 ± 0.13 %. Highest and lowest values in the estuary were recorded in E6 (0.36 %) during Mon and in E8 (0.003 %) during Pre-M respectively (Fig.3.5). In the coast, highest and lowest values were detected in C8 (0.38 %) during Mon and C4 (0.009 %) during Pre-M respectively. Spatial and temporal variations were not significant in the case of TN in the estuarine sediments. Although TN lacked temporal variability in its distribution, spatial variation was highly significant.

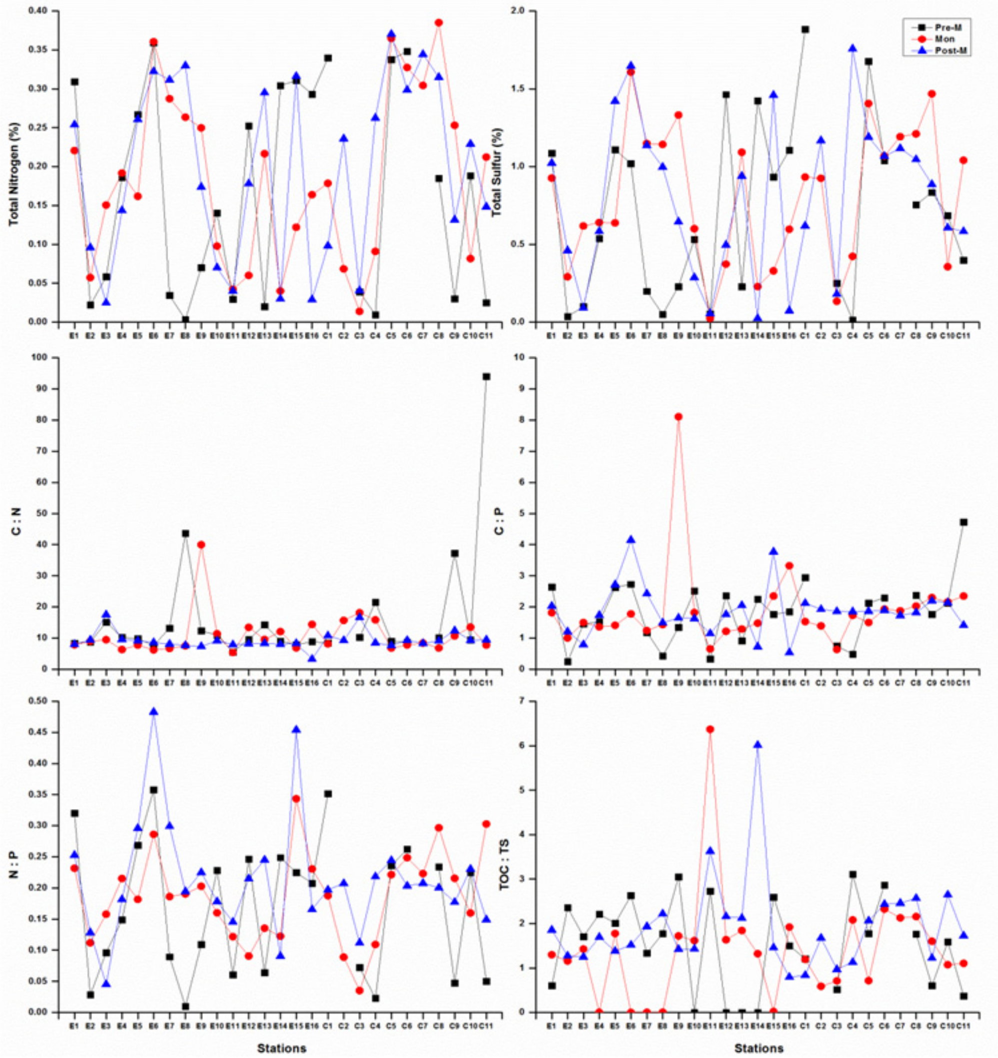

Figure 3.5 Spatial and temporal variations of total nitrogen, total sulfur and elemental ratios in the sediments of Cochin estuarine and coastal system

d) Total Sulfur (TS)

Total sulfur showed annual averages of 0.69 ± 0.49 % in the estuary and 0.90 ± 0.48 % in the coast. Highest and lowest values in the estuary were detected in E6 (1.65 %) during Post-M and E11 (0.023 %) during Mon

(Fig.3.5). Lowest and highest TS levels in the coast were recorded in C4 (0.014 %) and C1 (1.88 %) during Pre-M season. In the study area, TS was devoid of any significant spatial and temporal variability in its distribution.

Table 3.14 ANOVA results of the sedimentary parameters in the Cochin Estuary and its adjacent coast

Parameters	Estuary				Coast			
	Spatial (*df*=15)		Temporal (*df*=2)		Spatial (*df*=8)		Temporal (*df*=2)	
	F	P-value	F	P-value	F	P-value	F	P-value
Temperature	0.70	NS	11.47	0.000**	3.00	0.029*	72.00	0.000**
pH	0.78	NS	25.84	0.000**	3.14	0.024*	18.18	0.000**
Eh	2.15	0.035*	32.17	0.000**	1.47	NS	14.19	0.000**
Sand	1.71	NS	0.03	NS	3.36	0.018*	2.27	NS
Silt	1.77	NS	0.03	NS	0.79	NS	1.08	NS
Clay	1.59	NS	0.07	NS	5.03	0.002**	2.12	NS
TC	0.93	NS	0.29	NS	3.81	0.010**	0.12	NS
TP	0.74	NS	0.45	NS	5.81	0.001**	1.73	NS
TN	1.86	NS	0.08	NS	4.36	0.005**	0.73	NS
TS	1.67	NS	0.19	NS	2.01	NS	0.04	NS
C : N	0.91	NS	0.97	NS	0.94	NS	1.74	NS
C : P	1.23	NS	0.34	NS	1.38	NS	0.63	NS
N : P	3.92	0.000**	2.62	NS	2.06	NS	0.42	NS
TOC : TS	1.12	NS	1.06	NS	3.03	0.028*	0.54	NS
TOM (%)	1.73	NS	0.08	NS	3.27	0.02*	0.36	NS
CHO (mg/g)	1.89	NS	0.53	NS	2.39	NS	0.77	NS
LPD (mg/g)	1.63	NS	1.68	NS	5.69	0.002**	0.93	NS
PRT (mg/g)	3.35	0.002**	3.29	NS	2.66	0.046*	3.35	NS
TAN & LIG (mg/g)	1.22	NS	1.02	NS	4.03	0.008**	7.35	0.005**
BPC (%)	2.22	0.031*	0.47	NS	3.42	0.017*	0.16	NS
PRT : CHO	1.76	NS	2.71	NS	2.53	NS	12.80	0.000**
LPD : CHO	0.72	0.75	1.38	0.27	6.54	0.000**	2.10	0.15

** Significant at the 0.01 level, * Significant at the 0.05 level, NS Not Significant

Ratios of Carbon, Nitrogen, Sulfur and Phosphorus

Nutrient enrichment in the sedimentary environment was evaluated using the elemental ratios of organic matter. Carbon to nitrogen ratios are natural source indicators of sedimentary particulate organic matter (Ruiz-

Fernandez *et al.,* 2002). They are used to identify organic matter provenance in estuarine and near-shore marine environments (Burnett and Schaeffer, 1980; Sweeney and Kaplan, 1980; Thornton and MacManus, 1994) and source discrimination of the pollutants. Higher C : P and N : P ratios in sediments are indicative of increased anthropogenic input of nitrate and phosphate (Emeis *et al.,* 2000). It is also reported that the changes in the C : N and C : P molar ratios are the result of changes in carbon content, rather than in the content of nitrogen and phosphorus (Ruttenberg and Goni, 1997). Many aquatic ecosystems were reported to be shifted from their original phosphorus-limited condition to a nitrogen-limited condition due to the anthropogenic phosphorus inputs (Fisher *et al.,* 1995; Reddy *et al.,* 1999). Vitousek and Howarth (1991) reported that climate warming might increase the availability of N relative to P by accelerating decomposition and N mineralisation.

C : N Ratio

Bulk geochemical proxy such as C : N ratio has been commonly used to distinguish source and fate of organic matter in the marine environments (Meyers, 1994; Schelske and Hodell, 1995; Cloern *et al.,* 2002; Goni *et al.,* 2003) as it is governed by the mixing of terrestrial and autochthonous organic matter in aquatic systems (Muller, 1977; Rashid and Reinson, 1979; Nakai *et al.,* 1982; Ostrom and Macko, 1992; Thornton and McManus, 1994; Meyers, 1997; Yoshikazu Sampei, 2001). C : N ratio between 8 and 12 was reported for estuaries, lagoons and oceans throughout the world by Trask (1932). The range of C : N values are typically higher for terrestrial organic matter than for aquatic organic matter (Meyers and Lallier-Verges,1999) and the ranges were 6.0-9.0 for planktonic organisms (Meyers, 1994), 10–14 indicate organic carbon of terrestrial origin (Calvert and Pedersen, 1992) and 20.0-100.0 for terrestrial plant tissue and soil (Jasper and Gagosian, 1989; Meyers, 1994;

Tyson, 1995; Manju Mary *et al.,* 2012). This distinction arises from the abundance of cellulose in vascular plants and its absence in algae. However, the selective degradation of the different minerals in sediments during early diagenesis can affect the C : N ratios of organic matter (Muller, 1997; Lehmann *et al.,* 2002). Discrepancy arises also from the fact that in shallow coastal ecosystems, most of the organic carbon and nitrogen produced by microphytobenthos and macroalgae rather than phytoplankton (Barranguet *et al.,* 1996; Lucas *et al.,* 2000). Microbial immobilisation of nitrogenous material accompanied by the remineralisation of carbon may also result in lower C : N ratios (Sollins *et al.,* 1984).

The C : N ratios have been widely used to distinguish the origin of organic matter based on the generalisation that algal organic matter has atomic C : N ratios between 4 and 10, whereas organic matter from terrestrial vascular plants has C : N ratios equal to or greater than 20(Prahl *et al.,* 1980; Ishiwatari and Uzaki, 1987; Meyers, 1994; Twichell *et al.,* 2002). Annual average of C : N ratio in the estuary was 10.57 ± 7.12. Lowest ratio was found in E16 (3.24) during Post-M and the highest value was in E8 (43.66) during Pre-M season (Fig.3.5). Stations, E8 (during Pre-M) and E9 (during Mon) were the only stations with C : N ratios higher than 20. Highest value (43.66) was reported in station E8 with very low nitrogen level in the sediments which may be due to the utilization of nitrogenous compounds and lower nitrogen fixation (Anu Gopinath, 2002). E9 was recorded with high carbon content during Mon seasons which resulted in the highest C : N ratio in this station (39.97). C : N ratio between 2.5 and 16.9 has been reported in the sediments of the Cochin estuary (Sankaranarayanan and Panampunnayil, 1979).

C : N ratio showed an annual average of 14.16 ± 15.96 in the coast. Lowest and highest ratio in the coast were found in C5 (6.88) during Mon and

C11 (94) during pre-M respectively (Fig.3.5). Bhosle *et al.,* (1978) observed a high C : N ratio (37.50) for the shelf sediments of the Arabian Sea which can be attributed to the degradation of complex protein. During Pre-M, stations C4, C9 and C11 exhibited C : N ratios higher than 20, representing the vascular input to the coastal area. These ranges are intermediate values characteristic for autochthonous and terrestrial input of organic matter (Muri *et al.,* 2004). Based on, C : N =13 and C : N=16 for the marine and terrestrial end members, respectively (Colombo *et al.,* 1995), it could be inferred that organic matter in the study area are of mixed origin with a major contribution from vascular plants. Very high C : N ratios obtained in the stations C9 and C11 could be due to the utilisation of nitrogenous compounds and lower nitrogen fixation (Anu Gopinath, 2002). Seasonal averages clearly indicated the terrestrial or higher plant inputs of organic matter into both the estuary and its adjacent coast. Hence it can be said that the organic matter of terrestrial origin predominates in the Cochin estuarine and coastal system. The C : N ratio of surface sediments of Cochin estuary and the adjacent coast is comparable with other aquatic environments (Table 3.15), which have terrestrial organic material as the main source of OM to the sediments.

The C : N ratio has also been used as an organic matter quality indicator (Huston and Deming, 2002) with low values indicating fresh ‘‘high quality’’ (i.e. labile) particulate organic matter (Harmelin *et al.,* 2010), although this elemental quantification do not give any information about the chemical features of the organic matter and this over estimates the nutritionally available nitrogen due to the abundance of indigestible nitrogenous compounds like humic material (Mayer *et al.,* 1995). Organic matter in the sediments of Cochin estuary was reported to be highly reactive, with a reactivity index ranging from 2.4–7.4, suggesting rapid remineralisation. Dominance of bacterial biomass in the sediments of the study area have been reported to cause the lowering of C : N ratios when compared to that of terrestrial OM (Verma and Subramanian, 2002). Irrespective of the higher TC values, lower C : N ratios observed in the study area could be attributed to the high bacterial activity and the degradation of vascular plant detritus in the sedimentary environment.

Table 3.15 C : N Ratio of various aquatic environments around the world

Surface Sediments (Marine)		
Dobab Bay, Washington, DC	8.60–13.40	Prahl *et al.,* (1980)
Amazon River estuary	9.20–17.0	Artemyev (1993)
Arabian Sea shelf	2.48–37.50	Bhosle *et al.,* (1978)
Godavari estuary, India	8.50–12.0	Gupta *et al.,* (1997)
Mangroves, Brazil	11.7	Jennerjahn and Ittekkot (1997)
Recent siliciclastic shelf, Brazil	9.8	Jennerjahn and Ittekkot (1997)
Carbonate shelf, Brazil	7.8	Jennerjahn and Ittekkot (1997)
Vembanad Lake, Kerala	12.7 (1.02–21.8)	Verma and Subramanian (2002)
Cochin Estuary	(5.49-43.66) 12.19	Present study
Cochin Coast	(8.40-94.00) 23.20	Present study
Surface Sediments (Fresh Water)		
Sedimentary humic acids, Lake Ontario	8.6	Kemp and Mundrochova (1973)
Sedimentary fulvic acids, Lake Ontario	5.7	Kemp and Mundrochova (1973)
Vascular plants	53.4	Cowie and Hedges (1992)
Macrophytes	12.9	Cowie and Hedges (1992)

According to Russel- Hunter (1970), organic matter should have a C : N ratio lower than 17 in order to be of nutritional use to invertebrates. Majority of the sediments in the study period exhibited C : N ratios lower than 17 which suggested that the organic matter in the study area is of high nutritional value and represented a high- energy source for benthic organisms (Albertelli *et al.,*1998).

C : P Ratio

C : P values above the Redfield ratio (Redfield *et al.,* 1963) indicate a mixture of continental and marine sources (Ruttenberg and Goñi, 1997). The C

: P ratios lower than the Redfield ratio pointed to the enrichment of phosphorus in the organic matter (Hecky *et al.,* 1993).

Annual averages of C : P ratio in the estuarine and coastal sediments were 1.83 ± 1.24 and 1.93 ± 0.73 respectively. In the estuary, lowest ratio was found in E2 (0.25) during Pre-M and highest ratio was found in E9 (8.11) during Mon season. Stations C4 (0.49) and C11 (4.73) showed lowest and highest C : P ratio respectively in the coast (Fig.3.5). Spatial and temporal variations in C : P ratio were not significant in the study area. The C : P values of the present study are lower when compared to other tropical environments located on the Amazonian shelf (38-161), and on Mexican (14-79) and Indian (11-36) estuaries. This indicated the significant addition of P to the Cochin estuary and its adjacent coastal environment. This was reported earlier by many authors (Lizen & Chandramohanakumar, 2003; Gireesh Kumar, 2013). C : P ratios in the coastal and estuarine sediments are lower although the aquatic plant material has a high C : P ratio and this can be attributed to phosphorus contributions from the land. The C : P values of the present study are lower when compared to earlier studies in Cochin estuary also. C : P ratios reported in some previous studies are 22.61 to 60.4 (Qasim and Sankaranarayanan, 1972), 2.25 - 37.51 with an average of 41 (Sankaranarayanan and Panampunnayil, 1979), 15.37 - 36.77 with an average of 21.34 (Lizen and Chandramohanakumar, 2003). Lowering of C : P ratio over the years indicated the increased addition of phosphorus to the Cochin estuary which will lead to the eutrophication of the aquatic system. The main sources of the phosphorus to this ecosystem are the unscientific and uncontrolled applications in agriculture, industrial and municipal wastes. This might have to be controlled for the sustainable management of this versatile aquatic environment.

N : P Ratio

The N : P ratio 16:1, is expected in highly productive waters. N : P ratios have proved useful to investigate shifts from N to P limitation because they are easily determined and compared across studies (Güsewell & Koerselman, 2002; Olde Venterink *et al.,* 2003). Slow moving rivers and some reservoirs exhibit relatively high N : P ratios (> 30:1) and such waters are dominated by noncyanobacterial species (Paerl, 1988).

Annual average of N : P ratio in the estuary was 0.19 ± 0.10. Lowest ratio was found in E8 (0.01) during Pre-M and the highest ratio was found in E6 (0.48) during Post-M season (Fig.3.5). In the estuarine sediments N : P ratio showed highly significant spatial (p value = 0.0007) variations. However, N : P lacked temporal variations. In the coast, N : P ratio showed an annual average of 0.19 ± 0.08. Lowest (0.02 in C4) and highest (0.35 in C1) ratio were associated with Pre-M season (Fig.3.5). Temporal and spatial variation were absent in the case of N : P in the coastal sediments. N : P ratios in the present study were lower than the Redfield ratio indicating that the organic matter is enriched with phosphorus and it tends to accumulate in surface sediments (Hecky *et al.,* 1993). The input of organic matter enriched with P from the feeding rivers and industrial, agricultural and aquaculture activities resulting in a large scale accumulation of refractory organic P in the surface sediments of the Cochin estuary have been reported (Gireesh Kumar, 2013). Nitrogen is the primary limiting nutrient for phytoplankton production in most coastal waters (Downing, 1997). When the total nitrogen to total phosphorus ratio moves below 10, nitrogen may become limiting. Hence it can be said that the study area is also under nitrogen limited condition.

TOC : TS Ratio

TOC : TS ratios reflect the importance of sulfide reduction in the decomposition of organic matter, and thus can be used to get a qualitative indication of the redox status of the depositional environment when TS concentrations are high (Raiswell *et al.,* 1987). Under anoxic conditions dissolved sulfate is reduced to hydrogen sulfide gas, which then reacts with iron minerals to form iron sulfides. More Sulfide means less oxygen ie, anaerobic condition/reducing atmosphere in which heavy metals stay as sulfides. It was reported that marine sediments undergoing sulfate reduction under euxinic/ inhospitable bottom conditions (*e.g.* anoxic bottom waters with high H_2S concentrations) typically have TOC : TS ratios lower than 1.5 (Berner, 1983; Craft *et al.,* 1991; Niffy Benny, 2009). Marine sediments undergoing sulfate reduction below an oxygenated water column typically have TOC : TS ratios in the range from 1.5 to 5.0 (Berner, 1983; Hedges and Keil, 1995) and aerobic marine sediments typically have TOC : TS ratios greater than five.

Annual average of TOC : TS ratio in the estuarine sediments was 1.64 ± 1.30. Station E6 (0.0006) and E11 (6.37) during Mon was associated with lowest and highest ratio in the estuary (Fig.3.5). Majority of the estuarine stations exhibited TOC : TS ratio higher than 1.5 during Pre-M, suggesting sulphate reduction below an oxygenated water column (Berner, 1983; Hedges and Keil, 1995). Northern (except E1) and central (except E7) estuarine stations were associated with higher TOC : TS ratio during Pre-M season compared to the southern stations (except E11, E15 and E16) suggesting sediments were deposited under periodic anoxia. Stations E10, E12-E14 were associated with very low TOC : TS ratio indicating highly anoxic conditions. These were the flow restricted stations during Pre-M favouring accumulation of organic matter. During Mon, 56 % of the stations were associated with TOC : TS ratio lower than 1.5 suggesting anaerobic condition and rest of the stations were associated with ratios higher than 1.5. Whereas during Post-M season, 44 % of the estuarine stations were associated with TOC : TS ratio lower than 1.5 indicating an oxic condition prevailing in the sediments. During Mon, estuarine stations around Wellingdon Island (E4, E6-E8) were found to be with very low TOC : TS ratio, suggesting highly anoxic environment in the sediment surface layers. Stations E11 during Mon and E14 during Post-M exhibited TOC : TS ratio greater than 5 indicating an aerobic, oxidising environment prevailing there. Station E11 exhibited higher TOC : TS ratio irrespective of the seasons indicating an aerobic condition in that area.

Annual average of TOC : TS ratio in the coastal sediments was 1.59 ± 0.76. In the coast, station C4 was associated with highest (3.11) TOC : TS ratio and C11 was associated with the lowest (0.37) ratio (Fig.3.5). During Pre-M and Post-M, majority of the coastal stations were associated with TOC : TS values between 1.5 and 5 indicating organic matter degradation under periodic anoxic conditions. But during Mon season, majority of the stations were with TOC : TS value less than 1.5 indicating anoxic conditions during this season. Low ratio observed during this season can be attributed to the upwelling phenomena during Mon season, which results in oxygen decrease of subsurface waters and surface sediments. Coastal stations to the south of bar mouth (C4-C8) exhibited TOC : TS ratios higher than 1.5 and those north of the bar mouth (C1-C3) were associated with TOC : TS ratio less than 1.5 during the study period.

From the TOC : TS ratio ranges it could be suggested that the sediments in the study area were deposited under periodic anoxia and the sediments undergo sulphate reduction below an oxygenated water column (Hedges and Keil, 1995; Renjith *et al.,* 2011; Gireesh Kumar, 2013). Generally, the TOC : TS ratios were lower in the Cochin estuary and its adjacent coast suggesting a noticeable reducing environment in the sediment surface. Negative Eh values of the sediments of the study area attested the above conclusion.

3.2.3 Biochemical Composition of Sedimentary Organic Matter

The organic matter in the estuaries and coastal sediments are either terrestrial or aquatic in origin. The chemical constituents of organic matter can be grouped into the following (Stevenson, 1994); I) Non-humic substances like carbohydrates, proteins, and fats II) Phenolic substances like lignins and tannins III) Humic substances– heterogeneous mixtures of high molecular weight aromatic structures that result from secondary synthesis reactions. Organic matter undergoes complex cycling in wetlands, and its fate depends on substrate quality and various environmental factors. In general, easily degradable (labile) fractions are decomposed rapidly, whereas recalcitrant pools are accreted as new organic matter layers in sediments. Organic matter accumulation regulates the following key functions in wetland ecosystems; potential energy source to microbial communities, long-term storage of associated compounds (nutrients, heavy metals and organics) and major component of the global carbon cycle and source/sink for greenhouse gases.

The biodegradability of the organic materials may range from easily decomposable (labile) to highly resistant (refractory). Decomposition is regulated by substrate quality (substrate size, percentage of C, type of C, lignin cellulose ratio), electron acceptors, limiting nutrients, and environmental factors such as temperature. The labile organic compounds, simple and/or combined organic biopolymer molecules such as proteins, lipids and carbohydrates in sediments represent the fraction of organic matter available to the benthic organisms (Mayer *et al.,* 1995; Fabiano *et al.,* 1995; Dell Anno *et al.,* 2002) and are rapidly mineralised (Venturini *et al.,* 2012). Organic biochemical components vary faster than the more conservative total organic carbon in response to spatio-temporal changes in the benthic trophic status associated to both natural and anthropogenic environmental modifications (Pusceddu *et al.,* 2003, 2009; Dell Anno *et al.,* 2002; Joseph *et al.,* 2008).

The spatial and seasonal distributions of biochemical components in the estuarine and coastal surface sediments are presented in Appendix 10.

3.2.3.1 Total Organic Matter (TOM)

Total organic matter in the estuarine sediments showed an annual average of 2.00 ± 1.46 %. Organic matter was found to be lowest in E16 (0.99

%) during Post-M and highest value was found in E6 (4.62 %) during Pre-M (Fig.3.6). Significant temporal and spatial variations were not observed in the case of TOM in the estuarine sediments. Annual average of TOM in the coastal sediments was 2.53 ± 1.71 %. Lowest (0.08 % in C4) and highest (5.13 % in C6) values were found during Pre-M season (Fig.3.6). TOM in the coastal sediments exhibited significant spatial variation whereas temporal variations were not significant during the study period.

3.2.3.2 Total Carbohydrates (CHO)

Carbohydrates are the most abundant class of biopolymers on earth (Aspinall, 1983) and consequently represent significant components of water column particulate organic matter and dissolved organic matter in aquatic environments (Cowie and Hedges, 1984a & b; Arnosti *et al.,* 1994; Aluwihare *et al.,* 1997; Bergamaschi *et al.,* 1999; Opsahl and Benner, 1999; Burdige *et al.,* 2000; Hung *et al.,* 2003a & b). In sediments, carbohydrates have been estimated to be approximately 10 to 20 % of the total organic matter (Hamilton and Hedges, 1988; Cowie *et al.,* 1992; Martens *et al.,* 1992). Carbohydrates which are important structural and storage molecules and so critical in the metabolism of both the terrestrial and aquatic organisms (Aspinall, 1970). Cellulose is a major constituent in vascular plants and is generally absent in algal and microbial tissue. Some carbohydrates can also represent significant components of other structural (e.g., lignins) and secondary compounds (e.g., tannins) found in plants (Zucker, 1983).

Annual average of CHO in the estuary and coast were 0.22 ± 0.14 and 0.28 ± 0.13 % respectively. Lowest (0.008 % in E16) and highest (0.50 % in E13) values were found in the southern estuary during Post-M (Fig.3.6). In the coast, station C4 showed lowest (0.02 %) and highest (0.56 %) values during Pre-M and Post-M seasons respectively.

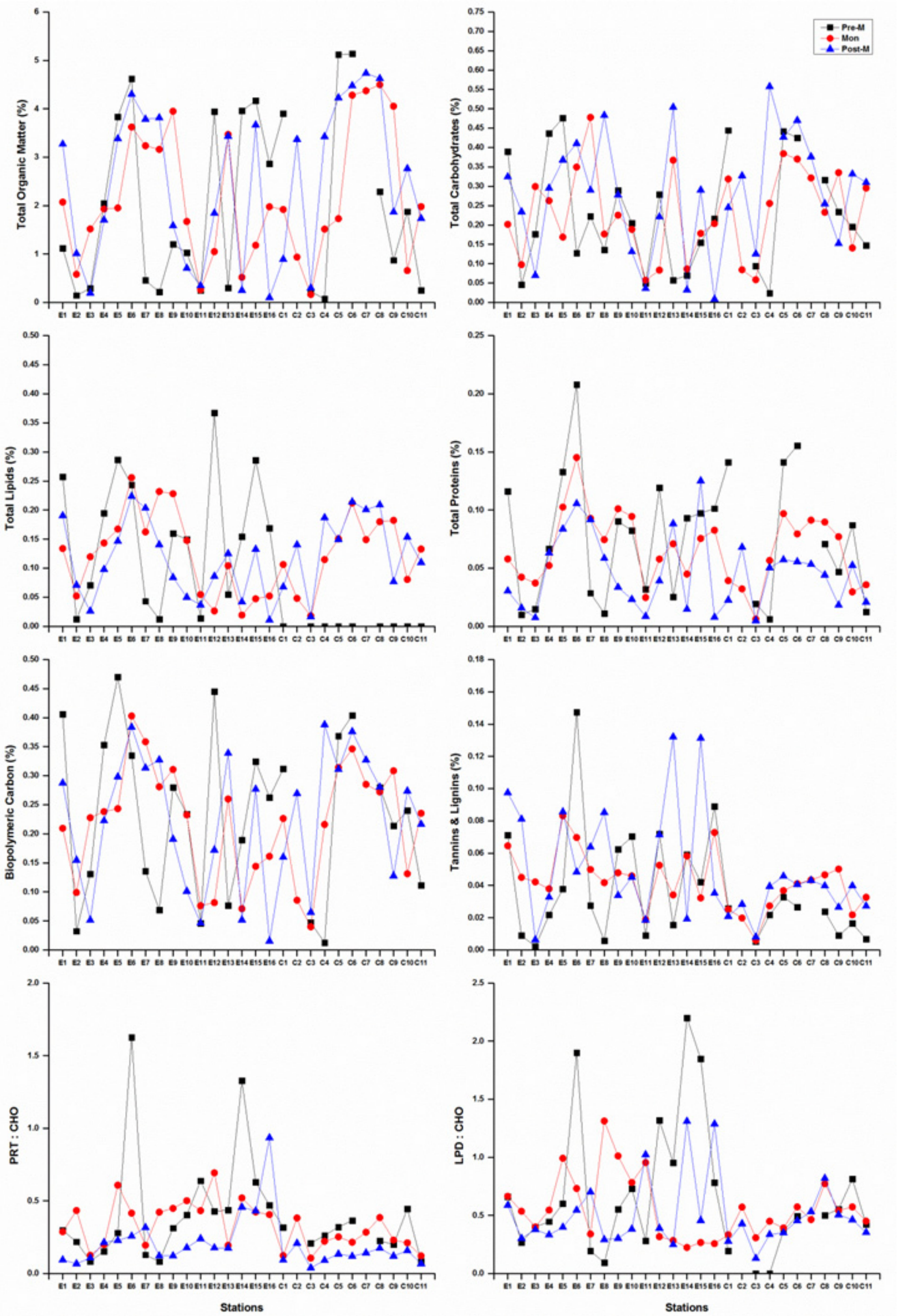

Figure 3.6 Spatial and temporal variations of total organic matter, its biochemical components and their ratios in Cochin estuarine and coastal system

3.2.3.3 Total Lipids (LPD)

Lipids are an important component of organic matter with a diversity of compound classes (e.g., hydrocarbons, fatty acids, n-alkanols, and sterols) that have been used as effective biomarkers of organic matter in coastal and estuarine systems (Volkman and Maxwell, 1984; Prahl, 1985; Volkmann and Hallegraeff, 1988; Yunker *et al.,* 1993 & 1995; Canuel *et al.,* 1995 & 1997; Canuel, 2001; Sun *et al.,* 2002). These energy-rich compounds represent a significant component of the carbon flux through trophic pathways in coastal/estuarine systems (Sargent *et al.,* 1977). In fact, the term geolipid has been used to describe decay-resistant biomarkers in sediments because lipids are typically recalcitrant compared to other biochemical components of organic matter, making them more long-lived in the sedimentary records (Meyers, 1997).

Total lipids showed an annual average of 0.13 ± 0.09 and 0.09 ± 0.08 % in the estuarine and coastal sediments respectively (Fig.3.6). In the estuary, highest and lowest values were found in stations E12 (0.37 %) during Pre-M and E16 (0.01 %) during Post-M respectively. Lowest concentration was detected in C1 (0.000087 %) during Pre-M and highest value was found in C6 (0.214 %) during Post-M.

3.2.3.4 Total Proteins (PRT)

In sediments, proteins account for approximately 7 to 25 % of organic carbon (Degens, 1977; Burdige and Martens, 1988; Keil *et al.,* 1998 & 2000). Preferential adsorption of basic amino acids to fine particulate matter in river/estuarine systems occurs because of the attraction between the net positive charge of the amine group and the negative charge of the aluminosilicate clay minerals (Gibbs, 1967; Rosenfield, 1979; Hedges *et al.,* 2000; Aufdenkampe *et al.,* 2001). Redox conditions have also proven to be an important controlling factor in determining the decay rates and selective utilisation of amino acids.

Annual average of PRT in the estuary and coast were 0.07 ± 0.04 and 0.06 ± 0.04 % respectively. Highest and lowest concentrations of total protein were found in estuarine stations E6 (0.21 %) during Pre-M and E3 (0.007 %) during Post-M (Fig.3.6). In the coast, lowest concentration was found in C3 (0.0049 %) during Post-M and highest value was found in C6 (0.16 %) during Pre-M season.

3.2.3.5 Biopolymeric Carbon (BPC)

The sum of PRT, CHO and LPD carbon is denoted as biopolymeric carbon (BPC) (Fichez, 1991; Fabiano *et al.,* 1995). PRT, CHO and LPD concentrations were converted to their carbon equivalents by using the following conversion factors: 0.49, 0.40 and 0.75 g of C/g, respectively (Fabiano and Danovaro, 1994). The biopolymeric carbon, BPC has been generally reported as the fraction of total organic carbon potentially available to the benthic consumers (Pusceddu *et al.,* 2009). Annual average of BPC in the estuarine sediment was 0.22 ± 0.12 % and that of coastal sediments was 0.23 ± 0.11 % (Fig.3.6).

3.2.3.6 Tannins & Lignins (TAN & LIG)

Tannins & Lignins come under the relatively unavailable fraction (refractory) of organic substrates. They are highly resistant to biological degradation and persist in water and get buried in the bottom sediment. TAN & LIG are high molecular weight polycyclic aromatic compounds widely distributed throughout the plant kingdom (Schnitzer and Khan, 1972; Finar, 1976; Field and Lettinga, 1987). They are the major classes of Folin phenol active substances, so their identification and quantification is easier.

Tannins occur in plant roots, bark, wood, leaves, fruits and buds (Kraus *et al.,* 2003), and are estimated to be the fourth most abundant compound types produced by vascular plant tissue after cellulose, hemicellulose and lignin (Hernes and Hedges, 2000). In addition to having a biomarker potential, tannin greatly contributes to the properties of bulk organic matter including colour, astringency and reactivity (Lin *et al.,* 2006). Lignin is a structural component of plant tissues where it occurs as a three-dimensional network together with cellulose. It is a macromolecular condensation product of three different propenyl (C3-substituted) phenols (one type of few biogenic aromatic compounds). It is preserved, even during transport from land to ocean and during sedimentation to the seafloor where it occurs predominantly in humic organic matter of deltaic environments. Lignins are considered to be some of the most stable compounds in vascular plant tissues and are usually preserved selectively in terrestrial (Bates and Hatcher, 1989) and aquatic environments (Moran and Hodson, 1989; Opsahl and Benner, 1995; Bianchi *et al.,* 1999 & 2002). Hence lignin can be considered as a useful chemical biomarker for vascular-plant inputs into the estuarine and coastal margin sediments (Gardner and Menzel, 1974; Hedges and Parker, 1976; Goni and Hedges, 1992; Hedges *et al.,* 1997; Louchouaran *et al.,* 1997; Bianchi *et al.,* 1999 & 2002).

Annual average of TAN & LIG in the estuarine sediments was 0.05 ± 0.03 and that of the coastal sediments was 0.03 ± 0.01 %. Pre-M season was associated with the lowest (0.002 % in E3) and highest (0.15 % in E6) TAN & LIG concentrations in the estuary (Fig.3.6). In the coast, lowest concentration was found in C3 (0.005 %) during Pre-M and highest concentration was detected in C9 (0.05 %) during Mon season.

Biochemical composition of sedimentary organic matter in the study area exhibited a dominance of carbohydrates, followed by lipids and proteins.

Biochemical composition of sedimentary organic matter in the study area seems to be quite different from other coastal systems, which is usually characterized by dominance of proteins and carbohydrates over lipids (Meyer-Reil, 1983; Sargent *et al.,* 1983; Fabiano and Danovaro, 1994). Significantly higher values of LPD in the study region might be attributed to its preservation under highly anoxic conditions (Sun *et al.,* 2002; Manju *et al.,* 2012). Highly significant positive correlations of LPD with total sulphur support this argument.

Carbohydrates in the estuarine sediments represented a major biochemical class in the labile organic matter (LOM) pools during Pre-M (50.64 %), Mon (52.01 %) & Post-M (58.42 %). This is followed by lipids during Pre-M (31.64 %), Mon (28.47 %) & Post-M (28.67 %) and proteins during Pre-M (17.72 %), Mon (19.52 %) & Post-M (12.91 %). In the coastal sediments also, carbohydrates were a major biochemical class of organic matter during Pre-M (62.97 %), Mon (58.81 %) & Post-M (65.82 %). This is followed by lipids during Pre-M (20.67 %), Mon (28.22 %) & Post-M (26.47 %) and proteins during Pre-M (16.36 %), Mon (12.97 %) & Post-M (7.70 %).

Carbohydrates which include polyhydroxyllated compounds ranging in size from 5-6 carbon sugars to large biopolymers (starch, cellulose) are much lower in algae than in vascular plants (Cowie and Hedges, 1984a). Dominance of carbohydrates over lipids and proteins in the northern estuarine zone indicated lower nutritive aspect of the organic matter and its aged and refractory nature. Dominance of CHO over LIP and PRT concentrations in the study region may be attributed to the accumulation of aged organic detritus due to the faster utilisation of proteins than carbohydrates by micro-organisms (Joseph *et al.,* 2008; Venturini *et al.,* 2012, Gireesh Kumar, 2013). Proliferation of alien weeds like Eichhornia crassipes, Salvinia molesta exerts great pressure on the biodiversity of the system. Weed infestation is a major ecological problem in the Cochin estuary during Mon and Post-M seasons; decay and decomposition of these weeds also contribute to the higher concentrations of CHO observed in the estuary.

Lipids in sediments are derived from aquatic biota and higher plant wax. Lipids are abundant in the surface sediments of eutrophic systems compared to the oligotrophic systems and it, also indicates the productivity of the system like proteins (Gremare *et al.,* 1997). Although lipids are consumed by microheterotrophs in both the fresh and marine ecosystems, they contribute significantly to the bacterial production (Rich *et al.,* 1996). Mangrove forests lying near the estuary contribute to the higher lipid content observed in the estuarine sediments. The higher lipid levels found in the study region suggested the higher biological activity associated with the productive nature of the environment.

Numerous fish peeling and processing units situated in the banks of the estuary (Vasudevan, 2000; Balasubramaniam *et al.,* 2012), where tissues undergo decomposition to liberate protein, which are finally adsorbed/settled into the surface sediments. Protein sources in the estuary can be attributed to the wastes from this industry.

Labile nitrogen is considered as the major limiting factor for deposit feeders and the quantity of protein nitrogen estimated by multiplying the protein content with the factor 0.16 (Mayer *et al.,* 1986). Contribution of labile nitrogen to total nitrogen in the estuarine sediments ranged from 4.06 to 53.19, 3.96 to 18 and 1.92 to 7.86 % during Pre-M, Mon and Post-M seasons respectively. In the coastal sediments it ranged from 6.12 to 24.98, 2.7 to 9.98 and 1.91 to 4.62 % during Pre-M, Mon and Post-M seasons respectively. The labile fraction in the sediments was less even though total nitrogen was found to be in higher concentrations. This indicated that in the study area, the major fraction of the sedimentary nitrogen is refractory in nature. Although proteins and peptides have been considered as part of the labile fraction, there are studies on the resistance of microbial degradation of proteins in the sedimentary environments and incorporation of a portion of the nitrogen from the active nitrogen pool into the biologically refractory material (Knicker and Hatcher, 2001; Nguyen and Harvey, 2001; Zang *et al.,* 2001).

Lower contribution of protein nitrogen to total nitrogen in the study area is indicative of a relatively lower nutritive value of the sediments. However TOM, TN, and biochemical components were found to be very high in the study area which is sufficient enough to support the benthic organisms. Sedimentary nitrogen in the estuary was more refractory than the coastal sediments.

The contribution of labile organic matter to total organic matter pool in estuarine sediments ranged from 8.01 to 90.00 (40.10 ± 24.43), 14.04 to 52.60 (23.91 ± 9.54) and 14.95 to 53.14 (24.44 ± 9.83) % during Pre-M, Mon and Post-M seasons respectively. Whereas in the coastal sediments it ranged from 14.57 to 87.38 (35.48 ± 23.80), 11.17 to 50.51 (24.79 ± 12.48) and 10.98 to 48.92 (21.78 ± 11.73) % during Pre-M, Mon and Post-M seasons respectively. Irrespective of the higher content of total organic matter, the labile organic matter was low in majority of the estuarine and coastal surface sediment samples. Hence in the study area, a considerable fraction of total organic matter represented refractory material or is uncharacterised. The uncharacterised fraction probably contains recalcitrant humic-type geopolymers, which usually account for a major fraction (10-70%) of TOM in sediments (Mayer, 1985).

The quantification of the phenolic compounds such as tannin and lignin in sediments provide information on the input of land-derived organic detritus in marine systems. From this study, it can be found that the concentrations of tannin & lignin are higher in the estuarine stations than the coastal stations irrespective of the seasons. Abundance of TAN & LIG in the sediments pointed to the influence of land derived organic matter in the study area. The occurrence of higher TAN & LIG content in the sediments of the study region could be attributed to the higher vascular plant inputs including mangrove forests lying north to the Cochin estuarine system. Wide spread coconut husk retting activities also contribute to the higher tannin content observed in the estuarine area. In estuaries, it is common to find a gradient of vascular plant inputs of particulate organic matter with decreasing concentrations moving from the head to the mouth of the system (Bianchi and Argyrou, 1997; Goni and Thomas, 2000). The higher abundance of tannin and lignin in estuarine stations showed that the estuary is acting as a sink for the terrigenous organic matter and a little terrigenous organic matter is reaching the coastal stations.

Spatial and temporal variations in the distribution of biochemical components during Pre-M, Mon and Post-M seasons was tested using two way ANOVA. Results of ANOVA of different biogeochemical parameters in the study area are given in the Table 3.14. Total organic matter distribution was devoid of any temporal and spatial variation in the estuary. TOM showed significant spatial variation ($p < 0.05$) in its distribution in the coastal sediments, however temporal variations were lacking in coastal area also. In the study area, significant spatial and temporal variations were absent in the case of CHO. LPD distribution in the estuarine sediments was devoid of any significant spatial and temporal variations during the study period, while in the coastal sediments spatial variations were significant at 99 % confidence level (p value < 0.01).

Although temporal variations were not significant in PRT distribution in the study area, significant spatial variations were shown by both the estuarine (p value < 0.01) and coastal sediments (p value < 0.05). BPC exhibited significant spatial variations (p value < 0.05) in the study area, which might be attributed to the changes in organic matter deposition in sediments associated with the strong river discharge in upper reaches of the estuary. While temporal variations were absent in BPC distribution. Spatial and temporal variations were lacking in TAN & LIG distribution in the estuarine sediments. But, TAN & LIG in the coastal sediments exhibited highly significant temporal (p value < 0.01) and spatial (p value <0.05) variations.

The results of correlation analysis of estuarine sedimentary biogeochemical parameters are presented in Tables 3.16 to 3.18. In the estuary, sand showed strong negative correlations with all the biochemical parameters except CHO during Pre-M and TAN & LIG during Mon. All the biochemical parameters except CHO exhibited strong positive correlations with silt and clay during Pre-M. Silt showed strong positive correlations with LPD, PRT, BPC; weak positive correlations with CHO during Mon. Clay exhibited strong positive correlations with CHO, LPD, BPC and weak positive correlation with PRT. TAN & LIG did not show significant correlations with silt and clay during Mon. During Post-M, clay and silt showed strong positive correlations with all the biochemical parameters. From these observations, it is understood that sediment texture is one of the main factors influencing organic matter accumulation in the study region. This phenomenon could be attributed to the close hydraulic equivalence of both organic and mud particles and/or to the relatively high absorptive capacity of fine particles for organic molecules (Cotano and Villate, 2006).

Table 3.16 Pearson correlation matrix of sedimentary parameters in Cochin estuary during pre-monsoon (n=16)

	CHO	LPD	PRT	TAN & LIG	BPC	TOM	TC	TP	TN	TS	Sand	Silt	Clay	pH	Eh	Temperature
CHO	1															
LPD	.594*	1														
PRT	0.377	.818**	1													
TAN & LIG	0.141	.611*	.898**	1												
BPC	.790**	.955**	.802**	.575*	1											
TOM	0.237	.817**	.833**	.663**	.718**	1										
TC	0.453	.867**	.850**	.711**	.831**	.880**	1									
TP	0.328	.697**	.600*	0.475	.639**	.782**	.852**	1								
TN	0.362	.838**	.872**	.747**	.784**	.885**	.982**	.856**	1							
TS	0.342	.846**	.784**	.666**	.765**	.871**	.942**	.766**	.920**	1						
Sand	-0.412	-.873**	-.860**	-.734**	-.822**	-.893**	-.972**	-.819**	-.974**	-.960**	1					
Silt	0.395	.838**	.808**	.645**	.785**	.912**	.961**	.842**	.957**	.960**	-.985**	1				
Clay	0.418	.882**	.888**	.811**	.834**	.837**	.949**	.761**	.958**	.924**	-.979**	.930**	1			
pH	-0.448	-0.419	-0.426	-0.345	-0.491	-0.119	-0.282	-0.178	-0.291	-0.194	0.330	-0.244	-0.418	1		
Eh	-0.108	-0.075	0.039	-0.05	-0.078	0.094	0.079	0.17	0.088	0.101	-0.017	0.076	-0.053	0.011	1	
Temperature	-0.278	-0.252	-0.137	0.106	-0.275	-0.074	-0.004	-0.095	-0.056	0.089	-0.020	0.016	0.023	0.244	-0.159	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.17 Pearson correlation matrix of sedimentary parameters in Cochin estuary during monsoon (n=16)

	CHO	LPD	PRT	TAN & LIG	BPC	TOM	TC	TP	TN	TS	Sand	Silt	Clay	pH	Eh	Temperature
CHO	1															
LPD	.527*	1														
PRT	0.485	.683**	1													
TAN & LIG	0.075	0.224	.543*	1												
BPC	.826**	.906**	.756**	0.241	1											
TOM	.740**	.815**	.714**	0.210	.904**	1										
TC	0.236	.526*	0.413	0.094	0.467	.657**	1									
TP	.803**	.717**	0.483	0.113	.843**	.913**	0.436	1								
TN	.781**	.843**	.701**	0.281	.936**	.919**	0.464	.856**	1							
TS	.728**	.861**	.738**	0.296	.927**	.964**	.584*	.882**	.954**	1						
Sand	-.737**	-.857**	-.684**	-0.289	-.921**	-.974**	-.594*	-.932**	-.927**	-.960**	1					
Silt	.550*	.847**	.749**	0.448	.840**	.899**	.681**	.772**	.828**	.892**	-.935**	1				
Clay	.831**	.743**	.514*	0.076	.874**	.913**	0.414	.968**	.898**	.893**	-.924**	.728**	1			
pH	-0.417	-0.288	0.279	0.352	-0.311	-0.151	-0.023	-0.342	-0.308	-0.185	0.234	-0.098	-0.347	1		
Eh	0.118	0.071	0.202	0.354	0.125	0.057	0.008	-0.006	0.186	0.199	-0.057	0.199	-0.104	-0.122	1	
Temperature	-0.120	-0.264	0.082	0.210	-0.192	-0.100	-0.472	0.023	-0.158	-0.150	0.076	-0.100	-0.038	0.401	-0.206	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.18 Pearson correlation matrix of sedimentary parameters in Cochin estuary during post-monsoon (n=16)

	CHO	LPD	PRT	TAN & LIG	BPC	TOM	TC	TP	TN	TS	Sand	Silt	Clay	pH	Eh	Temperature
CHO	1															
LPD	.787**	1														
PRT	.728**	.767**	1													
TAN & LIG	.705**	.538*	.629**	1												
BPC	.950**	.931**	.844**	.681**	1											
TOM	.889**	.940**	.871**	.707**	.976**	1										
TC	.906**	.914**	.895**	.728**	.978**	.993**	1									
TP	.865**	.626**	0.473	.609*	.774**	.739**	.754**	1								
TN	.904**	.909**	.866**	.729**	.971**	.990**	.993**	.781**	1							
TS	.823**	.912**	.898**	.662**	.935**	.956**	.958**	.582*	.936**	1						
Sand	-.893**	-.932**	-.867**	-.723**	-.974**	-.989**	-.985**	-.734**	-.984**	-.952**	1					
Silt	.808**	.893**	.901**	.685**	.920**	.965**	.956**	.605*	.947**	.970**	-.960**	1				
Clay	.889**	.857**	.695**	.675**	.915**	.883**	.887**	.815**	.899**	.791**	-.916**	.768**	1			
pH	-0.048	-0.155	-0.098	0.052	-0.104	-0.054	-0.022	0.077	-0.026	-0.094	0.063	-0.100	-0.001	1		
Eh	-.646**	-0.485	-.501*	-.554*	-.608*	-.598*	-.602*	-.543*	-.629**	-.557*	.648**	-.520*	-.741**	-0.021	1	
Temperature	-0.178	0.025	0.028	0.006	-0.077	-0.064	-0.071	-0.247	-0.068	-0.052	0.020	0.007	-0.055	-0.108	0.284	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

The results of correlation analysis of sedimentary biogeochemical parameters in the coast are presented in Tables 3.19 to 3.21. Sand exhibited significant negative correlations with all the biogeochemical parameters except TAN & LIG during Pre-M season. Silt showed strong positive correlation with BPC and weak positive correlations with CHO, LPD, PRT and TOM during Pre-M. TAN & LIG did not show any significant relationship with silt in the coastal sediments during the study period. During Mon, silt did not show any significant relationships with any of the biochemical parameters. During Post-M, silt was correlated to PRT and BPC only. Clay exhibited significant positive relationship with all the biochemical parameters in the entire study period. Unlike the estuary, silt fraction did not have much importance as the finer clay fraction, in the transport of biochemical components in the coastal sediments.

Table 3.19 Pearson correlation matrix of sedimentary parameters in Cochin coast during pre-monsoon (n=9)

	CHO	LPD	PRT	TAN & LIG	BPC	TOM	TC	TP	TN	TS	Sand	Silt	Clay	pH	Eh	Temperature
CHO	1															
LPD	.749*															
PRT	.938**	.751*	1													
TAN & LIG	.707*	0.514	.761*													
BPC	.956**	.904**	.942**	.692*	1											
TOM	.938**	.741*	.976**	.825**	.933**											
TC	.874**	.707*	.822**	0.582	.857**	.839**	1									
TP	.890**	.774*	.943**	.763*	.917**	.977**	.811**	1								
TN	.917**	.688*	.983**	.816**	.903**	.973**	.807**	.928**								
TS	.927**	0.552	.874**	0.643	.829**	.842**	.794*	.789*	.851**	1						
Sand	-.946**	-.752*	-.958**	-0.659	-.937**	-.956**	-.907**	-.945**	-.948**	-.861**	1					
Silt	.789*	.684*	.775*	0.443	.799**	.745*	.722*	.755*	.799**	.700*	-.868**					
Clay	.911**	.686*	.941**	.709*	.891**	.957**	.898**	.934**	.909**	.843**	-.941**	0.649	1			
pH	-.862**	-.837**	-.830**	-0.385	-.906**	-.776*	-.685*	-.793*	-.748*	-.766*	.839**	-.784*	-.752*			
Eh	-0.639	-0.519	-0.605	-0.071	-0.627	-0.540	-.792*	-0.571	-0.537	-.678*	.735*	-0.664	-.674*	.687*	1	
Temperature	0.268	0.519	0.373	0.188	0.411	0.414	0.612	0.522	0.343	0.172	-0.489	0.345	0.514	-0.269	-0.595	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.20 Pearson correlation matrix of sedimentary parameters in Cochin coast during monsoon (n=11)

	CHO	LPD	PRT	TAN & LIG	BPC	TOM	TC	TP	TN	TS	Sand	Silt	Clay	pH	Eh	Temperature
CHO	1															
LPD	.847**															
PRT	.756**	.854**	1													
TAN & LIG	.759**	.936**	.887**													
BPC	.951**	.965**	.880**	.902**	1											
TOM	.647*	.882**	.802**	.911**	.813**	1										
TC	.816**	.939**	.960**	.958**	.939**	.887**										
TP	.787**	.790**	.955**	.800**	.859**	.724*	.918**	1								
TN	.780**	.883**	.906**	.876**	.889**	.818**	.954**	.911**								
TS	.725*	.748**	.779**	.850**	.787**	.721*	.853**	.836**	.839**	1						
Sand	-.719*	-.827**	-.861**	-.869**	-.831**	-.841**	-.916**	-.888**	-.928**	-.918**						
Silt	0.222	0.277	0.141	0.381	0.251	0.458	0.292	0.225	0.274	.607*	-0.570	1				
Clay	.751**	.854**	.959**	.854**	.871**	.783**	.953**	.951**	.974**	.802**	-.918**	0.198	1			
pH	-0.186	-0.152	-0.311	-0.088	-0.200	-0.222	-0.309	-0.460	-0.462	-0.258	0.416	-0.108	-0.444			
Eh	-0.387	-0.412	-0.435	-0.474	-0.427	-0.379	-0.524	-0.461	-0.530	-0.535	0.474	-0.222	-0.458	0.596	1	
Temperature	0.290	0.230	0.046	0.107	0.243	0.040	0.094	0.123	0.199	0.219	-0.301	0.391	0.171	-0.096	-0.049	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 3.21 Pearson correlation matrix of sedimentary parameters in Cochin coast during post-monsoon (n=11)

	CHO	LPD	PRT	TAN & LIG	BPC	TOM	TC	TP	TN	TS	Sand	Silt	Clay	pH	Eh	Temperature
CHO	1															
LPD	.746**	1														
PRT	.731*	.805**	1													
TAN & LIG	.742**	.901**	.792**	1												
BPC	.934**	.932**	.851**	.882**	1											
TOM	.658*	.942**	.835**	.905**	.863**	1										
TC	.617*	.963**	.821**	.896**	.851**	.983**	1									
TP	.656*	.924**	.774**	.902**	.847**	.980**	.947**	1								
TN	.702*	.896**	.844**	.944**	.865**	.973**	.929**	.969**	1							
TS	.780**	.717*	.695*	.689*	.806**	.721*	.693*	.675*	.713*	1						
Sand	-.697*	-.865**	-.847**	-.854**	-.848**	-.903**	-.888**	-.858**	-.888**	-.849**	1					
Silt	0.555	0.567	.676*	0.517	.617*	0.585	0.564	0.538	0.576	.811**	-.848**	1				
Clay	.650*	.912**	.788**	.939**	.841**	.958**	.951**	.927**	.942**	.674*	-.887**	0.507	1			
pH	-.832**	-.799**	-.851**	-.915**	-.886**	-.814**	-.770**	-.801**	-.879**	-.671*	.804**	-0.498	-.874**	1		
Eh	0.268	0.185	0.199	0.014	0.244	0.150	0.148	0.074	0.070	0.023	-0.167	0.049	0.228	-0.205	1	
Temperature	-0.056	0.001	-0.145	0.059	-0.043	-0.120	-0.026	-0.102	-0.171	-0.271	0.178	-0.413	0.071	-0.072	0.109	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

In the estuary, sediment pH was not found to be with any significant correlations with any of the biochemical parameters during the study period. Unlike the estuarine sediments, coastal sediment pH showed significant negative correlations with all the biochemical parameters during Post-M and Pre-M (except TAN & LIG during Pre-M) seasons. But during Mon, pH did not correlate to any of the biochemical parameters. Eh was not correlated to any of the biochemical parameters in the estuarine sediments during Pre-M and Mon seasons. During Post-M, Eh of the estuarine sediments exhibited significant negative correlations with all the biochemical parameters except LPD content, suggesting the anoxic preservation of organic matter due to the decreased rate in organic C, N and P mineralisation as the sediments became more reduced. It was reported that organic matter turn over and nutrient cycling appears to be strongly correlated with electron acceptor availability and redox conditions in the wetland soils (McLatchey and Reddy, 1998). Eh of the coastal sediments lack significant relationships with any of the biochemical parameters during the study period. Sediment temperature did not exhibit significant correlation with any of the biogeochemical parameters.

In the estuarine sediments, CHO exhibited weak positive correlation with LPD and strong positive correlation with BPC during Pre-M. During Mon season, CHO showed strong positive correlations with BPC, TOM, TP, TN, TS and weak positive correlation with LPD. LPD content showed significant positive correlations with all the biochemical parameters during Pre-M and Mon seasons except the non-significant relationship with TAN & LIG during Mon. PRT showed significant positive correlations with all the biochemical parameters except CHO during Pre-M; CHO, TC and TP during Mon season. TAN & LIG exhibited positive correlations with all the parameters except CHO and TP during Pre-M season, whereas during Mon, it was correlated to PRT content only. BPC showed positive relationships with other parameters during Pre-M and Mon except the non-significant relations with TAN & LIG and TC during Mon. In the estuary, Post-M season was featuring highly significant positive relationships among all the biochemical parameters, TOM, TN, TC, TP & TS exception being the non-significant positive association of PRT with TP. In the coastal sediments, biochemical parameters exhibited significant positive relationships with each other except the non-significant LPD – TAN & LIG, LPD - TS, TAN & LIG - TS relationship during Pre-M. The presence of significant correlations of the sedimentary biochemical parameters suggested same source of origin and similar diagenetic pathways for these parameters in the coastal sediments.

PRT : CHO Ratio

Protein : carbohydrate ratio (PRT : CHO) is used to determine the origin of organic matter in the sediments and to distinguish between fresh and aged sedimentary organic matter (Danovaro *et al.,*1993; Cividanes *et al.,* 2002). Since proteins are more readily used by bacteria than carbohydrates (Williams and Carlucci, 1976; Newell and Field, 1983), high PRT : CHO ratios indicate living organic matter or “newly generated” detritus (Danovaro *et al.,*1993). PRT : CHO ratio > 1 has been attributed to the presence of fresh materials of recent origin, while PRT : CHO ratio < 1 indicated to the predominance of aged organic matter in surface sediments (Danovaro *et al.,* 1993) and the role of proteins as a potential limiting factor for benthic consumers (Fabiano *et al.,* 1995). This ratio can also be used for classifying benthic trophic status which in turn reflects the patterns of nutrient enrichment (Dell Anno *et al.,* 2002). Dominance of carbohydrate over protein resulting in a protein to carbohydrate ratio < 1, is a typical feature of detrital-heterotrophic environments and PRT/CHO < 1 is reported in extremely oligotrophic environments where proteins reach very low levels (Danovaro, 1996; Danovaro *et al.,* 1993), so that differences between oligotrophic and detrital-heterotrophic systems cannot be easily identified.

The PRT : CHO ratio was found to be less than 1 in the study area (except E6 & E14 during Pre-M) during the study period (Fig.3.6) which suggested the accumulation of aged organic matter in the estuarine and coastal sediments. So in the study area, proteins are mobilised more rapidly than carbohydrates resulting in low values of the PRT : CHO ratio which indicated the presence of aged (i.e., not freshly produced) organic detritus (Pusceddu *et al.,* 2000). Low PRT : CHO ratios observed during the study suggested, protein as a potentially limiting factor for the benthic community. Low PRT : CHO ratios observed even in the bar mouth, where strong hydrodynamic conditions operate, pointed to the huge input of terrigenous organic load into the estuary and the adjacent coast.

Thus it can be said that the presence of aged or less degradable matter indicated the source of organic matter in the study area is terrestrial or vascular plant inputs. Both the seasonal and temporal variations in the PRT : CHO ratio were absent in the estuary. However in the coast, seasonal variation in the PRT : CHO ratio was observed; Pre-M is with higher ratio followed by Mon and Post-M seasons.

LPD : CHO Ratio

The lipid content and LPD : CHO have been used as good indices to describe the energetic (food) quality of the organic matter in the sediments (Gremare *et al.,* 1997; Fabiano and Pusceddu, 1998; Gremare *et al.,* 2002). Moreover, lipid contents have been associated with the most labile fraction in sediments and it is the best descriptor for meiofauna abundance and biomass over enzymatically hydrolysable amino acids or protein contents (Gremare, *et al.,* 1997; Cartes *et al.,* 2002; Gremare *et al.,* 2002). Seasonal average of LPD : CHO ratio of the estuarine sediments 0.83 ± 0.65, 0.60 ± 0.33 and 0.56 ± 0.35 during Pre-M, Mon and Post-M seasons respectively (Fig.3.6). In the coast, the seasonal average of LPD : CHO ratio was 0.37 ± 0.27, 0.49 ± 0.14 and 0.41 ± 0.19 during Pre-M, Mon and Post-M seasons respectively (Fig.3.6). Higher LPD : CHO ratios were observed for the middle and southern estuarine stations (E6, E12, E14 & E15 during Pre-M; E8 & E9 during Mon and E11, E14 & E16 during Post-M seasons) which suggested the high quality of labile organic matter to support benthic fauna in the estuary. Compared to the estuarine sediments, lower LPD : CHO ratio were observed in the coastal sediments. This indicated the estuarine sediments which receive huge amount of lipids from the run off and from the nearby mangrove forests, act as trap for these lipids and hence the transport to the nearby coastal system was not considerable which resulted in the lower LPD : CHO ratios. In the study area, temporal variations in LPD : CHO ratio were not significant. Spatial variation in the LPD : CHO ratio was observed in the coastal stations only.

3.2.3.7 Benthic Trophic Status

Although the assessment of trophic status have been based on the predictive variables like water column turbidity, inorganic nutrients and responsive variables like Chlorophyll-a (Zurlini, 1996; Cloern, 2001; Coelho *et al.,* 2007), they are insufficient to provide better insights into the trophic status of aquatic ecosystems (Izzo *et al.,* 1997; Cognetti, 2001; Dell Anno *et al.,* 2002; Pusceddu *et al.,* 2011). Contribution of Chlorophyll-a from the re-suspension events and benthic primary production by microphytobenthose and macroalgae (Dell Anno *et al.,* 2002) in shallow ecosystems create discrepancies in the assessment of trophic status (Conde *et al.,* 1999; Pusceddu *et al.,* 1999). Due to these Nixon (1995) proposed a new approach for the assessment of trophic status based on the supply of total organic carbon in terms of $gCm^{-2}y^{-1}$. But it does not consider the differential reactivity of wide range of organic compounds within the sediments (Pusceddu *et al.,* 2009).

In this study, the benthic trophic status of sampling stations were established based on PRT and CHO threshold levels proposed by Dell Anno *et al.,* 2002 (Hypertophic (H): PRT > 4 and CHO > 7 mg/g, eutrophic (E): PRT 1.5-4 mg/g and CHO = 5.7 mg/g and Meso-oligotrophic (MO): PRT < 1.5 mg/g and CHO < 5 mg/g).The benthic trophic classifications of the stations are presented in

Table 3.22. Majority of the stations in the estuary were classified meso-oligotrophic using both the PRT (exception was E6 during Pre-M) and CHO (exception was E13 during Post-M) threshold levels. Stations, E6 and E13 showed eutrophic conditions based on the PRT and CHO threshold levels respectively.

Table 3.22 Benthic trophic classification of the sampling sites based on PRT and CHO concentrations

Stations	PRT			CHO		
	Pre-M	Mon	Post-M	Pre-M	Mon	Post-M
E1	MO	MO	MO	MO	MO	MO
E2	MO	MO	MO	MO	MO	MO
E3	MO	MO	MO	MO	MO	MO
E4	MO	MO	MO	MO	MO	MO
E5	MO	MO	MO	MO	MO	MO
E6	E	MO	MO	MO	MO	MO
E7	MO	MO	MO	MO	MO	MO
E8	MO	MO	MO	MO	MO	MO
E9	MO	MO	MO	MO	MO	MO
E10	MO	MO	MO	MO	MO	MO
E11	MO	MO	MO	MO	MO	MO
E12	MO	MO	MO	MO	MO	MO
E13	MO	MO	MO	MO	MO	E
E14	MO	MO	MO	MO	MO	MO
E15	MO	MO	MO	MO	MO	MO
E16	MO	MO	MO	MO	MO	MO
C1	MO	MO	MO	MO	MO	MO
C2	-	MO	MO	-	MO	MO
C3	MO	MO	MO	MO	MO	MO
C4	MO	MO	MO	MO	MO	E
C5	MO	MO	MO	MO	MO	MO
C6	E	MO	MO	MO	MO	MO
C7	-	MO	MO	-	MO	MO
C8	MO	MO	MO	MO	MO	MO
C9	MO	MO	MO	MO	MO	MO
C10	MO	MO	MO	MO	MO	MO
C11	MO	MO	MO	MO	MO	MO

MO-Meso-oligotrophic, E-Eutrophic

Among the coastal stations, C6 based on PRT during Pre-M and C4 based on CHO during Post-M, were the only stations with eutrophic status. All other stations were found to be meso-oligotrophic based on both PRT and CHO threshold levels. Almost the entire study area was found to be in meso-oligotrophic classification based on both PRT and CHO threshold levels. BPC levels greater than 3 mg g^{-1}as proposed by Pusceddu *et al.,* 2011 was also used in assessing trophic status of the study area. Based on this, many of the estuarine stations were found to be eutrophic. E6 was eutrophic in the entire study period. Stations around Wellingdon Island showed eutrophic nature. E12, E13 and E15 were also found to be eutrophic in nature based on the BPC levels. Among the coastal stations, C5 & C6 were found to be eutrophic during all the seasons.

3.2.3.8 Principal Component Analysis (PCA)

The quality and quantity of organic matter mostly control the biogeochemical processes taking place in an aquatic system. Some of the major biogeochemical processes which involve organic matter in the aquatic environments are diagenesis, allochthonous/autochthonous additions and sorption/desorption processes. Diagenesis, a redox process, which release organic carbon by mineralisation, is largely mediated by microorganisms. Diagenetic reactions in aquatic sediments include aerobic respirations, nitrification, denitrification, manganese reduction, iron reduction, sulphate reduction and methane production (Aller, 1982). Organic matter remineralisation regenerate nutrients in the sediment and the regenerated nutrients diffuse or transport back to the overlying water column and support water column production (Dunn *et al.,* 2008). Suitable indicators of diagenetic processes are organic carbon, TN and TS. During early diagenesis, thermodynamically unstable iron sulphide minerals like greigite which were formed under low dissolved oxygen levels will transform to pyrite (Berner, 1970). Sulfate reduction is reported to be the typical predominant process responsible for the mineralisation of organic carbon in anaerobic marine sediments (Jorgensen & Sorensen, 1985; Seitzinger & Giblin, 1996). It generally accounts for 5—50% of the total mineralisation of organic matter in shallow coastal sediments (Jorgensen & Sorensen, 1985; Berelson *et al.,* 1996) and in marine environments, anaerobic sulfate reduction is very much significant due to the high abundance of sulfate (Jorgensen, 1982; Skyring, 1987). Organic matter decomposition results in increase in pH as mineralisation and ammonification processes release OH- ions and consume H+ ions (Ritchie and Dolling, 1985). The relationship of sedimentary parameters with grain size can give indication about the sorption/desorption processes. Trace metal concentrations in clay surface soils were reported to be higher than that in the sandy soils (El-Ghawi *et al.,* 2005) as the organic matter in clayey soils capture these elements. Organic matter form coating on minerals and finely dispersed particle surfaces.

Although the system characteristics vary widely among stations, PCA was applied to find out various geochemical variables which affect organic matter dynamics which in turn affect the trace metal dynamics in an aquatic system. The parameters for the PCA were selected in such a way that the components of the analysis give indication of the significance of the processes. Varimax rotation was used to identify the more significant variables based on the significance of their correlations that are expressed as factor loading (Buckley *et al.,* 1995; Davis, 2002). Parameters with factor loading > 0.50 and components with eigen values > 1 are considered for interpretation in the present study. The Eigen-values for different factors, percentage variance accounted, and cumulative percentage variances are given in Tables 3.23 and 3.24 respectively. Component plots of PCA of the estuarine sediments are represented in Fig. 3.7 to 3.9 and that of the coastal sediments are represented in Fig. 3.10 to 3.12.

Table 3.23 Factor loadings showing eigen values of sedimentary parameters in the Cochin estuary

Variables	**Components**							
	Pre-monsoon			**Monsoon**			**Post-monsoon**	
	PC1	**PC2**	**PC3**	**PC1**	**PC2**	**PC3**	**PC1**	**PC2**
CHO	0.139	**0.894**	-0.066	**0.768**	-0.382	0.154	**0.926**	0.137
LPD	**0.748**	**0.577**	-0.158	**0.877**	0.026	0.086	**0.918**	-0.182
PRT	**0.844**	0.238	-0.313	**0.710**	0.490	0.302	**0.872**	-0.186
TAN & LIG	**0.783**	-0.071	-0.472	0.219	**0.574**	**0.608**	**0.746**	0.233
BPC	**0.639**	**0.719**	-0.174	**0.951**	-0.086	0.163	**0.986**	-0.033
TOM	**0.900**	0.198	0.042	**0.983**	0.058	0.002	**0.990**	-0.032
TC	**0.938**	0.314	0.019	**0.617**	0.298	-0.191	**0.992**	0.005
TP	**0.807**	0.247	0.305	**0.919**	-0.215	-0.032	**0.768**	0.358
TN	**0.943**	0.153	0.020	**0.940**	-0.095	0.209	**0.990**	0.030
TS	**0.915**	0.255	0.035	**0.966**	0.033	0.169	**0.950**	-0.149
Sand	**-0.939**	-0.309	0.048	**-0.987**	-0.015	-0.055	**-0.993**	0.015
Silt	**0.925**	0.301	0.062	**0.901**	0.233	0.191	**0.948**	-0.154
Clay	**0.916**	0.307	-0.176	**0.935**	-0.223	-0.100	**0.918**	0.186
pH	-0.149	**-0.586**	-0.014	-0.238	**0.877**	-0.067	-0.076	**0.846**
Eh	0.034	-0.107	**0.908**	0.012	-0.081	**0.910**	**-0.661**	-0.305
% of Variance	**59.89**	**17.55**	**8.93**	**63.61**	**11.68**	**10.06**	**77.32**	**7.75**
Cumulative %	**59.89**	**77.44**	**86.36**	**63.61**	**75.29**	**85.35**	**77.32**	**85.06**

PCA analysis of estuarine sedimentary parameters yielded 3 principal components during Pre-M, with 86.36 % cumulative variance. PC1 accounted for 59.89 % of the cumulative variance was characterised by positive loadings of all the biochemical parameters except CHO, pH and Eh. Sand was loaded negatively in this component and from this PC, it could be understood that grain size is the main factor influencing the deposition of organic matter in surface sediments. This PC might also represent the diagenetic processes as the usual indicators of diagenesis (Organic carbon, TN and TS) were loaded in this component. Diagenesis and granulometric deposition processes are complementary. Product retention of diagenesis is with the finer fractions of the sediment, so all the sedimentary parameters load together. PC2 with 17.55 % of variance was loaded positively with CHO, LPD and BPC; negatively with pH, which suggested an entirely different pathway for CHO which contribute to the BPC pools in the estuarine sediments during Pre-M. LPD was loaded in two components indicating its complex behaviour in the estuary. PC3 with 8.93 % of the cumulative variance was positively loaded with Eh only indicating the redox conditions standing separately from other biochemical and geochemical processes in the sediments.

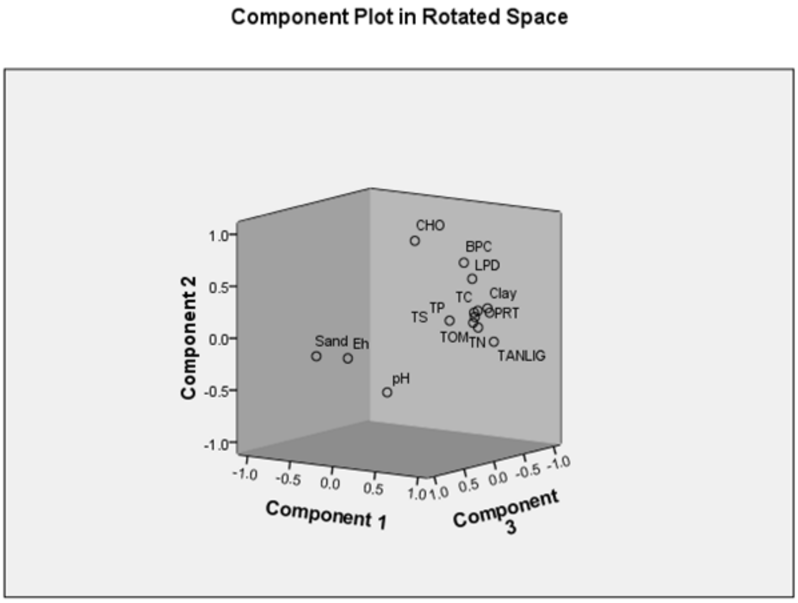

Figure 3.7 Ordination plot of principal components of estuarine sediments during pre-monsoon

During Mon, 3 principal components were obtained with 85.35% cumulative variance. PC1 with 63.61 % of the cumulative variance was characterised with positive loadings of CHO, LPD, PRT, BPC, TOM, TP, TN, TS, silt, clay and negative loading of sand. This PC gave indication of the geochemical processes affecting the labile organic matter deposition. PC2 which accounted for 11.68 % of the cumulative variance was loaded positively with pH and TAN & LIG. PC3 with 10.06 % of the cumulative variance was characterised by positive loading of Eh and TAN & LIG and this PC stood for the recalcitrant pool of organic matter.

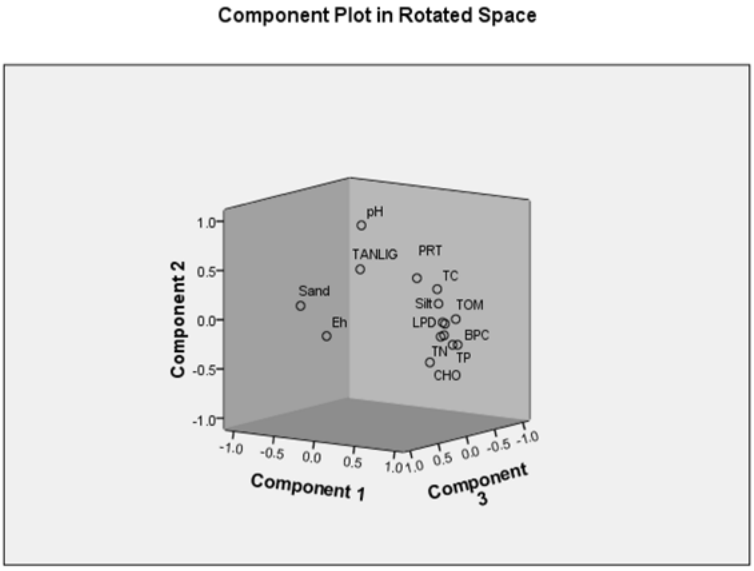

Figure 3.8 Ordination plot of principal components of estuarine sediments during monsoon

During Post-M, PCA yielded two PCs for the estuarine sediments which explained 77.32 and 7.75 % of the 85.06 % cumulative variance. PC1 was characterised with high positive loadings of all the biogeochemical parameters and moderate negative loading of Eh and sand explaining the diagenetic process in the surface sediments of estuary during Post-M season. PC2 was characterised with positive loading of pH only.

In the coastal sediments, PCA yielded two PCs during Pre-M, with 88.97 % cumulative variance. PC1 which accounted for 45.89 % of the cumulative variance was loaded positively with all the biochemical parameters, TOM, TC, TP, TN, TS and clay; negatively with sand. This factor clearly represented the geochemical process other than diagenesis, which include adsorption on to clay particles. PC2 which explained 43.08 % of the cumulative variance was characterised with positive loadings of all the biochemical parameters (except the refractory TAN & LIG), TOM, TC, TP, TN, TS, silt and clay; negative loadings of sand, pH and Eh. This PC stood for the diagenetic processes occurring in the coastal sediments during Pre-M season.

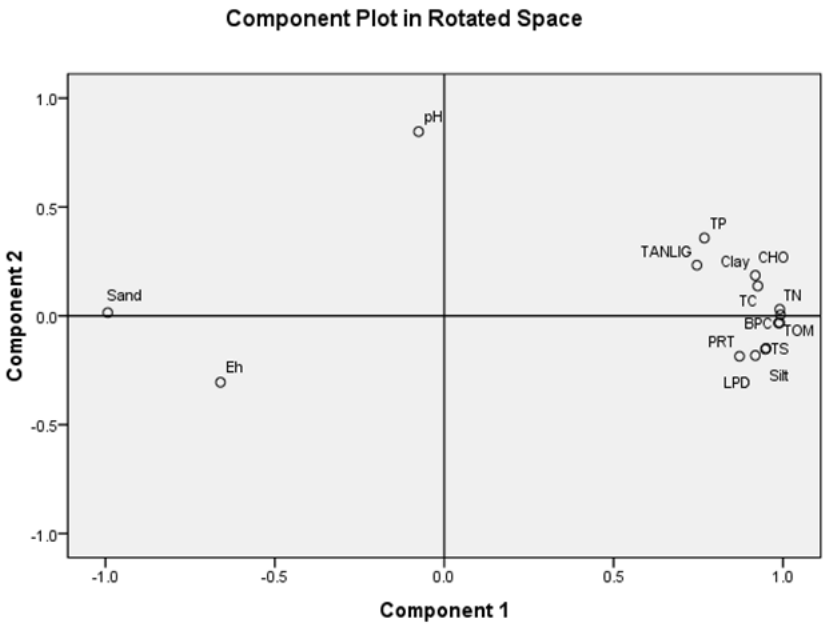

Figure 3.9 Ordination plot of principal components of estuarine sediments during post-monsoon

Table 3.24 Factor loadings showing eigen values of sedimentary parameters in the Cochin coast

Variables	**Components**							
	Pre-monsoon		**Monsoon**			**Post-monsoon**		
	PC1	**PC2**	**PC1**	**PC2**	**PC3**	**PC1**	**PC2**	**PC3**
CHO	**0.711**	**0.662**	**0.861**	0.100	0.077	**0.518**	**0.629**	0.345
LPD	**0.506**	**0.637**	**0.945**	0.060	0.167	**0.867**	0.389	0.134
PRT	**0.783**	**0.595**	**0.934**	0.253	0.016	**0.692**	**0.548**	0.178
TAN & LIG	**0.986**	0.009	**0.918**	0.061	0.307	**0.902**	0.349	-0.010
BPC	**0.695**	**0.684**	**0.958**	0.111	0.116	**0.742**	**0.558**	0.257
TOM	**0.846**	**0.522**	**0.817**	0.106	0.373	**0.912**	0.358	0.057
TC	**0.544**	**0.730**	**0.945**	0.252	0.177	**0.909**	0.329	0.052
TP	**0.786**	**0.558**	**0.865**	0.387	0.079	**0.923**	0.307	-0.008
TN	**0.830**	**0.515**	**0.882**	0.388	0.150	**0.909**	0.372	0.006
TS	**0.628**	**0.630**	**0.740**	0.265	**0.525**	0.452	**0.834**	-0.015
Sand	**-0.668**	**-0.729**	**-0.801**	-0.336	-0.447	**-0.702**	**-0.662**	-0.066
Silt	0.430	**0.750**	0.118	0.073	**0.979**	0.252	**0.907**	-0.045
Clay	**0.731**	**0.606**	**0.899**	0.366	0.062	**0.923**	0.284	0.146
pH	-0.421	**-0.812**	-0.089	**-0.948**	0.006	**-0.785**	-0.408	-0.228
Eh	-0.046	**-0.947**	-0.295	**-0.747**	-0.191	0.057	0.013	**0.967**
% of Variance	**45.89**	**43.08**	**63.07**	**14.99**	**12.10**	**56.21**	**26.34**	**8.38**
Cumulative %	**45.89**	**88.97**	**63.07**	**78.05**	**90.15**	**56.21**	**82.55**	**90.94**

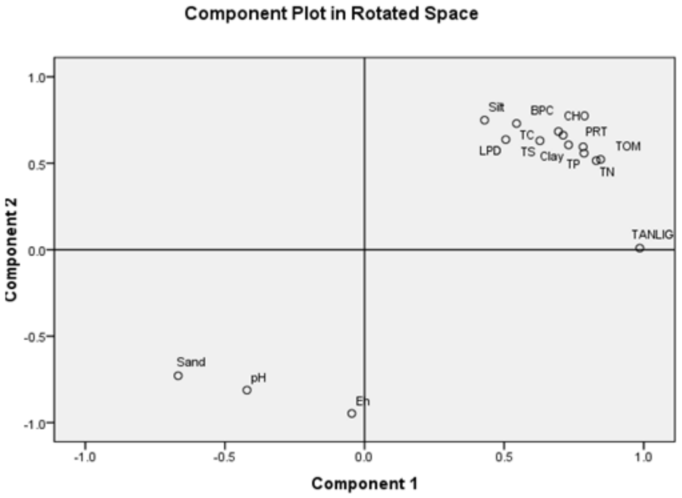

Figure 3.10 Ordination plot of principal components of coastal sediments during pre-monsoon

During Mon, all the biogeochemical parameters (except silt, pH and Eh) under consideration fell into PC1 which explained 63.07 % of the cumulative variance (90.15). This PC represented the geochemical process of adsorption and deposition. pH and Eh loaded negatively in PC2 which explained 14.99 % of the cumulative variance. PC3 was characterised with positive loading of TS and silt representing the siltation process occurring in the Mon season. This PC explained 12.10 % of the cumulative variance.

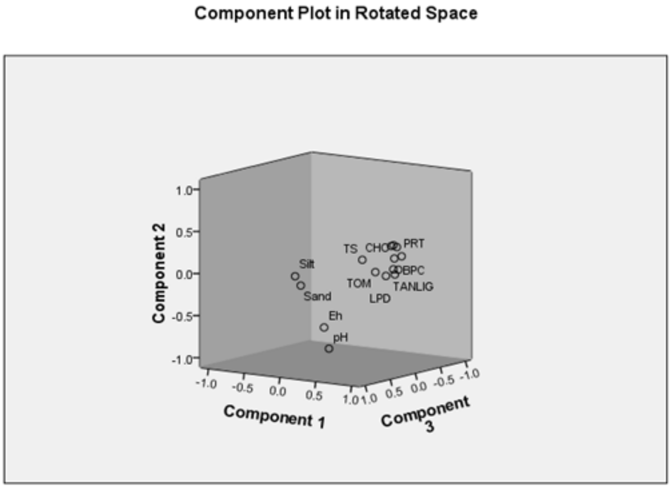

Figure 3.11 Ordination plot of principal components of coastal sediments during monsoon

During Post-M season, three PCs were obtained which explained 56.21, 26.34 and 8.38 % respectively of the cumulative variance (90.94). PC1 was characterised with positive loadings of all the biochemical parameters, TOM, TC, TP, TN, clay; negative loading of sand and pH pointing to the geochemical process of adsorption/desorption occurring in the sediments. PC2 was loaded positively with CHO, PRT, BPC, TS, silt and negatively with sand. This component stood for the diagenesis. PC3 was loaded positively with Eh only.

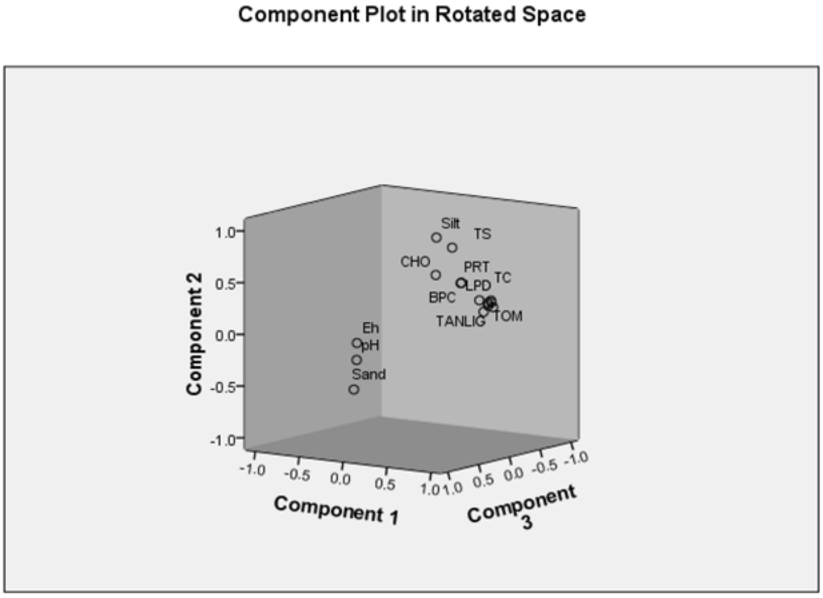

Figure 3.12 Ordination plot of principal components of coastal sediments during post-monsoon

From the PCA, it could be suggested that the deposition and accumulation of organic matter is prominent over the diagenetic processes in the anoxic estuarine sediments and the estuarine sediments act as a detrital trap. However in the coastal sediments, diagenetic processes were operative especially during Pre-M season. Eh was loaded separately in a PC both in the estuary and coast. Due to the oxygen rich conditions in the overlying waters, sediments show a meta stable redox status. Hence Eh was not loaded in both the PCs representing diagenesis and granulometric association.

3.3 Conclusions

Evaluation of the hydrographical and sedimentary parameters such as pH, redox conditions and organic matter contents reveals that the study area is favourable for metal precipitation and accretion. The presence of fine grained sediments also favours the accumulation of trace metals. Lower Eh and TOC : TS ratios suggests that surface sediments of the study area are associated with a noticeable reducing environment. Metal contaminants are strongly partitioned to sulfide or oxide phases in the sediment/water interface and suboxic zone. Once buried in the anoxic zone, these metal host phases are stable for long periods of time and are recalcitrant at near-neutral pH and do not undergo reductive dissolution unless and until they are disturbed by processes like dredging, bioturbation, storm and other marina activities. However, oxidation of the reduced sediments by any of the above said processes increase the dissolved metal concentrations. Yet, their inherent hazard to biota will be mitigated by their sorption to or co-precipitation with oxide substrates.

The input of allochthonus organic matter from the feeding rivers along with the organic wastes from domestic, industrial, agricultural and aquaculture sectors leads to accumulation of huge quantity of organic matter in the estuarine and coastal sediments. Tannins and lignins have very special significance as land-derived plant constituents and hence the extent of terrigenous organic matter input can be understood from the sedimentary TAN & LIG concentration. Higher abundance of tannin and lignin in estuarine sediments in comparison to the coastal sediments shows that the estuary is acting as a sink for the terrigenous organic matter and a little terrigenous organic matter is reaching the coastal stations. But the spatial variation of organic matter does not follow the same trend as tannin and lignin. Both the coastal and estuarine stations are comparable in their organic matter content and this implies that the origin of coastal organic matter is mainly marine and not terrestrial. The predominance of carbohydrates over sedimentary proteins indicates faster mineralisation of proteinaceous organic matter in surface sediments and the system behaves as a detrital trap for the accumulation of aged organic matter. PCA suggested deposition and accumulation of organic matter in the estuary while diagenetic process was active in the coastal area.

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Chapter 4

DISSOLVED AND SUSPENDED HEAVY METALS

Contents

4.1 Introduction

Coastal margins that are influenced by major rivers are an important source of dissolved and particulate material to the ocean and to global biogeochemical fluxes. However, large variability in the fluxes of suspended particulate matter (both organic and inorganic) in river-dominated margins leads to uncertainties in their contribution to global fluxes (Doxaran *et al.,* 2002). Heavy metal pollution in estuaries and other coastal systems is of major concern as they have deleterious effects on biota through mobilization and accumulation in various trophic levels. The dominant feature controlling the distribution, speciation and reactivity of chemical components within estuaries is the mixing of saline and fresh waters. Factors influencing heavy metal behaviour in estuaries are estuarine flushing time (Morris, 1990), complexation with dissolved inorganic (Comans and van Dijk, 1988) and organic (van den Berg *et al.,* 1987) species, and interactions with suspended solids (Turner *et al.,* 1993) and sediments (Evans *et al.,* 1977). One or more of these factors may be dominant in determining the dissolved heavy metal behaviour within a particular estuary and these factors may not be the same for different metals. Owing to large gradients in the chemical composition of the estuarine water and to high biological activity and complex hydrodynamic processes within the estuary, the physico-chemical properties of river-borne and anthropogenic heavy metals may be significantly modified as they interact with the SPM. Knowledge of heavy metal composition of estuarine and coastal waters is necessary to understand the marine geochemical budget, as these systems supply dissolved and particulate matter to the oceans (Riley and Chester, 1971).

Generally the dissolved metal concentrations are often low due to their fast and efficient removal from the water column through hydrolysis and adsorption by suspended particulate matter. The colloidal material present in river waters flocculate upon mixing with sea water, which results in the conversion of dissolved riverine metals to a particulate phase in the estuarine zone (Mayer *et al.,* 1984). The fine-size particles transported in suspension have a relatively large surface area and include clay minerals. These surface active fractions carry heavy metals together with them. Clay minerals of a river suspended matter are capable of adsorbing certain heavy metals in fresh water and partially desorbing them upon contact with seawater (Kharkar *et al.,* 1968; Borole *et al.,* 1977; Graham *et al.,* 1976, Evans *et al.,* 1977). The suspension and deposition behaviour of fine particles in rivers is of high environmental relevance and depends on numerous physical and chemical factors (Lick, 1982). Flow turbulence, particle size distribution, particle surface charge, ionic strength, and the concentration of organic matter are key parameters associated with these processes (Amos *et al.,* 1992; Buffle and Leppard, 1995a & b). Because of the high organic content in suspended particulate matter, they act as a food source for planktonic and benthic organisms. Aquatic organisms are well known for their ability to take up heavy metals from solution and particulates (Bowen, 1966; Riley and Chester, 1971). Suspended particulate matter (SPM) plays an important role in primary production, pollutant transport, and other biogeochemical processes in coastal marine environments (Babin *et al.,* 2003). Since suspended matter can be transported over long distances, erosion and resuspension events may influence regions remote from the origin of the events. Fine particles can interact with organic and inorganic pollutants (Grolimund *et al.,* 1996; Roy and Dzombak, 1997; Kretzschmar *et al.,* 1999) and facilitate their transport in river systems, but they also may contribute to the immobilization of pollutants due to particle sedimentation.

Metals in the coastal system are partitioned between the sediments, SPM and the soluble phase and their partition coefficients vary with metals, sites and time because of the complex nature of the water chemistry that affect the partitioning of metals (James, 2002). Adsorption onto suspended particulate matter (SPM) and bottom sediments is an important process controlling dissolved metal concentrations, bioavailability, toxicity to biota, fate and transport of heavy metals (Jannasch *et al.,* 1988; Comber *et al.,* 1996). Partitioning among dissolved and particulate phases is dependent on the properties of the metal and the aquatic environment. In the fresh-water/seawater mixing zone in the estuary, some metals are removed from solution by biological uptake and chemical scavenging. Coagulation of colloids and small particles also contribute to removal during this estuarine mixing. Desorption of particulate metals are also taking place in this zone, in part due to their displacement from particle surfaces by competition from the major cations and by complexation with the major cations of seawater. Complexation by dissolved ligands competes for heavy metals with the adsorption to the particle surfaces, and the balance between these competing processes influences the overall biogeochemical behaviour of metals. Transformations between dissolved and particulate phases in surface waters often occur via colloidal intermediaries (Wells, 2002; Doucet *et al.,* 2007). Even the most insoluble metals (e.g., Th), are exchanged between dissolved and particulate phases scores of times before finally being deposited on the sediments and buried (Bacon and Anderson, 1982). If sedimentation occurs in the backwaters of lotic environments, sediment bound contaminants may be periodically remobilised by dredging, (Förstner and Calmano, 1998) or natural high flow events (Vignati *et al.,* 2003) until they reach a final sink i.e. lacustrine or oceanic sediments.

An improved understanding of heavy metal behaviour in coastal environments is valuable in assessing the extent to which natural cycles are perturbed or enhanced in systems like Cochin estuarine and coastal systems which are subjected to huge anthropogenic pressures. Understanding of the partitioning of heavy metals between soluble and particulate phases is essential to interpret accurately the geochemical behaviour of heavy metals in aquatic environments (Honeyman and Santschi, 1988; Buffle and Leppard, 1995a & b; Gustafsson and Gschwend, 1997; Buffle *et al.,* 1998).

This chapter deals with the evaluation of the spatial and seasonal variations of nine heavy metals (Cd, Pb, Cr, Ni, Co, Cu, Zn, Mn and Fe) in the dissolved and particulate compartments of Cochin estuarine and its adjacent coastal systems. Partition coefficients were determined to assess the contaminant retardation. Statistical analyses like, Pearson correlation, PCA and CA were also employed to find out the possible sources and behaviour of the above said metals and the classification of the stations based on the metal distribution.

4.2 Results & Discussions

4.2.1 Metal Distribution in Water

Concentrations of the dissolved metals (average ± standard deviation) analysed are given in appendix 11 to 16.

Cadmium

Annual average of Cd in the estuarine surface and bottom waters were 7.30 ± 9.09 and 7.29 ± 9.23 nM/L respectively. Highest concentration (21.13 nM/L) in the surface waters was detected in E2, E5 and E13 and that in the bottom water was in E2 (25.35 nM/L) during Pre-M season. In the coast, dissolved Cd showed annual averages of 5.51 ± 5.53 and 5.62 ± 5.87 nM/L in the surface and bottom waters respectively. Highest Cd concentrations detected in the coast were 16.24 nM/L (C9) in the surface and 20.02 nM/L (C10) in the bottom during Pre-M season.

Northern and some southern estuarine stations were found to be associated with higher Cd content compared to the middle stations during pre-M and Post-M seasons. Higher concentration of Cd found in the northern estuary can be attributed to the effluents from the northern industrial area (Joy *et. al.,* 1990; Robin *et al.,* 2012; Martin *et al.,* 2012). Higher concentrations of Cd in this area, has been reported by many authors (Sankaranarayanan *et al.,* 1978; Paul and Pillai, 1983a; Nair *et al.,* 1990; Ouseph, 1992; Shibu *et al.,* 1990; Shibu *et al.,* 1995; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; SCMC, 2004; Martin *et al.,* 2008; Deepulal *et al.,* 2012). Compared to the estuary, coast was found to be in lower ranges in Cd concentrations during Pre-M season, while during Mon and Post-M, many of the coastal stations showed higher Cd concentrations compared to the middle and southern estuarine stations (Fig. 4.1). Northern estuarine stations E1, E2, E4 and E5 were associated with higher dissolved Cd content compared to the coast, reinforcing the previous reports on industrial input of Cd from the industries lying upstream of these stations. Cd was below the detectable levels in all the estuarine surface stations (except E3) and bottom stations during Mon season. Coastal stations (C1 & C2) lying north to the bar mouth (station E3) always showed higher Cd content compared to station E3 during Mon. Surface-depth profile in the dissolved Cd distribution was not significant in the study area.

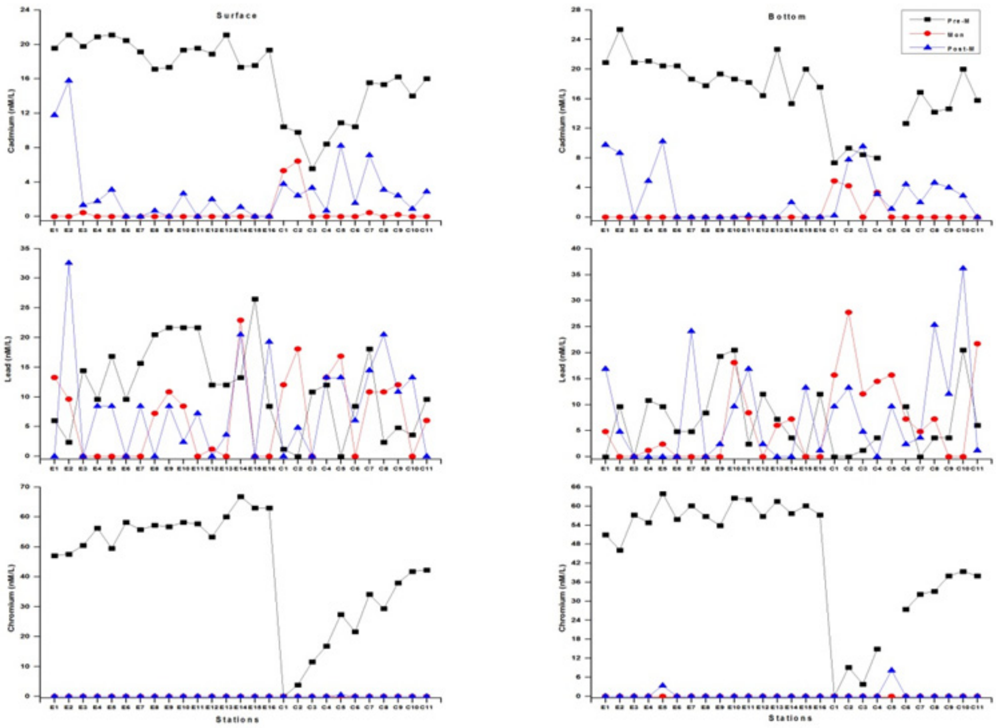

Figure 4.1 Spatial and temporal distribution of dissolved Cd, Pb and Cr

Lead

In the estuary, dissolved Pb in the surface and bottom showed annual averages of 8.87 ± 8.65 and 5.53 ± 6.66 nM/L respectively. Lead was detected in highest level in stations E2 (32.58 nM/L) in the surface and E7 (24.13 nM/L) in the bottom waters during Post-M season. In the coast, Pb showed an annual average of 8.12 ± 6.41 nM/L in the surface and 9.16 ± 9.20 nM/L in the bottom. Highest Pb content recorded in the coast was in station C8 in the surface (20.51 nM/L) and C10 in the bottom (36.20 nM/L) during Post-M season.

Estuary was found to be having higher concentrations of dissolved Pb compared to the coast during Pre-M season (Fig. 4.1). But during Mon and Post-M seasons, the scenario reversed and coastal dissolved Pb concentrations were observed to be higher. Surface-depth profile was significant only in the estuarine waters during Pre-M season. Some middle and southern end member stations were showing higher dissolved Pb compared to the northern estuarine stations. These middle stations probably may be receiving Pb from the nearby Cochin Shipyard and the southern end members from the boat building activities nearby.

Chromium

Annual average of Cr in the estuary was 18.77 ± 27.01 nM/L in the surface and 19.18 ± 27.39 nM/L in the bottom water samples. Highest Cr concentrations during the study period was detected in E14 (66.83 nM/L) in the surface and (63.95 nM/L) in the bottom during Pre-M period. In the coast, Cr showed an annual average of 8.10 ± 14.24 nM/L in the surface and 7.63 ± 13.74 nM/L in the bottom. Maximum concentration detected in the coast was 42.31 nM/L in the surface waters of C11 and 39.43 nM/L in the bottom waters of station C9.

Dissolved Cr was not in a detectable range in the study area during Mon and also in the surface estuarine waters during Post-M season. Dissolved Cr was higher in the estuary compared to the coastal waters (Fig. 4.1). Cr content in the northern estuarine stations was found to be lower than the other stations. Dissolved Cr in the coastal station, C1 was always found to be below the detectable levels. In the case of dissolved Cr, surface-bottom profile was not significant in the study area.

Nickel

In the estuary, Ni showed an annual average of 69.29 ± 57.23 nM/L in the surface and 71.19 ± 60.11 nM/L in the bottom. Highest concentration recorded in the surface and bottom estuarine waters were in E8 (153.77 nM/L) and E9 (166.12 nM/L) respectively during Pre-M season. Annual averages in the coastal surface and bottom waters were 79.20 ± 33.84 and 78.75 ± 34.80 nM/L respectively. In the coast, maximum Ni content during the study found was 160.15 nM/L in the surface (C8) during Post-M and 152.49 nM/L in the bottom (C10) during Pre-M.

During Pre-M season, estuarine stations were found to be with higher Ni content in comparison with the coastal stations. But this situation was reversed during Mon and Post-M seasons (Fig. 4.2). During Post-M, dissolved Ni was higher in the southern estuarine stations, which was almost comparable with the dissolved Ni content in the coastal waters. Surface to bottom variation in dissolved Ni content in the estuarine water was significant (95 % confidence level) only during Mon season. No such depth profile was obtained in the coastal waters.

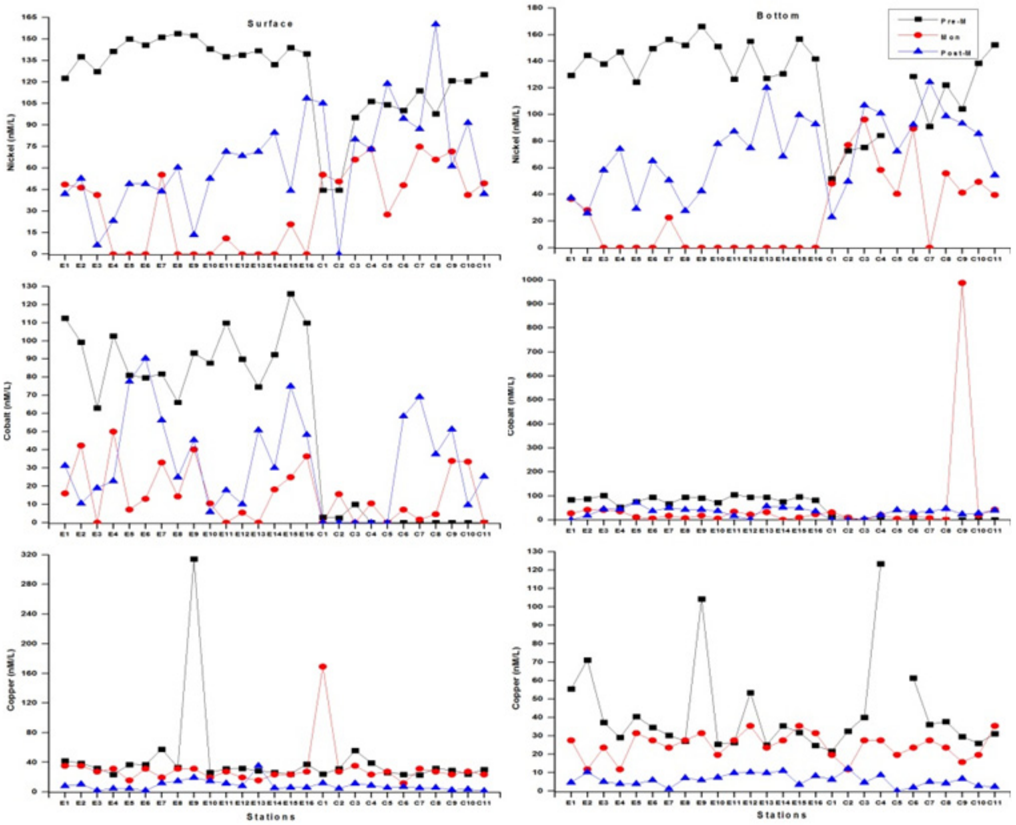

Figure 4.2 Spatial and temporal distribution of dissolved Ni, Co and Cu

Cobalt

Dissolved Co showed annual averages of 50.00 ± 36.84 and 48.22 ± 31.88 nM/L in the surface and bottom waters respectively in the estuary. Maximum Co concentrations detected in the surface and bottom waters were 125.99 nM/L (E15) and 105.20 nM/L (E11) respectively during Pre-M. In the coast, the annual averages were 11.36 ± 19.02 and 44.75 ± 172.74 nM/L in the surface and bottom waters respectively. Highest Co content found during the study was 69.15 nM/L (C7) in the surface during Post-M and 987.56 nM/L (C9) in the bottom during Mon.

During Pre-M, Co was detected only in stations north to the bar mouth (C1, C2 and C3). Compared to other stations, abnormally high value (987.56 nM/L) was observed in the bottom station C9 during Mon season. Estuarine water was found to be with higher dissolved Co levels compared to that in the coastal water during Pre-M and Mon, while during Post-M season, central coastal stations were associated with almost a comparable Co content with that in the estuary (Fig. 4.2). Surface-bottom profile of dissolved Co was not significant during the entire study period.

Copper

Annual average of dissolved Cu in the estuary was 29.35 ± 43.79 nM/L in the surface and 24.54 ± 19.05 nM/L in the bottom. Station E9 during Pre-M was associated with highest dissolved Cu both in the surface (314.34 nM/L) and bottom (104.26 nM/L) waters in the estuary. In the coastal waters, Cu showed annual averages of 25.48 ± 28.71 nM/L in the surface and 23.33 ± 23.13 nM/L in the bottom respectively. In the coastal waters, C1 (169.17 nM/L during Mon) and C4 (123.53 nM/L during Pre-M) were detected with highest Cu content in the surface and bottom respectively. Cu distribution was almost comparable both in the estuarine and coastal waters (Fig. 4.2). Surface-bottom variation was also not significant in the study area.

Zinc

Annual average of dissolved Zn in the estuary was 110.70 ± 238.94 & 113.57 ± 199.04 nM/L in the surface and bottom respectively. Highest Zn content was found in E2 in the surface (1425.29 nM/L) during Post-M and in

E2 in the bottom (1080.06 nM/L) during Pre-M. In the coast, Zn showed an annual average of 143.07 ± 595.44 nM/L in the surface and 155.32 ± 601.56 nM/L in the bottom waters respectively. Maximum Zn concentration detected in the surface was in C6 (3452.36 nM/L) and in C4 (3430.57 nM/L) during Pre-M.

Compared to the estuary, coastal waters were low in dissolved Zn except the abnormal higher values observed in the stations, C4 in the bottom and C6 in the surface (Fig. 4.3). During Pre-M, abnormally higher values observed for Zn in stations, C4 in the bottom and C6 in the surface, can be attributed to the effect of dredge spoil which is discharged at about 12 m depth on the south of the navigational channel (Balachandran, 2001). Higher values observed in the stations near the bar mouth can be attributed to the fluvial discharge through the estuary and also the effect of dumping of the dredge spoil. Surface-depth profile in the dissolved Zn distribution was not significant in the study area. In addition to the anthropogenic inputs in to the estuary (Sankaranarayanan *et al.,* 1978; Paul and Pillai, 1983a; Nair *et al.,* 1990; Ouseph, 1992; Shibu *et al.,* 1990; Shibu *et al.,* 1995; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; SCMC, 2004; Martin *et al.,* 2008; Deepulal *et al.,* 2012), association of zinc with organic matter (Paul and Pillai, 1983b) and dissolution of zinc from the sedimentary to the dissolved phases with increasing salinity may also be responsible for the generally higher concentration of dissolved zinc in the waterway (Ackroyd *et al.,* 1986).

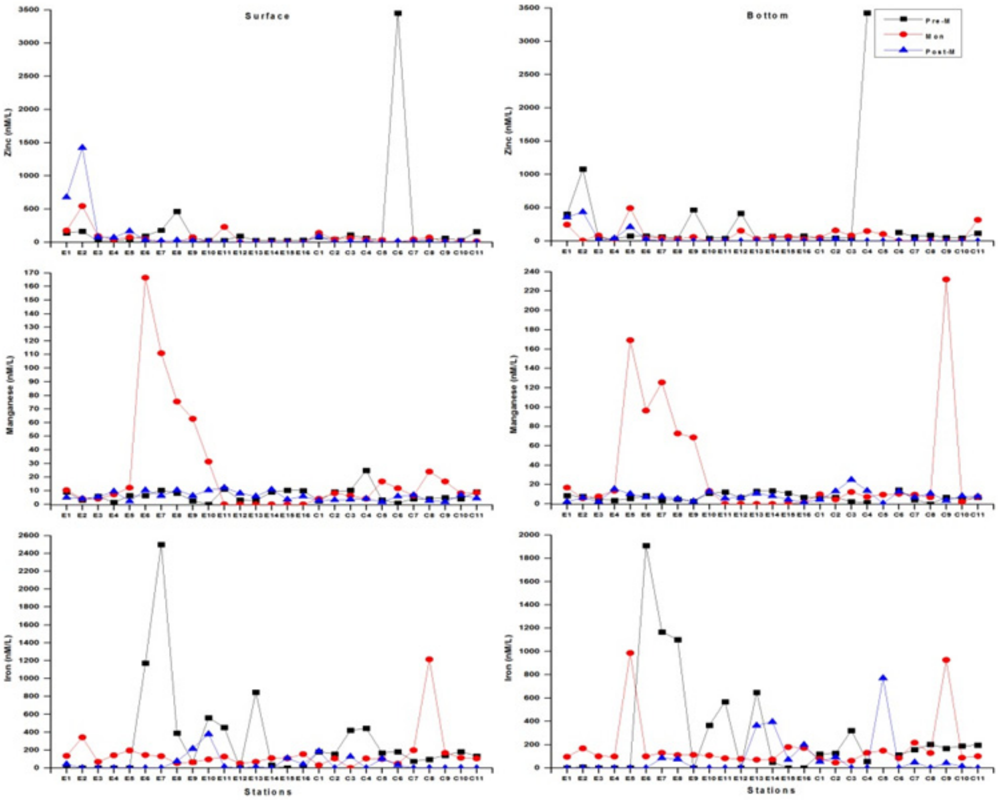

Figure 4.3 Spatial and temporal distribution of dissolved Zn, Mn and Fe

Manganese

Annual average of Mn in the estuarine surface and bottom waters were 14.66 ± 31.10 and 17.21 ± 33.40 nM/L respectively. Highest Mn concentrations detected in the surface was 166.55 nM/L (E6) and that in the bottom was 169.28 nM/L (E5) during Mon season. In the coastal waters, annual averages shown by dissolved Mn in the surface and bottom were 7.20 ± 5.89 and 14.82 ± 39.95 nM/L respectively. Highest Mn concentrations found in the coast was in station C4 (25.03 nM/L) in the surface during Pre-M and in C8 (232.08 nM/L) in the bottom during Mon.

Mon season was found to be with higher dissolved Mn compared to other seasons in the dynamic northern and central estuarine stations. But non-monsoon seasons were found to be with higher dissolved Mn concentrations in the comparatively less dynamic southern estuarine stations (Fig. 4.3). Surface-bottom variation in dissolved Mn distribution was found to be significant in the coastal area and bottom waters were associated with higher Mn content compared to the surface. Estuary was not showing significant surface-bottom variations in Mn content. During Mon, middle estuarine stations exhibited higher Mn concentration. Southern stations were below the detectable levels and this trend of concentration minimum has been reported in the low salinity region in the Cochin estuary (Unnikrishnan and Nair, 2004). This may be attributed to the oxidative precipitation, which is catalysed by an initial sorptive uptake onto suspended particles (Ackroyd *et al.,* 1986).

Iron

Fe in the estuarine waters shown annual averages of 185.99 ± 410.55 and 201.71 ± 377.23 nM/L in the surface and bottom respectively. Highest Mn concentrations detected in the surface was in E7 (2502.46 nM/L) and that in the bottom was in E6 (1911.54 nM/L) during Pre-M. Dissolved Fe in the coast was associated with annual averages of 147.08 ± 219.41 & 146.42 ± 200.35 nM/L in the surface and bottom waters respectively. In the surface, station C8 (1216.31 nM/L) and C9 (927.57 nM/L) showed maximum Fe content during Mon season.

Northern estuarine stations exhibited higher Fe content during Mon compared to Pre-M and Post-M, which could attributed to the industrial input along with the high runoff during Mon season (Fig. 4.3). During Mon, coastal bottom stations south to the bar mouth exhibited higher Fe than the estuarine stations. During Post-M also coastal stations were associated with higher dissolved Fe compared to the estuarine area. During Pre-M, dissolved Fe was higher in the middle estuarine stations (E6, E7, E8, E10, E11 and E13) compared to the north and south stations. Surface - bottom variation in the distribution of dissolved Fe was not significant in the study area.

4.2.1.1 Spatial and Temporal Variations of Dissolved Metals

Two-way ANOVA without replication was performed to examine the spatial and temporal variations in the distribution of dissolved metals (Table 4.1).

Cd which is a non-essential element showed highly significant temporal variation in the entire study area. In the study area, Pre-M season was found to be associated with high Cd content followed by Post-M and Mon seasons. Higher dissolved fraction during Pre-M and Post-M seasons can be due to the salinity induced desorption from the SPM and the formation of stable Cd-Chloro complexes (Bourg, 1987; Elbaz-Poulichet *et al.,* 1987; Comans and van Dijk, 1988). These stable complexes are less available from solution and hence Cd is more toxic in freshwater than in saltwater (Wright and Welbourn, 2002; Bradl, 2005). Pb exhibited highly significant temporal variation in the estuary and it lacked temporal variation in the coast. In the estuary, Pre-M season was found to be associated with higher Pb content and this can be attributed to the salinity induced desorption from the particulates. Although significant seasonal variations were absent in the coastal waters, Mon season was found to be in higher ranges for dissolved Pb followed by Post-M and Pre-M. This is indicative of the increased monsoonal estuarine inflow of Pb in to the stations near the bar mouth.

Essential metals like Cr and Ni exhibited temporal variations significant at 99 % confidence levels in the study area. Pre-M season was found to be in higher sides for these metals. During Mon season, majority of the estuarine stations were below the detectable levels for Ni. During Mon and Post-M seasons, Cr was below the detectable levels in the entire study area; exceptions being, stations E5 (in the bottom) and C5 (both in the surface and bottom) during Post-M. Co exhibited temporal variations significant at 99 % and 95 % confidence levels in the estuarine and coastal surface waters respectively. In the estuary, Pre-M season was associated with higher concentration of Co followed by Post-M and Mon seasons. However in the coast, Post-M season was detected with higher Co concentrations followed by Mon and Pre-M seasons. Dissolved Co in the bottom waters lacked significant temporal variations. In the study area, dissolved Cu showed temporal variations significant at 95 and 99 % confidence levels in the surface and bottom respectively. Pre-M season was associated with highest dissolved Cu followed by Mon and Post-M seasons. Mn showed significant temporal variation in the estuarine bottom waters only. Fe was the only element in the study area which was devoid of any significant temporal and spatial variations.

All the metals under study except Zn in the estuary lacked significant spatial variations in the study area. In the estuary, Zn showed spatial variation significant at 95 % confidence level both in the surface and bottom waters. Northern and middle stations in the estuary were showing higher levels of Zn compared to the southern stations. This spatial variation could be attributed to the influx of Zn from the industrial belt in the northern estuary (Sankaranarayanan *et al.,* 1978; Paul and Pillai, 1983a; Nair *et al.,* 1990; Ouseph, 1992; Shibu *et al.,* 1990; Shibu *et al.,* 1995; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* & 2006; SCMC, 2004; Martin *et al.,* 2008; Deepulal *et al.,* 2012; Shaiju, 2013; Bindu *et al.,* 2015).

Table 4.1 ANOVA results of the dissolved heavy metals in the Cochin estuary and its adjacent coast

Estuary	Spatial (*df*=15)				Temporal (*df*=2)			
	Surface		Bottom		Surface		Bottom	
	F	P-value	F	P-value	F	P-value	F	P-value
Cd	1.33	NS	1.85	NS	256.70	0.000**	341.58	0.000**
Pb	0.83	NS	1.02	NS	6.65	0.000**	2.24	0.000**
Cr	1.00	NS	1.22	NS	1607.81	0.000**	2610.34	0.000**
Ni	0.44	NS	0.51	NS	139.56	0.000**	178.23	0.000**
Co	1.38	NS	0.53	NS	60.74	0.000**	60.15	NS
Cu	1.16	NS	1.08	NS	4.26	0.023*	27.82	0.000**
Zn	2.49	0.016*	2.35	0.022*	0.74	NS	2.55	NS
Mn	1.06	NS	0.93	NS	3.71	NS	4.80	0.015*
Fe	0.94	NS	0.79	NS	2.87	NS	2.45	NS
Coast	Spatial (*df*=10)				Temporal (*df*=2)			
Cd	0.86	NS	0.22	NS	43.91	0.000**	25.35	0.000**
Pb	0.96	NS	0.73	NS	0.53	NS	1.33	NS
Cr	1.00	NS	1.00	NS	29.59	0.000**	24.15	0.000**
Ni	1.27	NS	0.99	NS	5.70	**0.01****	5.93	**0.01****
Co	0.95	NS	1.00	NS	4.23	0.03*	1.11	NS
Cu	1.05	NS	1.22	NS	4.84	0.02*	12.54	0.000**
Zn	0.96	NS	1.07	NS	4.84	0.02*	1.23	NS
Mn	0.37	NS	0.92	NS	3.14	NS	0.98	NS
Fe	0.62	NS	1.02	NS	1.77	NS	3.05	NS

** Significant at the 0.01 level, * Significant at the 0.05 level, NS Not Significant

4.2.1.2 Correlation among the Dissolved Metals and other Hydrographic Parameters

Pearson correlation analysis was performed to find out inter metallic relationships and the relationships of dissolved metals with other hydrochemical parameters in the estuary (Tables 4.2 to 4.7) and coast (Tables 4.8 to 4.13).

In the estuary, temperature showed weak negative correlations with dissolved Mn in the surface waters during Mon season. During Pre-M, pH showed strong and weak negative correlations with Ni and Fe respectively in the surface and Fe in the bottom. Weak negative correlations were obtained for pH with Ni and Mn in the surface and Cu in the bottom during Post-M. DO exhibited strong negative correlations with Mn in the surface; strong and weak positive correlations with Cd and Zn respectively in the bottom during Pre-M. DO showed weak negative correlations with Pb during Mon. In the surface waters, strong negative correlation was obtained for DO with Mn during Post-M. In the bottom waters, weak positive correlation was exhibited by DO and Cr during this season. Salinity was correlated negatively to Zn in the bottom waters during Pre-M suggesting that the origin of Zn is riverine. During Mon, strong positive correlation was shown by the pair Mn-salinity. Salinity showed weak positive correlation with Co both in the surface and bottom waters during Post-M season.

During Pre-M season, significant negative correlations were shown by the following metallic pairs; Cd - Pb in the estuarine surface waters (Table 4.2) and Cr – Cu, Cr – Zn and Ni – Mn (Table 4.3). Negative correlations observed among the metals indicated their entirely different origin or behaviour during this season. Significant positive correlation observed among Zn and Cu indicated a common anthropogenic source for these metals. During Mon season, the following metallic pairs in the estuary exhibited significant positive correlations; Zn –Ni, Zn – Cu and Zn – Fe in the surface waters (Table 4.4) and Zn –Mn, Zn- Fe, Mn – Fe in the bottom waters (Table 4.5). Strong positive correlations observed between Zn and Fe indicated a common pathway for these two metals in the estuary which might be the adsorption on to the surface of freshly formed hydrated oxides of Fe which are known to have strong scavenging action for Zn because of their high specific surface area (Jenne, 1968). The highly significant Fe-Mn correlation observed during this season revealed the formation of stable Fe–Mn oxy-hydroxides. Although Fe and Mn hydrous oxides act as scavengers for metals, highly significant positive correlation with Fe suggested predominance of Fe oxides over Mn oxides and thus Mn oxides might only be a minor host phase for the metals (Rengasamy Alagarsamy, 2006) in the estuary. It has been reported that the Flocculation properties of Fe and Mn is very much dependant on salinity (Sholkovitz, 1978; Balachandran *et al.,* 2005); Fe gets precipitated at low salinity (< 20 ppt) and Mn requires salinity > 20 ppt (Richard *et al.,* 1981; Balachandran *et al.,* 2006). Weak positive correlations observed for Zn with Ni and Cu suggested a similar origin/behaviour of these metals in the estuary. During Post-M season, significant inter-metallic correlations observed were Zn – Cd, Zn – Pb in the surface (Table 4.6) and Cd – Zn, Cd – Cr, Cd – Ni, Zn – Ni in the estuarine bottom waters (Table 4.7). Strong positive correlations observed for Cd and Zn indicated a common source for these metals. In Cochin estuary, strong association of these metals due to the disposal of untreated or partially treated industrial effluents has already been reported (Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Deepulal *et al.,* 2012; Bindu *et al.,* 2015). Negative correlation observed for Cd and Zn with Ni indicated its entirely different origin/behaviour in the estuary.

Table 4.2 Pearson correlation matrix of metals and hydrographic parameters in the surface waters of Cochin estuary during pre-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	-.574*	1												
Cr	-0.483	0.382	1											
Ni	-0.181	0.475	0.219	1										
Co	-0.117	0.007	0.173	-0.256	1									
Cu	-0.368	0.251	-0.033	0.359	0.003	1								
Zn	-0.319	-0.007	-0.214	0.349	-0.352	-0.024	1							
Mn	-0.354	0.164	0.234	-0.116	0.305	-0.215	0.182	1						
Fe	0.080	0.075	0.111	0.406	-0.330	-0.048	0.218	0.187	1					
Temp.	0.272	-0.111	-0.178	0.492	-0.438	0.033	0.416	0.095	0.449	1				
pH	0.174	-0.484	-0.416	-.771**	0.263	-0.180	-0.145	-0.091	-.587*	-0.207	1			
DO	0.429	-0.198	-0.288	-0.092	-0.205	-0.061	-0.133	-.671**	-0.109	-0.182	0.063	1		
Salinity	-0.278	0.223	0.212	-0.073	-0.192	-0.238	0.043	0.299	-0.070	0.116	0.105	-.583*	1	
SPM	-0.095	0.027	0.210	-0.085	-0.105	-0.180	0.187	0.199	0.108	0.200	0.050	-0.461	.677**	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.3 Pearson correlation matrix of metals and hydrographic parameters in the bottom waters of Cochin estuary during pre-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	-0.088	1												
Cr	-0.417	0.001	1											
Ni	-0.141	0.437	-0.223	1										
Co	0.029	-0.329	0.000	-0.066	1									
Cu	0.235	0.334	-.602*	0.352	0.139	1								
Zn	0.475	0.194	-.795**	0.177	0.112	.751**	1							
Mn	-0.073	-0.299	0.276	-.501*	0.287	-0.383	-0.158	1						
Fe	-0.043	-0.140	0.170	0.161	0.145	-0.341	-0.315	0.043	1					
Temp.	-0.026	-0.186	-0.482	0.153	-0.112	0.198	0.363	-0.272	-0.079	1				
pH	0.285	-0.397	-0.433	-0.456	-0.027	0.066	0.227	0.131	-.508*	0.261	1			
DO	.664**	0.170	-0.393	-0.067	0.216	0.295	.611*	0.153	0.093	0.016	-0.076	1		
Salinity	-0.394	-0.408	0.259	0.007	-0.232	-0.363	-.609*	-0.259	-0.108	0.141	0.183	-.718**	1	
SPM	-0.487	-0.145	0.075	0.415	0.041	-0.221	-0.347	-0.158	0.316	0.271	-0.201	-.498*	.549*	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.4 Pearson correlation matrix of metals and hydrographic parameters in the surface waters of Cochin estuary during monsoon (n=16)

	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1												
Pb	-0.180	1											
Ni	0.345	0.029	1										
Co	-0.318	0.144	0.140	1									
Cu	0.060	0.289	0.269	0.459	1								
Zn	0.021	0.169	.499*	0.207	.523*	1							
Mn	-0.142	-0.111	0.015	0.093	0.164	-0.189	1						
Fe	-0.210	0.058	0.373	0.431	0.301	.786**	-0.078	1					
Temp.	-0.051	-0.005	0.120	0.168	-0.076	-0.171	-.501*	-0.209	1				
pH	-0.125	0.059	-0.037	0.155	0.146	0.103	-0.065	0.272	0.168	1			
DO	-0.016	0.103	-0.063	-0.001	-0.119	0.172	-0.229	0.424	-0.100	.624**	1		
Salinity	0.210	-0.164	-0.135	0.115	0.352	-0.196	.772**	-0.253	-0.300	0.081	-0.285	1	
SPM	-0.153	0.284	-0.353	0.062	0.079	-0.062	-0.137	-0.319	-0.043	-0.299	-.585*	0.054	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.5 Pearson correlation matrix of metals and hydrographic parameters in the bottom waters of Cochin estuary during monsoon (n=16)

	Pb	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Pb	1											
Ni	-0.097	1										
Co	-0.218	0.306	1									
Cu	-0.199	-0.318	-0.470	1								
Zn	-0.111	0.122	-0.149	0.399	1							
Mn	-0.261	0.042	-0.392	0.156	.538*	1						
Fe	-0.089	-0.084	-0.182	0.204	.837**	.658**	1					
Temp.	0.066	-0.086	-0.319	0.409	0.217	-0.133	0.209	1				
pH	-0.181	-0.135	0.165	-0.161	0.430	0.368	0.492	-0.435	1			
DO	.527*	-0.067	-0.173	-0.062	0.351	0.023	0.491	0.396	0.073	1		
Salinity	-0.418	0.054	0.300	-0.262	-0.160	0.271	-0.163	-.789**	0.457	-.744**	1	
SPM	0.087	-0.378	-0.195	0.396	0.147	-0.129	0.116	0.078	-0.127	0.108	-0.180	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.6 Pearson correlation matrix of metals and hydrographic parameters in the surface waters of Cochin estuary during post-monsoon (n=16)

	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1												
Pb	0.442	1											
Ni	-0.097	0.348	1										
Co	-0.348	-0.184	-0.008	1									
Cu	-0.100	-0.062	0.123	-0.100	1								
Zn	.962**	.563*	-0.097	-0.265	-0.065	1							
Mn	-0.364	-0.143	0.235	-0.354	0.003	-0.395	1						
Fe	-0.096	-0.203	-0.158	-0.195	0.280	-0.173	0.147	1					
Temp.	0.055	-0.086	0.267	-0.011	0.166	0.001	-0.207	-0.035	1				
pH	0.276	-0.190	-.501*	0.293	-0.251	0.302	-.533*	-0.267	-0.341	1			
DO	0.450	0.077	-0.312	0.272	0.150	0.445	-.757**	-0.156	-0.060	.530*	1		
Salinity	-0.222	-0.284	-0.233	.512*	-0.407	-0.229	0.014	-0.118	-.663**	.557*	0.042	1	
SPM	-0.251	-0.120	0.379	-0.181	0.220	-0.298	0.216	0.009	0.288	-0.278	-0.112	-0.374	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.7 Pearson correlation matrix of metals and hydrographic parameters in the bottom waters of Cochin estuary during post-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	0.013	1												
Cr	.551*	-0.194	1											
Ni	-.560*	0.002	-0.338	1										
Co	-0.110	-0.307	0.473	0.088	1									
Cu	-0.144	-0.366	-0.261	0.270	-0.344	1								
Zn	.894**	0.116	0.276	-.574*	-0.348	0.000	1							
Mn	0.143	-0.136	0.246	0.182	0.368	-0.031	-0.096	1						
Fe	-0.246	-0.232	-0.151	0.475	0.382	0.420	-0.291	0.089	1					
Temp.	0.072	-0.223	0.260	0.222	0.048	-0.102	0.028	-0.229	-0.148	1				
pH	0.187	-0.161	0.445	-0.364	0.318	-.584*	0.078	0.044	-0.395	0.219	1			
DO	0.237	-0.358	.559*	-0.110	-0.050	0.371	0.104	0.065	-0.116	0.339	-0.108	1		
Salinity	-0.050	-0.444	0.129	-0.336	.518*	-0.343	-0.165	0.195	-0.025	-0.303	.632**	-0.279	1	
SPM	-0.280	-0.114	-0.011	0.334	-0.349	0.445	-0.263	0.032	-0.041	0.309	-0.381	.559*	-.548*	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

In the coast, temperature showed negative correlations with Cd, Cr, Ni and positive correlation with Fe in the coastal surface waters during Pre-M. In the bottom waters also Cd, Pb and Ni exhibited significant negative correlations with temperature. During Mon, temperature showed negative correlation with Cd in the surface waters. During Pre-M, pH showed positive correlations with Cd, Cr and negative correlation with Fe in the surface waters. Weak positive correlations were shown by dissolved Cd, Cr and Ni with pH of the bottom waters. During Mon, pH showed positive correlations with Co in the surface waters. Pb was correlated positively to pH during Post-M season. DO showed weak positive correlation with Mn in the bottom waters during Pre-M. Salinity was correlated positively to Pb in the bottom waters during Pre-M. Salinity showed weak negative correlations with Cd, Cu and Zn in the surface during Mon season. SPM exhibited negative correlations with Cd, Cr, Ni and positive correlation with Co in the surface waters during Pre-M. During Post-M, SPM exhibited weak negative correlation with Co and positive correlation with Cu and Fe in the surface waters.

During Pre-M, significant positive correlations observed in the coastal surface waters were Cd – Cr, Cr – Ni, Co – Cu, Cu – Fe, Mn- Fe and negative correlations observed were Cd – Co, Cd – Cu and Cd – Fe (Table 4.8). In the bottom, following metallic pairs showed significant positive correlations (Table 4.9); Cd – Pb, Cd – Cr, Cd – Ni, Pb – Ni, Cr – Ni, Cr –Co, Ni – Co and Cu – Zn. During Mon season, Cu – Zn and Mn – Fe exhibited strong positive correlations in the surface waters (Table 4.10). In the bottom, Pb – Zn, Co – Mn, Co – Fe and Mn – Fe were the metallic pairs which showed strong positive correlations (Table 4.11). During Post-M season, the following metallic pairs in the coast exhibited significant positive correlations; Cd – Cr, Cu – Zn, Cu – Fe and Zn – Fe in the surface (Table 4.12) and Cd – Mn, Cr – Fe, Cu – Zn and Co – Cu in the bottom waters (Table 4.13).

Table 4.8 Pearson correlation matrix of metals and hydrographic parameters in the surface waters of Cochin coast during pre-monsoon (n=11)

	Cd	**Pb**	**Cr**	**Ni**	**Co**	**Cu**	**Zn**	**Mn**	**Fe**	**Temp.**	**pH**	**DO**	**Salinity**	**SPM**
Cd	1													
Pb	0.028	1												
Cr	.778**	0.251	1											
Ni	0.488	0.489	.901**	1										
Co	-.694*	0.067	-0.557	-0.368	1									
Cu	-.625*	0.230	-0.315	-0.013	.793**	1								
Zn	-0.154	0.121	-0.059	0.032	-0.138	-0.224	1							
Mn	-0.410	0.346	-0.197	0.068	0.127	0.571	-0.299	1						
Fe	-.799**	0.251	-0.415	-0.030	0.560	.781**	-0.032	.751**	1					
Temp.	-.729*	-0.241	-.832**	-.661*	0.553	0.576	-0.064	0.496	.604*	1				
pH	.939**	0.173	.817**	0.598	-0.534	-0.380	-0.164	-0.320	-.659*	-.728*	1			
DO	0.145	-0.187	0.453	0.482	-0.155	0.169	0.306	0.082	0.120	-0.089	0.242	1		
Salinity	-0.201	-0.151	-0.475	-0.551	0.140	-0.132	0.027	-0.201	-0.104	0.058	-0.218	-0.462	1	
SPM	-.664*	-0.092	-.745**	-.705*	.823**	0.454	0.039	-0.061	0.256	0.532	-.607*	-0.343	0.431	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.9 Pearson correlation matrix of metals and hydrographic parameters in the bottom waters of Cochin coast during pre-monsoon (n=10)

	Cd	**Pb**	**Cr**	**Ni**	**Co**	**Cu**	**Zn**	**Mn**	**Fe**	**Temp.**	**pH**	**DO**	**Salinity**	**SPM**
Cd	1													
Pb	.642*	1												
Cr	.915**	0.554	1											
Ni	.775**	.698*	.860**	1										
Co	-0.542	-0.379	-.669*	-.658*	1									
Cu	-0.382	-0.042	-0.161	-0.089	-0.307	1								
Zn	-0.381	-0.062	-0.188	-0.174	-0.168	.940**	1							
Mn	0.077	0.223	0.093	0.205	0.165	-0.173	-0.344	1						
Fe	0.181	0.024	0.041	0.142	-0.298	-0.504	-0.534	-0.313	1					
Temp.	-.648*	-.942**	-0.520	-.730*	0.283	0.168	0.192	-0.369	-0.054	1				
pH	.669*	0.489	.642*	.652*	-0.308	-0.625	-0.604	0.292	0.458	-0.558	1			
DO	0.153	0.529	0.222	0.506	-0.150	-0.123	-0.218	.676*	0.101	-0.617	.646*	1		
Salinity	0.449	.784**	0.175	0.244	-0.141	-0.299	-0.308	0.115	0.314	-.721*	0.373	0.313	1	
SPM	-0.426	-0.509	-0.595	-0.395	0.474	-0.336	-0.333	0.089	0.335	0.240	-0.114	-0.027	-0.213	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.10 Pearson correlation matrix of metals and hydrographic parameters in the surface waters of Cochin coast during monsoon (n=11)

	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1												
Pb	0.480	1											
Ni	-0.098	0.033	1										
Co	-0.034	-0.086	0.039	1									
Cu	0.591	0.167	-0.003	-0.270	1								
Zn	0.545	0.275	0.193	-0.478	.859**	1							
Mn	-0.329	0.172	-0.128	0.120	-0.350	-0.208	1						
Fe	-0.185	0.152	0.246	-0.060	-0.149	0.172	.737**	1					
Temp.	-.696*	-0.374	0.010	0.232	-0.476	-0.536	0.398	0.315	1				
pH	-0.150	-0.356	-0.162	.767**	-0.282	-0.364	0.083	0.134	0.422	1			
DO	-0.320	0.085	0.380	0.214	-0.507	-0.345	0.509	0.578	.731*	0.246	1		
Salinity	-.627*	-0.083	-0.309	0.355	-.658*	-.717*	0.531	0.313	0.579	0.405	0.313	1	
SPM	0.293	0.591	0.403	0.245	-0.150	0.000	-0.054	0.200	-0.392	-0.014	0.064	0.128	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.11 Pearson correlation matrix of metals and hydrographic parameters in the bottom waters of Cochin coast during monsoon (n=11)

	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1												
Pb	0.578	1											
Ni	0.157	0.252	1										
Co	-0.178	-0.427	-0.169	1									
Cu	-0.365	0.034	-0.158	-0.347	1								
Zn	0.224	.794**	0.056	-0.239	0.428	1							
Mn	-0.197	-0.438	-0.154	.998**	-0.349	-0.268	1						
Fe	-0.255	-0.499	-0.308	.980**	-0.294	-0.300	.983**	1					
Temp.	-0.456	-0.390	-0.227	0.429	0.087	0.012	0.396	0.404	1				
pH	0.192	-0.037	0.106	0.022	-0.315	-0.267	0.048	0.094	-0.345	1			
DO	0.404	0.362	0.299	0.060	-0.258	0.077	0.089	0.046	-0.262	.627*	1		
Salinity	0.038	0.215	-0.033	-0.180	0.252	0.384	-0.216	-0.176	0.118	0.076	-0.377	1	
SPM	0.020	-0.231	-0.248	-0.204	0.201	-0.327	-0.183	-0.084	-0.589	0.355	-0.237	0.301	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.12 Pearson correlation matrix of metals and hydrographic parameters in the surface waters of Cochin coast during post-monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	0.142	1												
Cr	.688*	0.213	1											
Ni	0.282	0.528	0.287	1										
Co	0.111	0.322	-0.283	0.161	1									
Cu	0.022	-0.292	-0.044	0.308	-0.409	1								
Zn	-0.027	-0.377	-0.205	0.242	-0.229	.688*	1							
Mn	-0.203	0.063	-0.398	-0.077	0.375	-0.150	-0.142	1						
Fe	0.340	-0.505	0.308	0.292	-0.471	.765**	.720*	-0.374	1					
Temp.	-0.176	0.456	0.056	0.229	0.158	-0.077	-0.418	0.222	-0.406	1				
pH	0.018	.681*	-0.239	0.325	0.564	-0.433	-0.210	0.231	-0.479	0.134	1			
DO	-0.358	0.130	0.000	0.338	0.192	-0.313	-0.022	0.028	-0.075	-0.092	0.298	1		
Salinity	0.404	0.005	0.071	0.150	0.501	-0.379	0.171	0.000	0.077	-0.600	0.436	0.414	1	
SPM	0.381	-0.359	0.482	0.018	-.681*	.636*	0.538	-0.395	.819**	-0.485	-0.555	-0.273	-0.050	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.13 Pearson correlation matrix of metals and hydrographic parameters in the bottom waters of Cochin coast during post-monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	0.075	1												
Cr	-0.277	-0.033	1											
Ni	0.328	-0.040	-0.109	1										
Co	-0.464	0.135	0.331	0.389	1									
Cu	0.425	-0.074	-0.490	-0.146	-.657*	1								
Zn	0.283	-0.050	-0.182	-0.295	-0.482	.669*	1							
Mn	.805**	-0.171	-0.462	0.333	-0.425	0.277	0.059	1						
Fe	-0.264	-0.025	.991**	-0.164	0.260	-0.401	-0.066	-0.498	1					
Temp.	0.361	-0.291	-0.149	0.564	-0.155	-0.013	0.089	0.468	-0.149	1				
pH	-0.079	.760**	-0.100	0.041	0.065	-0.215	-0.162	-0.079	-0.116	-0.149	1			
DO	-0.459	0.097	-0.287	-0.369	0.108	-0.331	-0.236	-0.285	-0.314	-0.518	0.320	1		
Salinity	-0.364	0.314	-0.307	-0.017	0.099	-0.197	-0.190	-0.431	-0.296	-0.143	0.537	.656*	1	
SPM	0.105	0.119	0.239	0.265	0.323	-0.040	0.131	-0.014	0.239	0.160	-0.354	-0.468	-0.576	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

4.2.1.3 Principal Component Analysis

The types of reactions that are likely to control the partitioning of metals in an aquatic environment are; adsorption and desorption, precipitation and solubilization, surface complex formation, ion exchange and biological mobilization or immobilization. Heavy metals in water column are associated with several distinct geochemical phases, like clay minerals and organic matter. There are many processes which remove the dissolved metal species, off which simplest is the passage of heavy metals bound with clay minerals through the water column without any interaction. Another process is the adsorptive scavenging and settling by the sinking particulates. Direct sorption to surface sediments is also a removal mechanism in the bottom waters. Exchange of metals from sediment to the overlying waters also occurs via diffusion or resuspension or biological pumping (irrigation). Coagulation and flocculation of colloids in estuaries may remove some dissolved ions from water column. Metal hydroxides can flocculate from dissolved or colloidal organic matter during the mixing of river-derived iron in the mixing zone of estuaries (Sholkovitz, 1976 & 1978; Boyle *et al.,* 1977; Mayer, 1982). Scavenging by hydrous oxides of iron and manganese also contribute to the removal of dissolved species.

Principal component analysis of dissolved heavy metals and other physicochemical parameters was performed to identify the various processes acting in the water column. Varimax rotation was applied to identify the variables that are more significant to each factor based on the significance of their correlations and are expressed as factor loading (Buckley *et al.,* 1995; Davis, 2002). Parameters with factor loading > 0.50 and components with eigen values > 1 are considered for interpretation. The loadings of each variable, percentage variance accounted by each component and cumulative percentage variances in the estuarine and coastal area are given in Table 4.14 and 4.15 respectively.

Table 4.14 Factor loadings showing eigen values of dissolved parameters in the Cochin estuary

Variables	Components																
	Pre-monsoon					Monsoon						Post-monsoon					
Surface	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**	**PC1**	**PC2**	**PC3**	**PC4**		
Cd	0.000	-0.202	**-0.825**	-0.363	0.053	0.087	0.081	-0.025	**0.926**	-0.070	0.034	0.320	**0.886**	-0.064	-0.030		
Pb	0.385	0.176	**0.674**	0.052	-0.253	0.098	-0.112	0.086	-0.063	**0.811**	-0.034	-0.120	**0.708**	0.064	0.420		
Cr	0.428	0.295	0.270	0.244	**-0.589**												
Ni	**0.749**	-0.082	0.421	-0.129	0.274	**0.744**	-0.015	-0.087	0.361	-0.222	0.217	-0.403	0.032	0.477	**0.579**		
Co	-0.322	-0.320	0.047	**0.581**	-0.460	0.427	0.295	0.038	**-0.563**	0.130	0.431	0.486	**-0.573**	-0.147	0.407		
Cu	0.009	-0.298	**0.706**	-0.150	0.166	**0.574**	0.491	0.017	0.035	0.479	0.182	0.093	-0.064	**0.562**	-0.427		
Zn	0.113	0.095	0.203	0.143	**0.791**	**0.881**	-0.143	0.069	0.003	0.209	-0.167	0.339	**0.903**	-0.084	0.050		
Mn	0.098	0.178	-0.020	**0.912**	0.056	-0.039	**0.839**	-0.084	-0.154	-0.224	-0.324	**-0.891**	-0.164	-0.083	-0.105		
Fe	**0.782**	0.000	-0.243	0.135	0.236	**0.810**	-0.134	0.320	-0.336	-0.060	-0.192	-0.196	-0.077	0.085	**-0.760**		
Temp	0.430	0.151	-0.212	-0.009	**0.701**	-0.114	-0.308	0.025	-0.003	-0.048	**0.907**	0.135	-0.002	**0.790**	0.095		
pH	**-0.907**	0.062	-0.248	0.009	0.049	0.013	0.125	**0.862**	-0.090	0.123	0.223	**0.685**	0.000	**-0.554**	0.019		
DO	-0.057	-0.482	-0.216	**-0.703**	-0.122	0.088	-0.261	**0.903**	-0.020	-0.044	-0.197	**0.871**	0.207	0.005	-0.041		
Salinity	-0.076	**0.926**	0.082	0.132	0.005	-0.144	**0.950**	-0.030	0.134	0.012	-0.054	0.128	-0.412	**-0.822**	0.172		
SPM	0.003	**0.838**	-0.080	0.120	0.102	-0.244	-0.025	-0.590	-0.169	**0.623**	0.000	-0.192	-0.228	**0.605**	0.064		
% of Variance	**18.90**	**15.83**	**15.38**	**14.05**	**13.80**	**20.15**	**16.70**	**15.69**	**11.55**	**11.25**	**10.41**	**21.31**	**21.02**	**19.76**	**11.52**		
Cumulative %	**18.90**	**34.73**	**50.11**	**64.16**	**77.95**	**20.15**	**36.85**	**52.54**	**64.09**	**75.34**	**85.75**	**21.31**	**42.33**	**62.09**	**73.61**		
Bottom	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**		**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**
Cd	**0.778**	0.255	-0.247	0.039	-0.192							0.037	**0.950**	0.108	-0.029	-0.063	0.173
Pb	0.214	-0.209	**0.813**	-0.196	-0.257	-0.190	0.069	**0.869**	0.067	-0.117		-0.163	0.056	-0.120	**-0.909**	-0.153	-0.048
Cr	-0.369	**-0.824**	-0.042	0.187	-0.026							0.248	0.454	**0.505**	0.200	-0.108	**0.554**
Ni	-0.183	0.353	**0.771**	0.234	-0.021	0.048	0.138	-0.144	**-0.794**	0.250		-0.320	**-0.648**	0.209	-0.165	0.474	0.103
Co	0.071	0.026	-0.095	0.093	**0.903**	-0.061	-0.239	-0.138	-0.215	**0.890**		**0.626**	-0.164	0.201	0.133	0.432	0.489
Cu	0.308	0.497	**0.503**	-0.445	0.204	0.206	0.479	-0.418	**0.504**	-0.359		**-0.690**	-0.027	-0.200	**0.542**	0.289	-0.123
Zn	**0.613**	**0.596**	0.228	-0.334	0.183	**0.916**	0.188	-0.080	0.038	-0.042		-0.084	**0.946**	-0.008	-0.076	-0.092	-0.134
Mn	0.148	-0.473	-0.468	-0.017	0.481	**0.642**	-0.247	-0.189	-0.198	**-0.593**		0.022	-0.041	-0.207	0.012	0.068	**0.887**
Fe	0.040	-0.078	0.037	**0.928**	0.095	**0.946**	0.059	0.100	0.065	-0.120		-0.095	-0.179	-0.099	0.176	**0.908**	0.053
Temp	-0.142	**0.782**	-0.099	0.030	-0.070	0.112	**0.893**	0.073	0.047	-0.101		-0.028	-0.035	**0.925**	0.068	-0.026	-0.181
pH	0.029	0.363	**-0.651**	**-0.549**	-0.071	**0.625**	**-0.645**	0.033	0.067	0.130		**0.784**	0.092	0.247	0.088	-0.372	0.055
DO	**0.895**	0.125	0.044	0.134	0.155	0.435	0.365	**0.772**	0.035	0.063		-0.437	0.201	0.448	**0.532**	-0.232	0.314
Salinity	**-0.821**	0.102	-0.289	0.017	-0.308	-0.071	**-0.844**	-0.485	-0.090	0.003		**0.832**	-0.081	-0.329	0.380	-0.073	0.105
SPM	**-0.729**	0.284	0.126	0.423	0.115	0.061	0.164	-0.009	**0.821**	0.084		**-0.726**	-0.348	0.315	0.229	-0.270	0.143
% of Variance	**23.92**	**18.55**	**17.05**	**12.92**	**9.83**	**23.60**	**20.80**	**15.50**	**13.91**	**11.69**		**22.17**	**19.05**	**12.74**	**12.39**	**11.73**	**11.26**
Cumulative %	**23.92**	**42.47**	**59.52**	**72.44**	**82.27**	**23.60**	**44.40**	**59.90**	**73.81**	**85.51**		**22.17**	**41.21**	**53.95**	**66.33**	**78.06**	**89.32**

Table 4.15 Factor loadings showing eigen values of dissolved parameters in the Cochin coast

Variables	**Components**														
	Pre-monsoon					**Monsoon**					**Post-monsoon**				
Surface	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**
Cd	**-0.754**	0.234	-0.499	0.086	-0.248	**0.702**	-0.222	**0.505**	0.104	-0.137	0.044	0.276	0.399	0.407	**0.761**
Pb	0.088	-0.007	0.048	**0.969**	0.042	0.162	0.224	**0.836**	-0.193	-0.073	-0.379	**0.817**	-0.001	-0.123	0.042
Cr	**-0.572**	**0.623**	-0.336	0.364	-0.121						-0.103	0.261	**0.853**	0.053	0.331
Ni	-0.261	**0.700**	-0.217	**0.588**	-0.033	0.076	0.063	0.115	-0.051	**0.966**	0.362	**0.883**	0.141	0.034	-0.094
Co	0.279	-0.140	**0.939**	0.000	-0.067	-0.224	-0.022	0.129	**0.911**	0.044	-0.338	0.396	**-0.588**	0.412	0.102
Cu	**0.535**	0.255	**0.724**	0.166	-0.224	**0.907**	-0.145	-0.025	-0.119	-0.100	**0.910**	0.000	0.044	-0.321	0.135
Zn	-0.007	0.064	-0.061	0.055	**0.980**	**0.917**	0.079	0.084	-0.291	0.085	**0.905**	-0.064	-0.081	0.202	-0.107
Mn	**0.834**	0.173	-0.084	0.282	-0.343	-0.255	**0.866**	0.050	-0.007	-0.229	-0.126	0.054	**-0.714**	-0.049	0.098
Fe	**0.860**	0.161	0.350	0.211	0.002	0.043	**0.922**	0.089	0.007	0.170	**0.852**	-0.093	0.417	0.145	0.103
Temp	**0.766**	-0.162	0.328	-0.399	-0.059	-0.497	0.478	**-0.561**	0.229	0.136	-0.309	0.451	-0.152	**-0.728**	0.059
pH	**-0.737**	0.349	-0.304	0.232	-0.276	-0.137	0.121	-0.206	**0.920**	-0.072	-0.327	**0.620**	-0.389	0.326	-0.124
DO	0.003	**0.889**	0.007	-0.198	0.262	-0.339	**0.667**	-0.066	0.178	0.465	-0.114	0.291	0.101	0.337	**-0.824**
Salinity	-0.088	**-0.759**	0.100	-0.098	0.106	**-0.768**	0.369	0.025	0.242	-0.299	-0.047	0.155	-0.034	**0.982**	-0.034
SPM	0.167	-0.495	**0.781**	-0.185	0.127	-0.111	-0.010	**0.884**	0.151	0.320	**0.642**	-0.258	**0.591**	0.055	0.259
% of Variance	**28.11**	**20.27**	**19.79**	**13.40**	**9.91**	**25.29**	**19.66**	**16.50**	**15.31**	**11.46**	**24.44**	**18.05**	**17.70**	**15.99**	**10.90**
Cumulative %	**28.11**	**48.38**	**68.17**	**81.57**	**91.48**	**25.29**	**44.95**	**61.45**	**76.76**	**88.22**	**24.44**	**42.48**	**60.19**	**76.18**	**87.07**
Bottom	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC1**	**PC2**	**PC3**	**PC4**		**PC1**	**PC2**	**PC3**	**PC4**	**PC5**
Cd	**0.832**	0.364	0.353	-0.036	-0.030	-0.118	**0.568**	**0.504**	-0.199		**0.793**	-0.402	-0.087	0.131	0.059
Pb	0.461	-0.057	**0.840**	0.257	-0.038	-0.339	0.186	**0.873**	-0.136		-0.114	-0.030	-0.011	**0.960**	0.162
Cr	**0.976**	0.149	0.112	0.069	-0.068						-0.160	0.225	**0.947**	-0.041	0.118
Ni	**0.835**	0.032	0.236	0.361	0.136	-0.264	0.116	0.151	**-0.548**		**0.622**	**0.527**	-0.213	0.051	0.346
Co	**-0.765**	0.347	-0.059	0.003	-0.444	**0.971**	-0.043	-0.120	-0.048		-0.286	**0.765**	0.061	0.076	0.460
Cu	-0.009	**-0.983**	-0.102	-0.030	-0.106	-0.370	-0.428	0.111	0.482		0.136	**-0.842**	-0.320	-0.080	0.093
Zn	-0.049	**-0.938**	-0.071	-0.168	-0.157	-0.151	-0.232	**0.909**	0.151		-0.020	**-0.809**	-0.050	-0.039	0.184
Mn	-0.028	0.216	0.052	**0.835**	-0.375	**0.962**	-0.017	-0.152	-0.068		**0.831**	-0.199	-0.282	-0.092	-0.095
Fe	0.039	0.409	0.109	-0.111	**0.888**	**0.964**	0.000	-0.210	0.058		-0.188	0.121	**0.954**	-0.036	0.126
Temp	-0.394	-0.081	**-0.763**	-0.424	0.007	0.488	**-0.715**	-0.005	0.010		**0.751**	0.151	-0.068	-0.213	0.068
pH	**0.539**	**0.538**	0.211	0.420	0.279	0.115	**0.821**	-0.094	-0.004		-0.025	0.169	-0.069	**0.885**	-0.311
DO	0.142	0.030	0.282	**0.906**	0.162	0.134	**0.561**	0.290	**-0.560**		**-0.603**	0.242	-0.412	0.111	-0.475
Salinity	0.050	0.202	**0.945**	0.016	0.132	-0.083	0.015	0.392	**0.727**		-0.370	0.309	-0.407	0.386	-0.469
SPM	**-0.637**	0.358	-0.281	0.179	0.350	-0.245	**0.535**	-0.395	**0.666**		0.083	0.001	0.156	-0.050	**0.924**
% of Variance	**28.72**	**20.05**	**18.64**	**15.37**	**10.23**	**26.86**	**18.43**	**18.17**	**14.69**		**21.09**	**19.28**	**17.26**	**13.98**	**13.17**
Cumulative %	**28.72**	**48.77**	**67.41**	**82.78**	**93.00**	**26.86**	**45.29**	**63.46**	**78.15**		**21.09**	**40.37**	**57.63**	**71.61**	**84.78**

In the estuary, 5 major components with 77.95 % cumulative variance were obtained for the surface samples during Pre-M (Fig. 4.4). PC1 which explained 18.90 % of the total variance was characterised by positive loadings of Ni & Fe and negative loadings of pH. PC1 indicated the pH-dependent precipitation of iron along with scavenging of Ni from the water. PC2 with 15.83 % of variance was characterised by positive loadings of salinity and SPM. This PC indicated the flocculation of suspended particulate matter with increase in salinity (Hakanson, 2006). PC3 was characterised by positive loadings of Pb, Cu; negative loading of Cd and this factor explained 15.38 % of the total variance. This PC gave an indication of similar behaviour/source of Pb and Cu in the estuary. PC4 was loaded with positive loading of Co and Mn; negative loading of DO and this factor explained 14.05 % of the cumulative variance. This PC represented the scavenging Co by the hydrous Mn oxides. Gradual oxidation of dissolved Mn to particulate Mn with the increase in dissolved oxygen in the lower estuary has been reported (Tien-Hsi Fang and Che-Liang Lin, 2002). Zn and temperature loaded positively; Cr loaded negatively in PC5 which explained 13.80 % of the total variance.

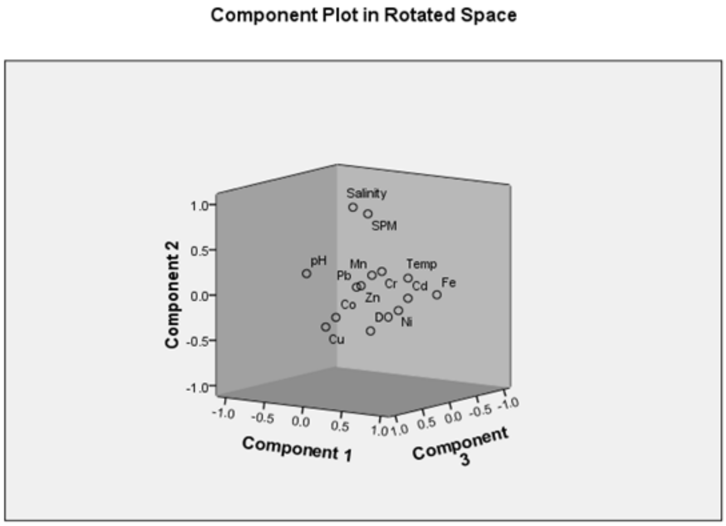

Figure 4.4 Ordination plot of principal components of estuarine surface waters during pre-monsoon

During Pre-M, 5 principal components with 82.27 % cumulative variance were obtained for the bottom samples (Fig. 4.5). PC1 was characterised with positive loadings of Cd, Zn, DO and negative loadings of salinity and SPM which stood for the riverine anthropogenic input. Input of industrial effluents with huge amount of Cd and Zn has already been reported in Cochin estuary (Joy *et al.,* 1990; Martin *et al.,* 2012). PC1 explained 23.92 % of the cumulative variance. PC2 with 18.55 % of variance was characterised with moderate positive loading of Zn and temperature and Cr was negatively loaded in this component. Pb, Ni & Cu were loaded positively and pH loaded negatively in PC3 which explained 17.05 % of the cumulative variance. PC4 which explained 12.92 % of cumulative variance was characterised with positive and negative loadings of Fe and pH respectively. PC5 with 9.83 % of the cumulative variance was loaded positively with Co alone.

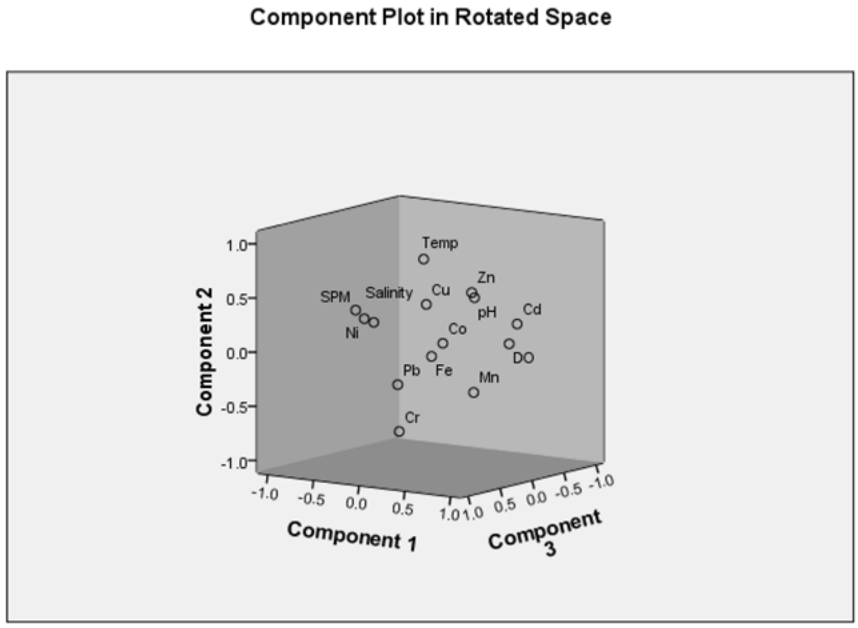

Figure 4.5 Ordination plot of principal components of estuarine bottom waters during pre-monsoon

During Mon, 6 factors with 85.75 % cumulative variance were obtained for the surface samples (Fig. 4.6). PC1 with 20.15 % of cumulative variance was loaded positively with Ni, Cu, Zn and Fe. This PC represented the metal scavenging by the hydrous Fe oxides. PC2 was characterised by positive loadings of Mn and salinity and it explained 16.70 % of the cumulative variance. This PC pointed the process of oxidative conversion of dissolved Mn to particulate Mn with increase in salinity (Roy Chester, 1990). PC3 with 15.69 % of total variance showed positive loadings of pH and DO; negative loading of SPM. Cd loaded positively and Co loaded negatively in PC4 which explained 11.55 % of the cumulative variance. PC5 was characterised with positive loadings of Pb and SPM and this PC explained 11.25 % of the total variance. This PC indicated the partitioning of Pb on to the particulate phase (Elbaz-Poulichet *et al.,* 1984; Balls, 1989). PC6 was characterised with positive loading of temperature and explained 10.41 % of the cumulative variance.

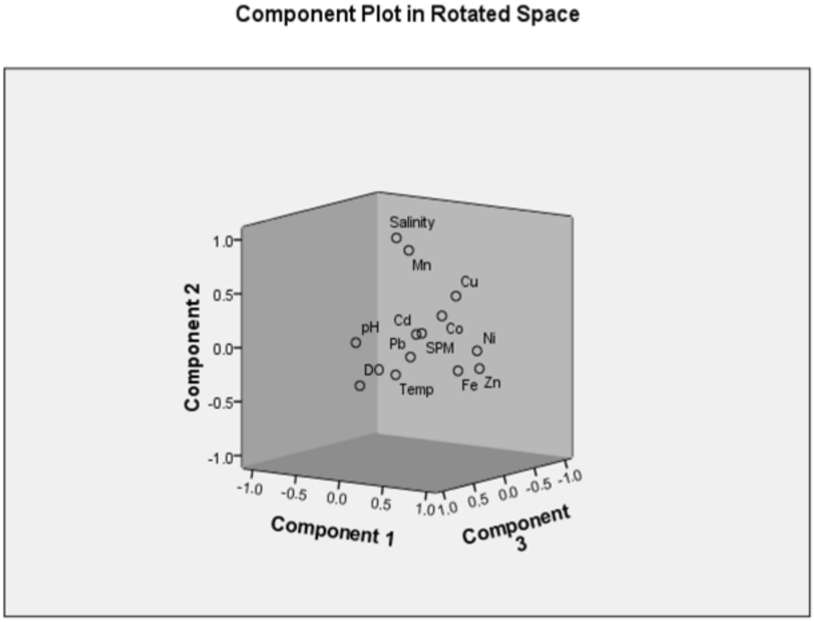

Figure 4.6 Ordination plot of principal components of estuarine surface waters during monsoon

For the bottom samples 5 principal components with 85.51 % cumulative variance were obtained (Fig. 4.7). PC1 with 23.60 % of the cumulative variance was loaded positively with Zn, Mn, Fe and pH. This component suggested the scavenging of Zn during the formation of hydrous oxides of Fe and Mn. PC2 which explained 20.80 % of the variance was characterised by positive loading of temperature and negative loading of pH and salinity. Pb and DO were loaded positively in PC3 which explained 15.50 % of the cumulative variance. PC4 which accounted for 13.91 % of the total variance was loaded positively with Cu and SPM; negatively with Ni. This PC might be representing the competitive removal of Cu from the SPM by Ni ions. Co and Mn were loaded positively and negatively in PC5, which explained 11.69 % of the total variance. PC5 represented the scavenging Co by the hydrous Mn oxides.

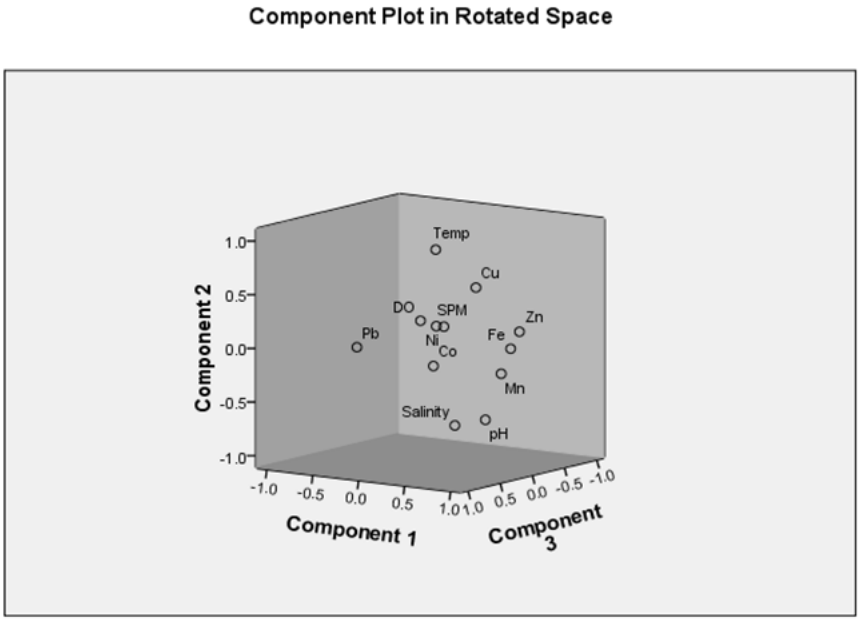

Figure 4.7 Ordination plot of principal components of estuarine bottom waters during monsoon

During Post-M season, 4 principal components were obtained for the surface stations which explained 73.61 % of variance (Fig. 4.8). PC1 which explained 21.31 % of variance was characterised with positive loadings of pH, DO and negative loading of Mn. This PC represented the oxidative precipitation of Mn. PC2 was characterised with positive loadings of Cd, Pb, Zn and negative loading of Co. This PC which explained 21.02 % of the total variance could be considered as the anthropogenic component. PC3 was characterised with positive loadings Cu, temperature, SPM; negative loading of pH and salinity. This component explained 19.76 % of total variance and represented the partitioning of Cu on to the SPM with increase in salinity. Positive and negative loadings were shown by Ni & Fe respectively in PC4 which explained 11.52 % of the cumulative variance.

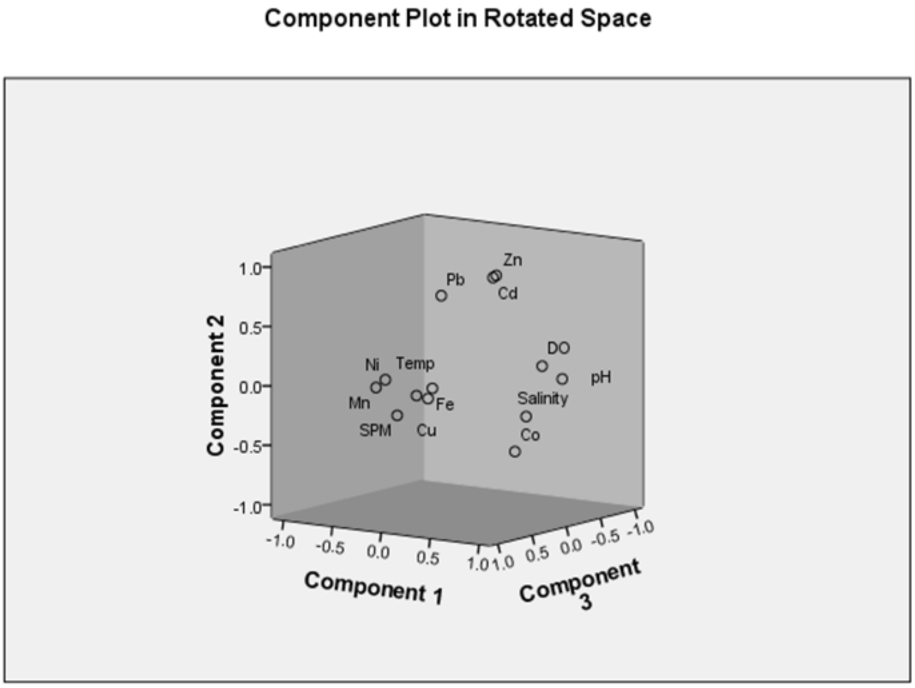
Component Plot in Rotated Space

Figure 4.8 Ordination plot of principal components of estuarine surface waters during post-monsoon

Bottom samples rendered 6 PCs with 89.32 % total variance (Fig. 4.9). PC1 was loaded positively with Co, pH, salinity; negatively with Cu and SPM. This PC which explained 22.17 % of total variance might be representing the competitive adsorption of Cu over Co on to SPM with increase in salinity and pH. PC2 with 19 .05 % of variance was characterised with high positive loading of Cd and Zn; moderate negative loading of Ni. PC2 can be considered as the anthropogenic component. PC3 was loaded positively with Cr and temperature and this component explained 12.74 % of the total variance. PC4 was characterised by negative loading of Pb; positive loading of Cu & DO and it explained 12.39 % of the cumulative variance. PC5 was characterised with high positive loading of Fe and explained 11.73 % of total variance. PC6 which explained 11.26 % of the cumulative variance showed high positive loading of Mn and moderate positive loading of Cr. This component represented the co-precipitation of Cr while the formation of hydrous Mn oxides.

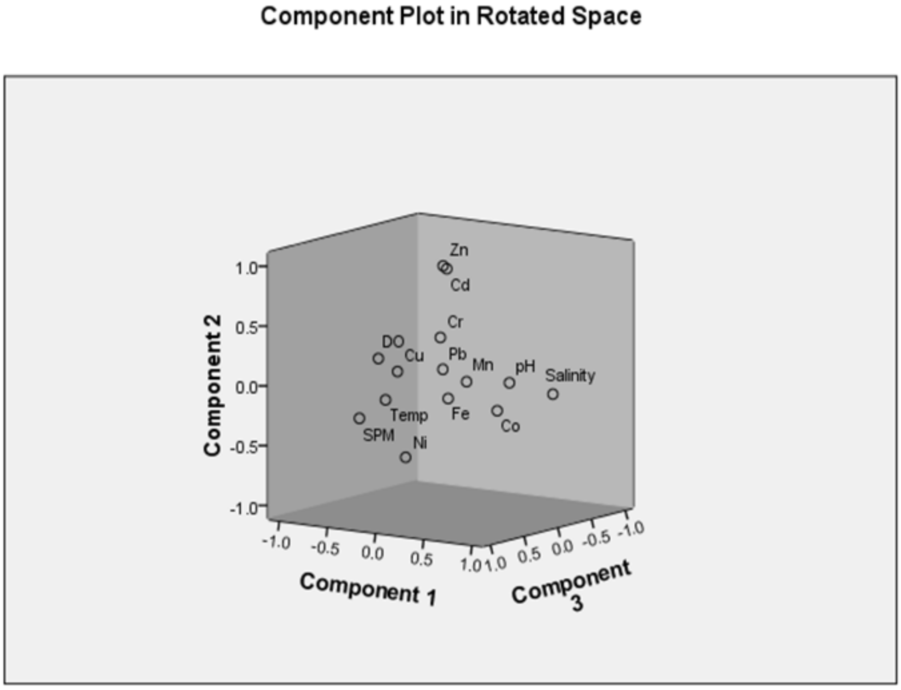

Figure 4.9 Ordination plot of principal components of estuarine bottom waters during post-monsoon

In the coast, 5 principal components whose eigen values are greater than one were extracted for both the surface (Fig. 4.10) and bottom (Fig. 4.11) coastal stations and they explained 91.48 and 93 % of cumulative variance respectively during Pre-M season. In the surface, PC1 with 28.11 % of total variance was characterised with positive loading of Cu, Fe, Mn, temperature; negative loading of Cd, Cr and pH. This PC explained the scavenging of Cu during the Fe-Mn oxy hydroxide formation with the increase in pH and desorption of Cd and Cr by the increased competition from the sea water cations. PC2 which explained 20.27 % of cumulative variance was loaded positively with Cr, Ni, DO and negatively with salinity. PC3 was loaded positively with Co, Cu & SPM and this PC explained 19.79 % of cumulative variance. This PC represented the adsorption of the above metals on the SPM. PC4 which explained 13.40 % of the total variance was characterised by positive loading of Pb and Ni. Zn was loaded positively in PC5 which explained 9.91 % of cumulative variance and this PC stood for the anthropogenic contribution from the estuary. PC1 in the bottom was loaded positively with Cd, Cr, Ni, pH and negatively with Co and SPM. This component explained 28.72 % of the cumulative variance. Cu & Zn showed high negative loading in PC2 and pH showed moderate positive loading in this component which explained 20.05 % of the variance. PC3 which accounted for 18.64 % of total variance was loaded positively with Pb and salinity; negatively with temperature. PC4 was characterised with positive loading of Mn and DO. This PC accounted for 15.37 % of the total variance and it stood for the oxidative precipitation of Mn. Fe exhibited high positive loading in PC5 which explained 10.23 % of the cumulative variance.

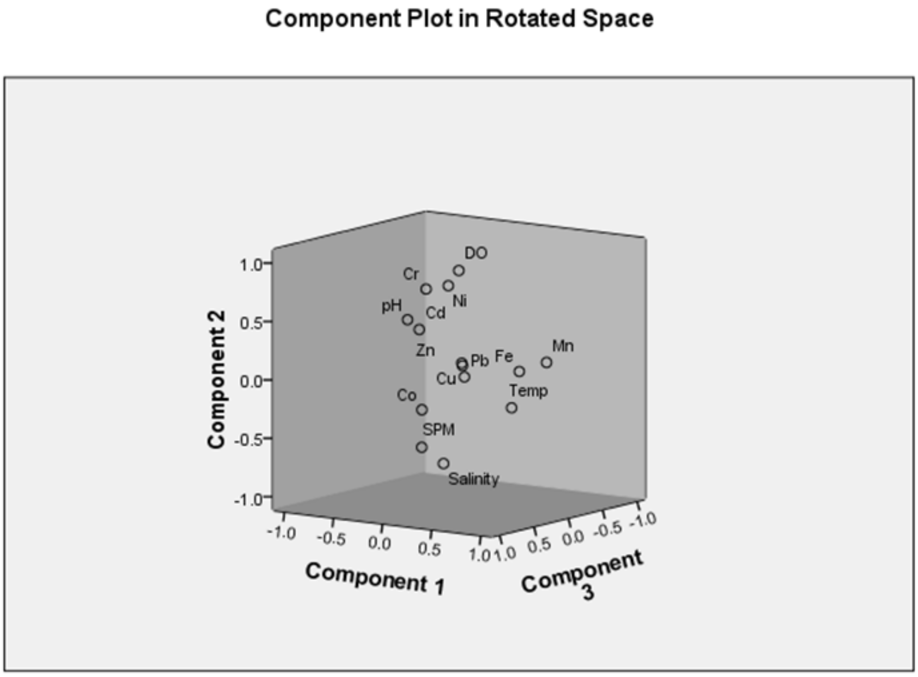

Figure 4.10 Ordination plot of principal components of coastal surface waters during pre-monsoon

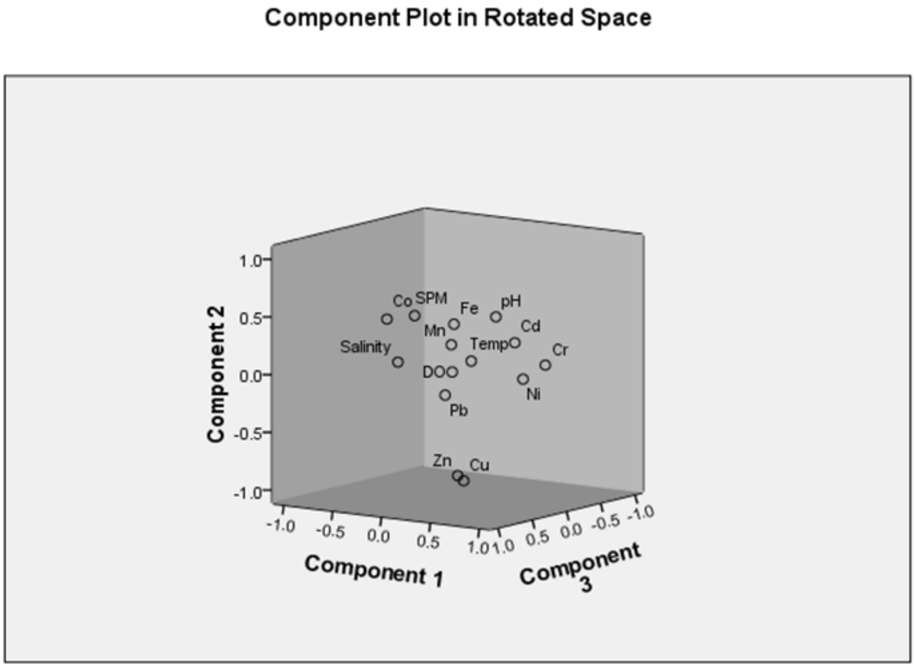

Figure 4.11 Ordination plot of principal components of coastal bottom waters during pre-monsoon

During Mon, 5 principal components with 88.22 % cumulative variance were obtained for the surface stations (Fig. 4.12). PC1 with 25.29 % of variance was loaded positively with Cd, Cu & Zn; negatively with salinity and this PC stood for the estuarine anthropogenic contribution during the season of high flow. PC2 which explained 19.66 % of the cumulative variance was characterised by positive loading of Mn, Fe and DO. This PC represented the oxidative precipitation of Fe and Mn. PC3 with 16.50 % of the total variance was loaded positively with Pb, SPM; negatively with temperature. This PC represented the adsorption of Pb by the particulates. Geochemical behaviour of particle reactive metals like Pb was strongly controlled by SPM (Balls, 1989; Vignati, 2004). PC4 was characterised by positive loading of Co & pH. PC4 explained 15.31 % of the total variance. PC5 with 11.46 % of variance was positively loaded with Ni. In the bottom, 4 principal components were extracted with 78.15 % cumulative variance (Fig. 4.13). PC1 was characterised with high positive loadings of Co, Fe & Mn and this component explained 26.86 % of the variance. This gave indication of the scavenging of Co by the Fe-Mn oxyhydroxides. PC2 which explained 18.43 % of total variance was characterised by positive loadings of Cd, pH, DO, SPM and negative loading of temperature. PC3 was loaded positively with Cd, Pb and Zn and explained 18.17 % of cumulative variance. This PC can be considered as the anthropogenic component. PC4 which accounted for 14.69 % of cumulative variance was loaded positively with salinity and SPM; negatively with Ni and DO.

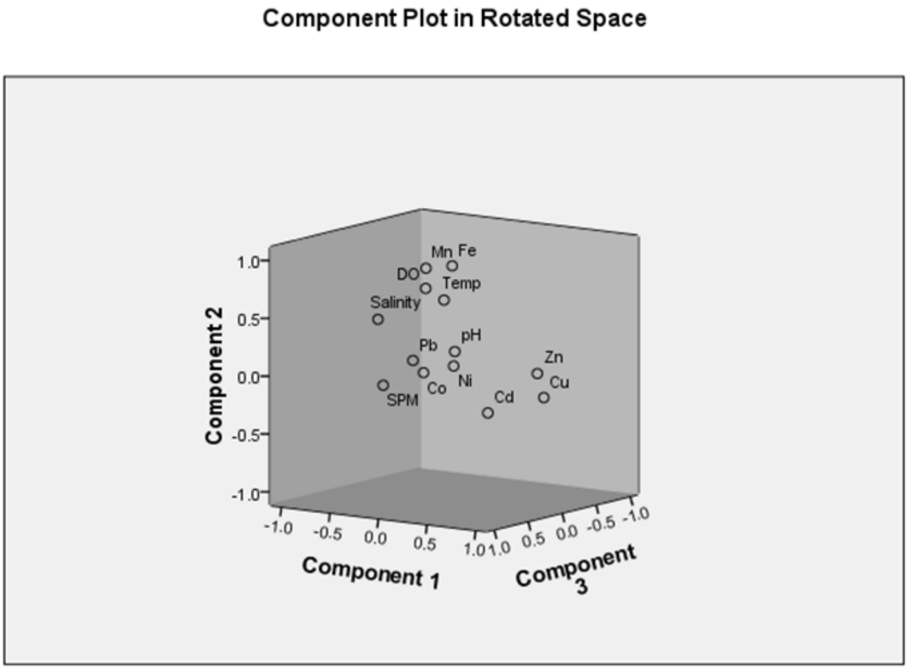

Figure 4.12 Ordination plot of principal components of coastal surface waters during monsoon

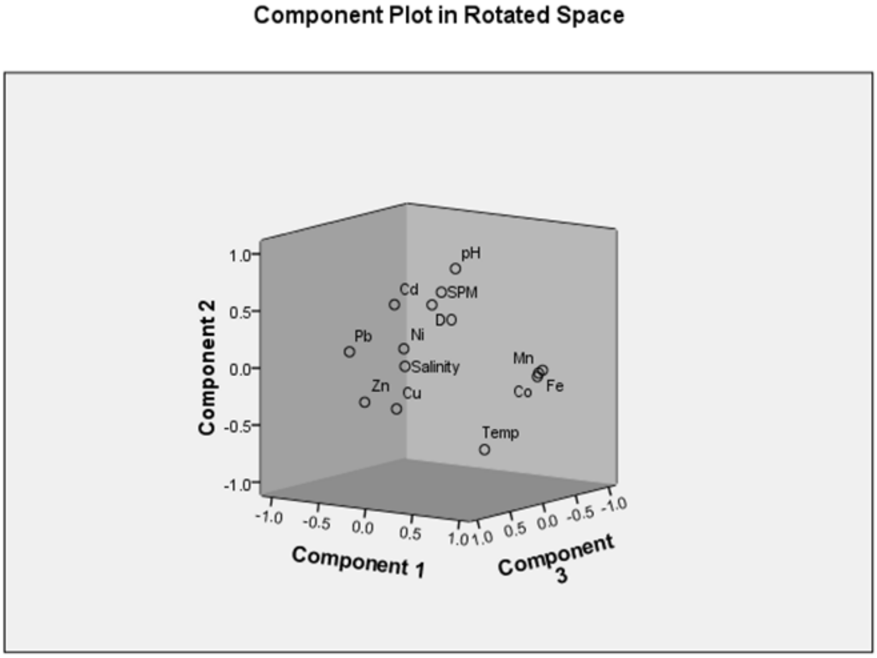

Figure 4.13 Ordination plot of principal components of coastal bottom waters during monsoon

During Post-M, five principal components were obtained for the surface (Fig. 4.14) and bottom (Fig. 4.15) stations which explained 87.07 and 84.78 % cumulative variance respectively. Cu, Zn, Fe & SPM were loaded positively in PC1 in the surface which explained 24.44 % of total variance. This component represented the scavenging of Zn and Cu by the hydrous Fe oxides and adhesion to SPM. PC2 with 18.05 % of variance was characterised with positive loading of Pb, Ni and pH. PC3 which explained 17.70 % of the cumulative variance was loaded positively with Cr, SPM; negatively with Co and Mn. PC4 which explained 15.99 % of total variance was characterised with positive loading of salinity and negative loading of temperature. PC5 was characterised by positive and negative loading of Cd and DO respectively. This component explained 10.90 % of the cumulative variance.

PC1 in the bottom waters was loaded positively with Cd, Ni, Mn & temperature; negatively with DO. PC1 explained 21.09 % of the cumulative variance. PC2 which accounted for 19.28 % of variance was characterised by positive loading of Ni and Co; negative loading of Cu and Zn. PC3 was characterised with high positive loadings of Cr & Fe and this component explained 17.26 % of total variance. PC4 which accounted for 13.98 % of the total variance was loaded positively with Pb and pH. PC5 was characterised with positive loading SPM only and this PC accounted for 13.17 % of the cumulative variance.

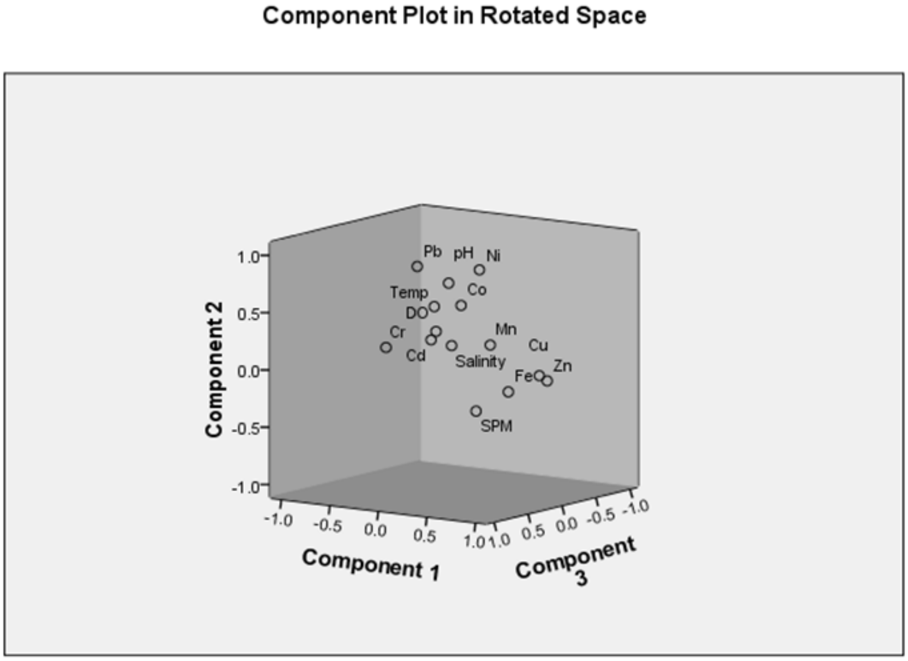

Figure 4.14 Ordination plot of principal components of coastal surface waters during post-monsoon

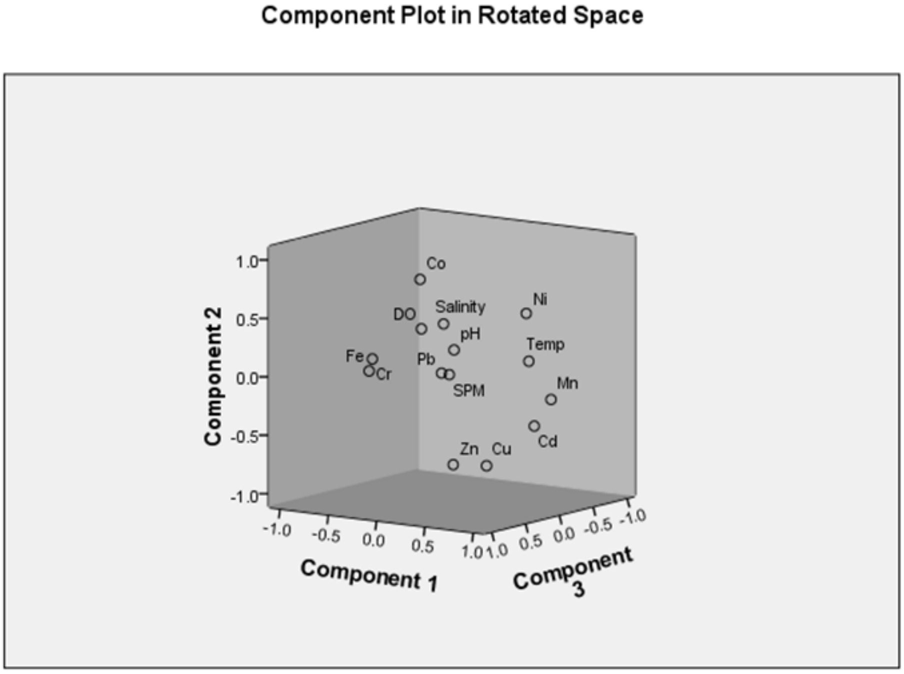

Figure 4.15 Ordination plot of principal components of coastal bottom waters during post-monsoon

In the estuarine surface, all the PCs were associated with almost comparable percentage of variance during Pre-M. While during Mon, PC1 which represented anthropogenic component was dominated. During Post-M, oxidative precipitation of Mn (PC1) and anthropogenic addition of Cd, Pb and Zn (PC2) were the dominating processes. In the estuarine bottom waters, PC1 during Pre-M and Mon which represented the anthropogenic additions were the leading processes. However during Post-M season, dominating processes were competitive adsorption of Cu over Co on to SPM (PC1) and the anthropogenic components influenced by Zn and Cd inputs (PC2).

In coastal surface waters PC1, which stood for anthropogenic addition of Zn was dominated during Mon and Post-M seasons. pH induced precipitation of Mn, Fe and Cu was dominated during Pre-M season. In the bottom, PC1 which represented the competitive adsorption of Co over Cd, Cr and Ni on to the suspended particulate matter, was the dominating process. During Mon season, scavenging of Co by the Fe-Mn oxy-hydroxides dominated other processes. Oxidative precipitation of Mn along with the scavenging of Ni and Cd dominated during Post-M season.

Although the first PCs have higher percentage of variance compared to rest of the PCs, they are low when compared to the cumulative variance. From this, it could be understood that there were no major processes dominating in the system.

4.2.1.4 Cluster Analysis

In the estuary, 2 and 3 major clusters were obtained in the surface and bottom respectively during Pre-M. It can be understood from the dendrogram that the clusters formed in the surface were mainly based on the differences in the distribution of Fe (Fig. 4.16). First major cluster was again sub divided in to two sub clusters; first sub cluster was constituted by stations with lowest Fe content and second cluster formed by stations having moderate Fe content.

Stations E1, E2, E5, E9, E12, E14, E15 and E16 constituted a cluster in the first sub cluster. Similarity in Fe distribution brought these stations together in a cluster. Fe was below the detectable level in all these stations except E14 (31.34 nM/L). Stations, E3 and E4 exhibited similar distribution for Fe and Zn; higher salinity and SPM, which brought them together in a cluster. Station E8 formed a simplicifolious cluster with the highest levels of Ni and Zn among the estuarine stations and moderate levels of Fe and SPM. E10, E11 and E13 were brought together in a sub cluster based on the comparable level of Zn and moderate levels of Fe compared to other estuarine stations. Station E6 formed a simplicifolious cluster based on higher level of Fe. Station E7 formed the second simplicifolious major cluster with the highest concentration of Fe observed in the estuary.

In the bottom, first major cluster was branched in to two sub clusters which again showed further branching (Fig. 4.16). Higher levels of salinity and lower Fe content brought stations E3, E4, E14 and E15 together in a cluster. Stations E4, E14 and E15 were clustered together based on the similarity in salinity. Station E3 showed similarity to the above sub cluster based on salinity distribution and the highest salinity reported was for this station (bar mouth). E12 formed a simplicifolious sub cluster with highest level of SPM, higher level of Zn and lower level of Fe. Stations E10, E11 and E13 brought together in a cluster based on the moderate levels of Fe compared to other estuarine stations. Similarity in the distribution of Zn, Mn, Fe, pH and SPM brought stations E5 and E16 together in a sub cluster. Similar levels of Fe, Cr and higher levels of Zn compared to other estuarine station brought E1 and E9 together. Second major cluster formed by station E2 was characterised by highest levels of Zn, Cd, DO and lowest level of Cr, salinity and SPM. As reported in earlier works (Sankaranarayanan *et al.,* 1978; Paul and Pillai, 1983a; Nair *et al.,* 1990; Ouseph, 1992; Shibu *et al.,* 1990; Shibu *et al.,* 1995; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; SCMC, 2004; Martin *et al.,* 2008; Deepulal *et al.,* 2012), this area may be receiving high amounts of Zn and Cd from the industrial belt of Cochin. Third major cluster formed by stations E6, E7 and E8 were characterised by higher levels of Fe compared to other estuarine stations. E6 was found to be with highest level of Fe (1911.54 nM/L).

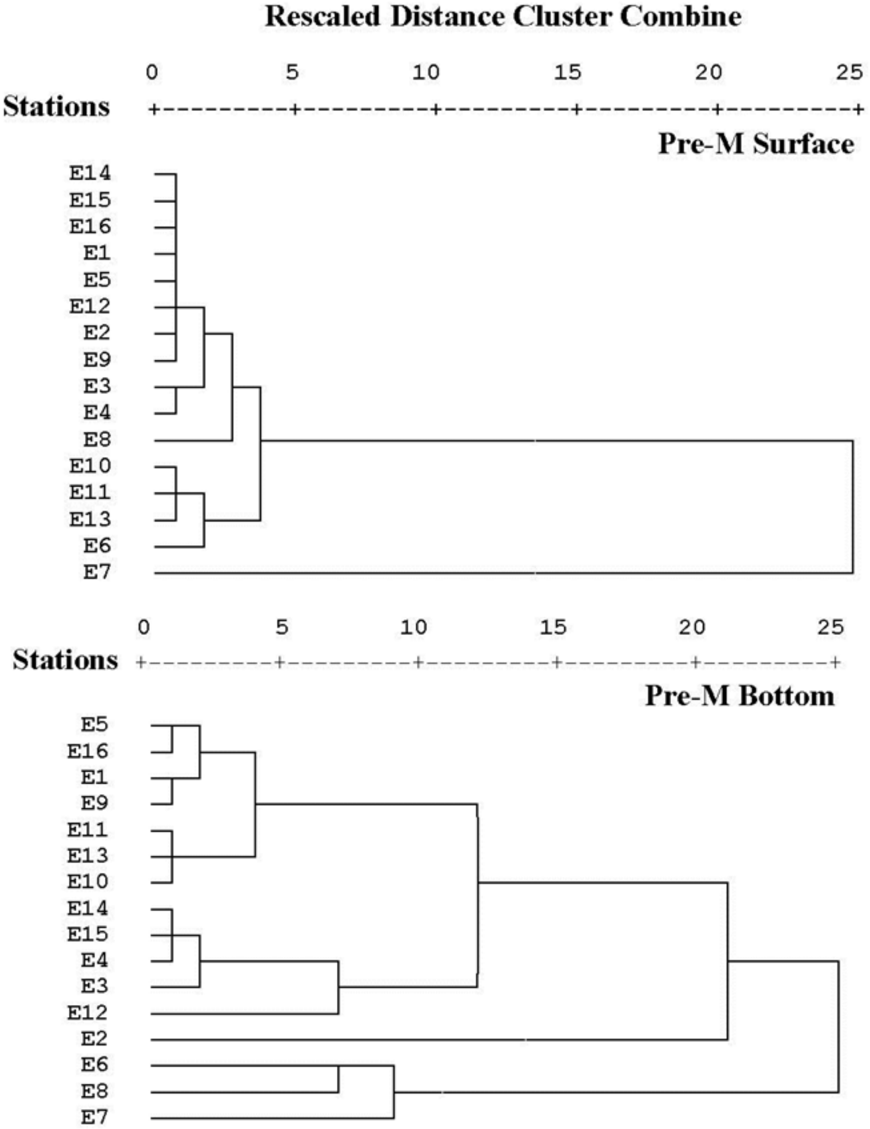

Figure 4.16 Dendrogram showing clusters of sampling locations in the estuary during pre-monsoon

Three major clusters of sampling stations were obtained in the surface during Mon season (Fig. 4.17). First major cluster was again split in to two sub clusters of which the first one showed further branching. Moderate and lower levels of SPM and salinity respectively grouped stations E10, E14, E15 and E16 together in a cluster. Stations, E7 and E8 were associated with lowest SPM content which made them cluster together. Lower SPM and higher salinity content in stations E3, E4, E5 and E13 made them cluster together. Highest Mn content and salinity made station E6 stood alone in a sub cluster. Stations E1 and E11 was characterised by similar levels of Fe, DO; lower levels of salinity and moderate levels of Zn compared to other stations. E12 and E9 formed the second major cluster and were characterised with higher level of SPM and lower level of DO compared to rest of the stations. Third major cluster formed by station E2 was characterised by highest levels of Cu, Zn and Fe.

Two major clusters were obtained in the bottom during Mon season (Fig. 4.17). First major cluster was again divided in to two sub clusters based on the SPM distribution. First sub cluster formed by stations E10, E12, E14 and E16 were associated with higher SPM content. E9 was detected with highest SPM content during this season. Second sub cluster constituted by stations E2, E6, E8, E11, E13 and E15 were associated with lower salinity and SPM levels. E1 was associated with highest Ni and moderately higher Zn content. Stations E3, E4 and E7 were clustered together based on higher salinity distribution. Highest levels of Zn, Mn, Fe, DO and pH compared to other estuarine stations made E5 stood alone in a cluster.

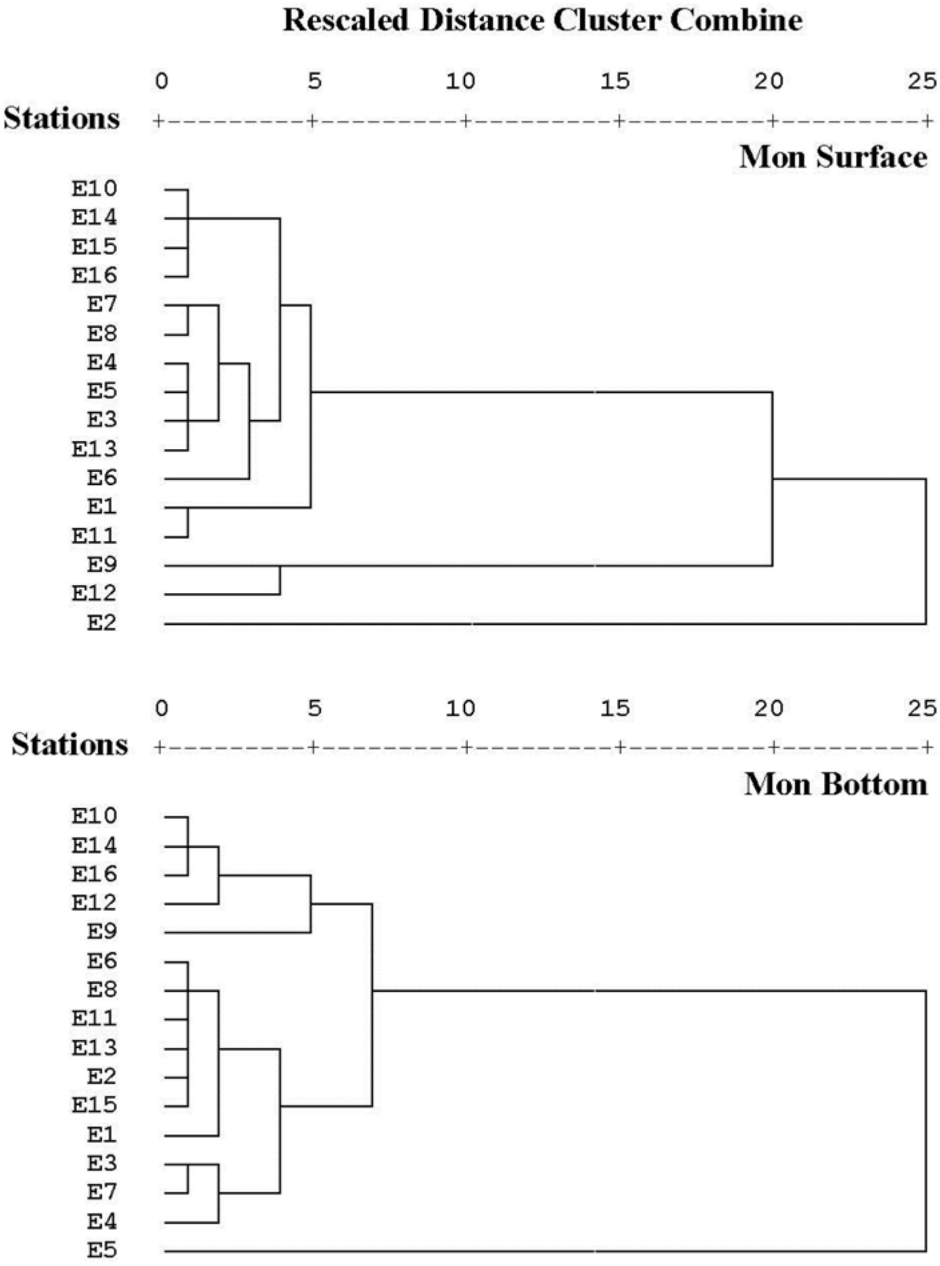

Figure 4.17 Dendrogram showing clusters of sampling locations in the estuary during monsoon

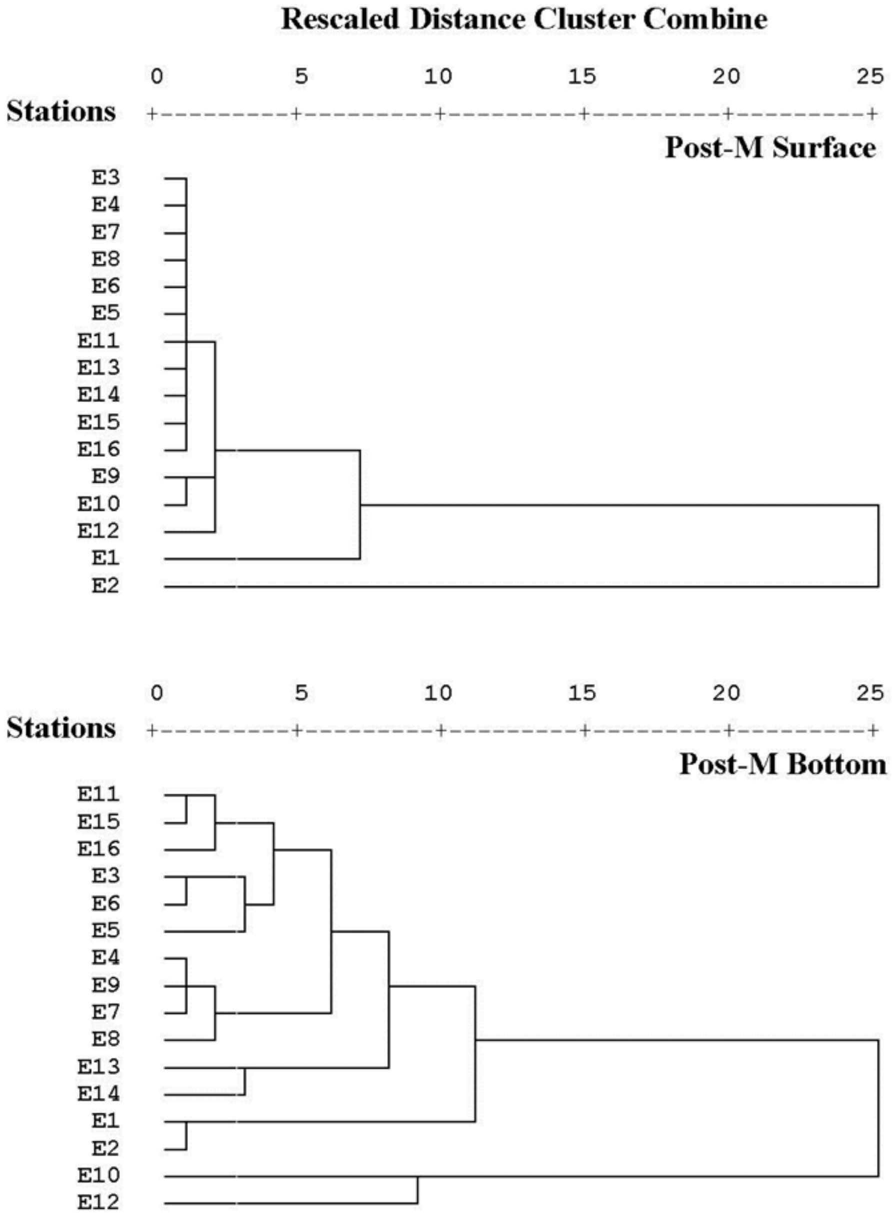

Figure 4.18 Dendrogram showing clusters of sampling locations in the estuary during post-monsoon

During Post-M season, 2 major clusters were obtained for the surface sampling stations (Fig. 4.18). First major cluster was again sub clustered in to 4 sub clusters. Sub cluster formed by stations E3-E8, E11 and E13-E16 were characterised by comparably higher Co content compared to rest of the stations. Stations E9 and E10 clustered together based on the higher Fe and moderately higher SPM content. E12 was characterised with highest Fe content. Simplicifolious cluster formed by E1 was characterised with higher levels of Cd and Zn. Second major cluster formed by station E2 was characterised with highest levels of Cd, Pb, Zn and lowest salinity among the entire stations. This suggested the inflow of fresh water containing industrial effluents along with the above said metals in to the estuary from the northern industrial catchment of Kochi (Sankaranarayanan *et al.,* 1978; Paul and Pillai, 1983a; Nair *et al.,* 1990; Ouseph, 1992; Shibu *et al.,* 1990; Shibu *et al.,* 1995; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; SCMC, 2004; Martin *et al.,* 2008; Deepulal *et al.,* 2012; Bindu *et al.,* 2015).

During Post-M season, 2 major clusters of sampling stations were obtained in the bottom (Fig. 4.18). First major cluster was again divided in to five sub clusters. Comparable levels of Ni, SPM and lower salinity content clustered stations E11, E15 and E16 together. Comparable levels of Ni, Co and Cu clustered stations E3 and E6 together, similarity in distribution of Cu and salinity brought E5 to the above cluster. Higher salinity, comparable levels of Co, DO and lower SPM content grouped stations E4, E7, E8 and E9 together in a sub cluster. Higher levels of Ni, Cu and Fe clustered stations E13 and E14 together. Sub cluster formed by stations E1 and E2 were characterised by highest Zn, higher Cd and Pb content and comparably lower salinity and SPM levels. Moderate levels of Pb, Ni, Cu, Mn, salinity and higher SPM content made E10 form a simplicifolious sub cluster in second major cluster. Station

E12, which was characterised by lowest salinity and highest SPM content formed the simplicifolious second sub cluster.

In the coast, two major clusters of stations were obtained in the surface during Pre-M (Fig. 4.19). Simplicifolious cluster formed by station C6 was characterised by highest level of Zn, DO and lowest Mn content compared to other coastal stations. In the bottom also two major clusters were obtained from cluster analysis (Fig. 4.19). First major cluster was again divided in to two sub clusters. Higher SPM compared to other stations brought stations C1, C2, C3 and C11 together in the first sub cluster. Second sub cluster formed by stations C6 - C10 was based on comparably higher Cd, Cr and Ni contents. Second major cluster formed by station C4 was based on the highest Cu and Zn contents.

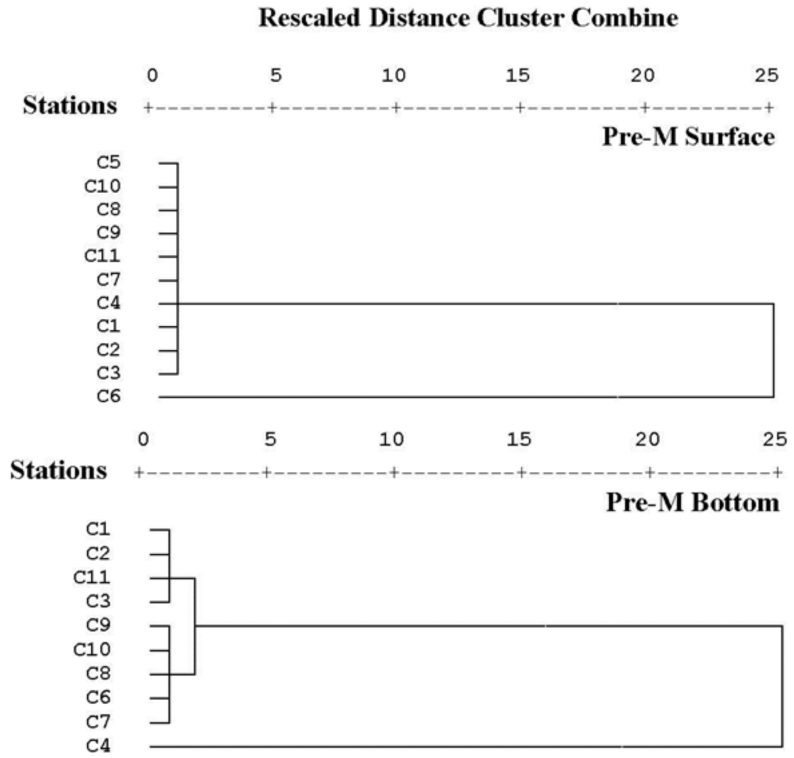

Figure 4.19 Dendrogram showing clusters of sampling locations in the coast during pre-monsoon

During Mon season, two major clusters were obtained in the surface (Fig. 4.20). First major cluster was again divided in to two sub clusters. Stations C2, C4, C5, C6, C7, C9, C10 and C11constituted first sub cluster and was characterised by higher salinity, Fe and lower Zn compared to other stations. Second sub cluster formed by stations C1 and C3 was characterised by higher levels of Zn, Cu and lower levels of Fe and salinity compared to other stations. Second major cluster was a simplicifolious cluster formed by C8 with highest content of Mn, Fe and DO among the coastal stations.

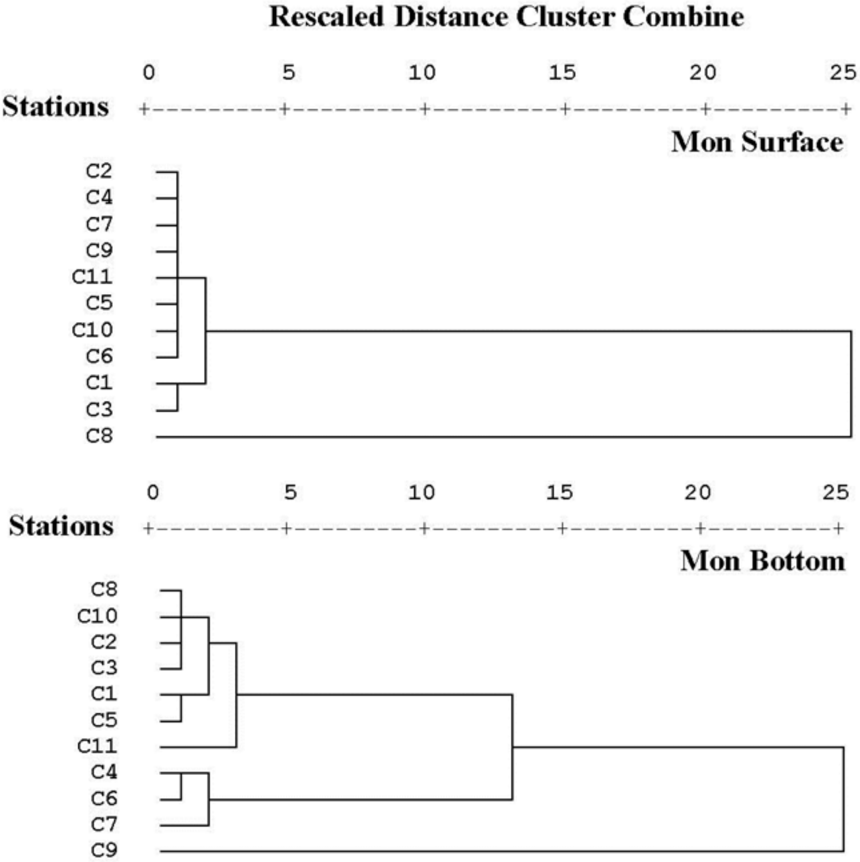

Figure 4.20 Dendrogram showing clusters of sampling locations in the coast during monsoon

In the bottom, two major clusters of sampling stations were obtained during Mon season (Fig. 4.20). First major cluster was again sub clustered in to two; of which first one showed further branching. C1 and C5 were clustered together based on similar distribution of Pb, Cu, Mn, DO, salinity and SPM. Cluster formed by C11 was characterised with highest Cu and Zn contents. Second sub cluster was constituted by coastal stations C4, C6 and C7 which might be based on similar levels of Cu, Mn, salinity and higher level of SPM compared to other stations. Second major cluster formed by station C9 was a simplicifolious sub cluster and was characterised by highest levels of Co, Mn and Fe. Cluster formed by stations C2, C3, C8 and C10 was characterised by comparatively lower Fe and Mn contents and lower SPM.

During Post-M season, two major clusters of sampling stations were obtained in the surface (Fig. 4.21). First major cluster was again branched. Higher levels of Co and lower SPM content brought stations C6, C7 and C9 together in a cluster. Similarity in Mn distribution and highest DO contents made C10 cluster together with the above stations. Simplicifolious cluster formed by C11 might be based on the lowest SPM content among the stations. Lowest Cd and lowest salinity content made C4 stood alone in a sub cluster. Cluster formed by C8 was characterised with highest Ni and Pb content compared to rest of the stations. Station C2 formed a simplicifolious sub cluster based on the Ni concentration which was below the detectable level in this station. Second major cluster was again branched in to two sub clusters and it was mainly based on the Fe distribution. Cluster formed by C1 was based on the highest concentrations of Cu, Zn, Fe and salinity. Cluster formed by C3 and C5 was characterised with comparably higher Fe, Ni and SPM contents.

In the bottom, three major clusters of sampling stations were obtained (Fig. 4.21). First major cluster was again divided in to 3 sub clusters. Comparable SPM levels grouped stations C1-C4 and C6 in to first sub cluster.

Station C7 formed a simplicifolious sub cluster based on the highest Ni and moderately higher SPM content among other stations. Third sub cluster formed by stations, C9, C10 and C11 was characterised by low SPM and high salinity. Highest Co and SPM contents made station C8 form the second major cluster. Station C5 formed the third major cluster based on highest Cr and Fe contents. Cr was not in detectable range in rest of the stations.

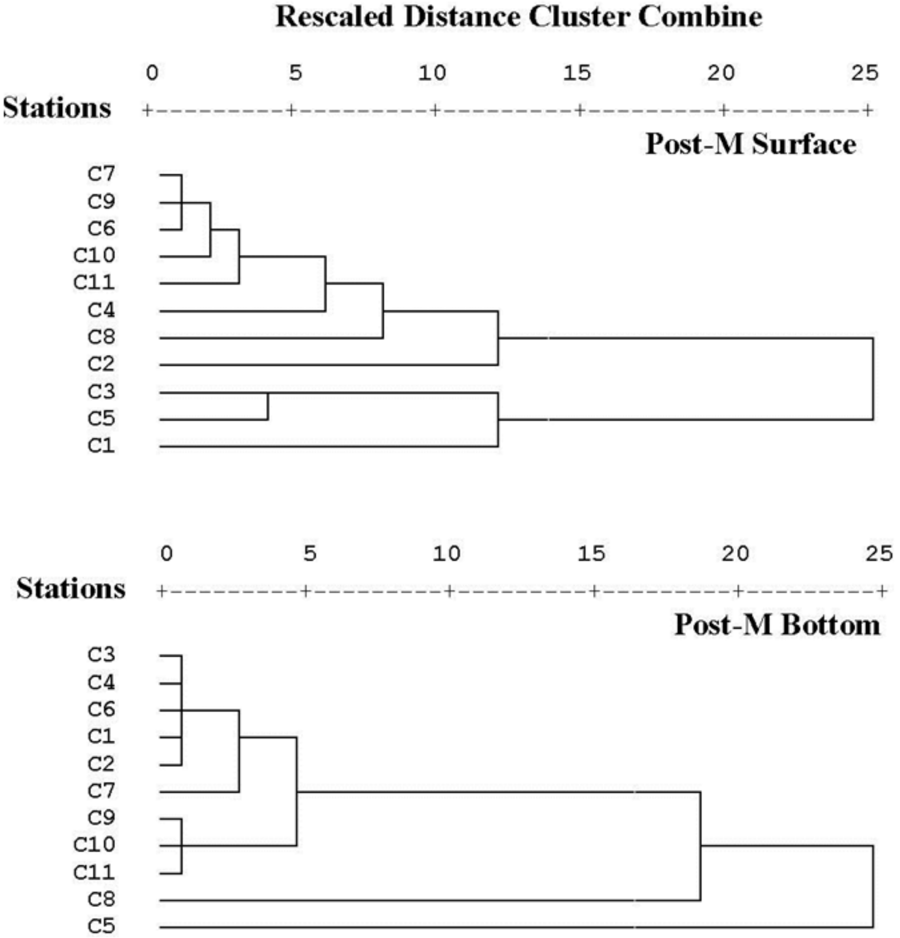

Figure 4.21 Dendrogram showing clusters of sampling locations in the coast during post-monsoon

4.2.2 Metal Distribution in Particulate Matter

Concentrations of the particulate metals (average ± standard deviation) analysed are given in appendix 17 to 22.

Cadmium

Annual average of Cd in the estuary was 0.11 ± 0.21 µM/g in the surface particulates and 0.22 ± 1.04 µM/g in the bottom particulates. Estuarine station E2 was associated with highest particulate Cd concentrations; 0.98 µM/g in the surface during Post-M and 7.23 µM/g in the bottom during Pre-M. In the coast, annual average of Cd shown by the surface and bottom particulates were 0.10 ± 0.18 µM/g and 0.06 ± 0.08 µM/g respectively. Highest Cd concentrations were found in the particulates of stations C3 (0.81 µM/g) in the surface during Mon and C9 (0.33 µM/g) in the bottom during Pre-M.

Cd was detected in more bottom stations compared to the surface stations; especially during the Mon and Post-M seasons (Fig. 4.22). No significant depth variation in Cd concentration was also observed during the entire study period.

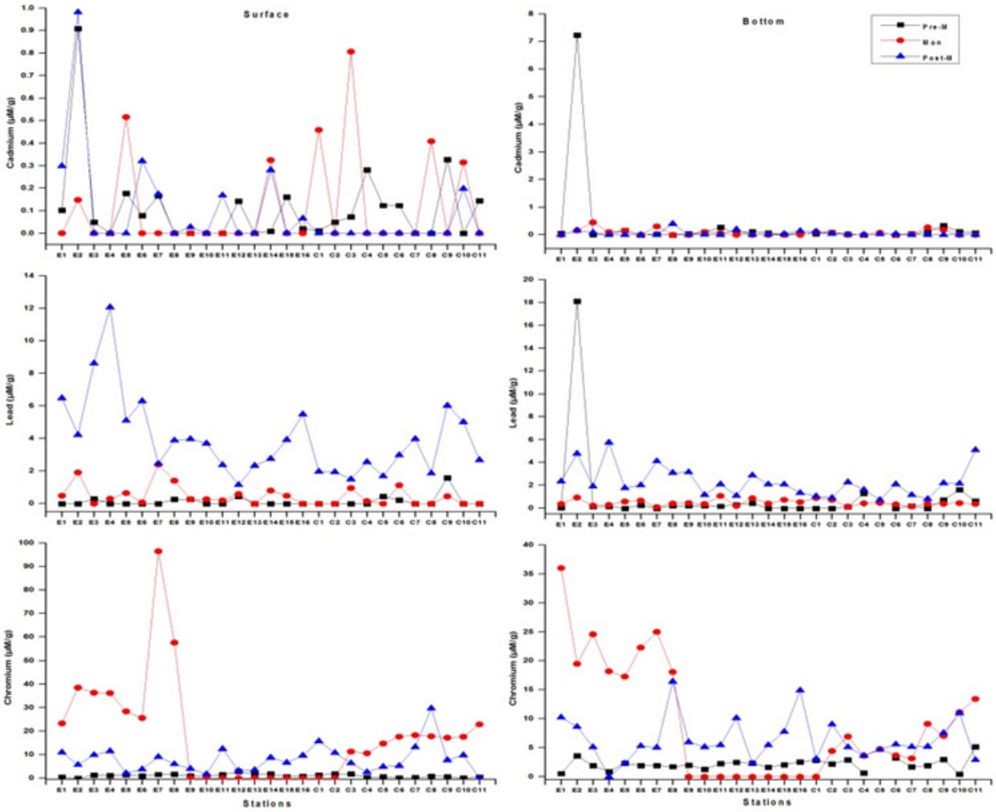

Figure 4.22 Spatial and temporal distribution of particulate Cd, Pb and Cr

Lead

In the estuary, Pb in the surface particulates showed an annual average of 1.79 ± 2.62 µM/g and in the bottom particulates, the annual average was 1.47 ± 2.79 µM/g. Highest Pb content in the surface particulates was recorded in E4 (12.07 µM/g) during Post-M and that in the bottom particulates was in E2 (18.10 µM/g) during Pre-M. Annual average of Cd in the coastal particulate was 1.13 ± 1.58 µM/g in the surface and 0.93 ± 1.03 µM/g in the bottom. Maximum Pb content was associated with stations C9 in the surface (6.33 µM/g) and C11 in the bottom (5.10 µM/g) during Post-M season.

Surface-bottom profile was very significant (99% level) during Post-M season indicating stratification during Post-M in the estuary (Fig. 4.22). Compared to the previous studies in Cochin estuary (Babukutty and Chacko, 1995), the concentrations of particulate Pb observed in the present study was higher. Resuspension of lead rich sediments, long range transport of lead-rich SPM and diffuse but enhanced atmospheric inputs of Pb were considered to have contributed to the elevated concentration of Pb observed in the estuary. The comparatively higher concentrations of particulate Pb during Mon season have been explained as partially due to the riverine input of lead rich SPM and partially due to the resuspension of lead-rich fine bottom sediments under the high flow conditions during Mon season (Unnikrishnan and Nair, 2004). Although not highly significant, there was a trend in the depth profile of Pb; Mon was associated with more particulate Pb in the bottom stations and Post-M in the surface stations.

Chromium

Chromium showed an annual average of 9.81 ± 17.91 µM/g in the surface estuarine particulates and 6.73 ± 8.39 µM/g in the bottom estuarine particulates. Highest concentration detected was in E7 (96.48 µM/g) in the surface and E1 (36.02 µM/g) in the bottom during Mon season. Depth profile was significant (99% level) in Pre-M season only; bottom samples were associated with higher values for Cr except in stations E2, E4, E12 and E14.

In the coastal particulate matter, Cr showed an annual average of 7.96 ± 8.19 µM/g in the surface and 4.83 ± 3.20 µM/g in the bottom. Maximum concentrations detected was in C8 (29.71 µM/g) in the surface during Post-M and in C11 (13.44 µM/g) in the bottom during Mon season. Mon season was lying in the higher sides for Cr followed by Post-M and Pre-M seasons (Fig. 4.22). During Mon season, coastal stations were associated with higher Cr content than the southern estuarine stations.

Variation in depth profile of Cr during Pre-M and Mon showed 99% significance. Pre-M season was found to be with high Cr content in bottom stations compared to surface. Cr was found to be high in surface stations during Mon except in the stations north of the bar mouth. Station C1 particulates were found not loaded with Cr in both surface and bottom. In station C2, Cr was detected only in the bottom stations. During Post-M, majority of the stations showed high Cr contents in the surface and stations C4, C6, C10 and C11 showed higher values in bottom.

Nickel

In the estuarine SPM, Ni showed annual averages of 0.92 ± 1.78 µM/g in the surface and 1.19 ± 1.67 µM/g in the bottom. Highest value was detected in E11 in the surface (8.26 µM/g) and E12 in the bottom (7.24 µM/g) during Post-M season. No significant depth profile was observed in any of the seasons. In the coast, respective annual average of Ni was 1.25 ± 2.15 µM/g in the surface particulate samples and 0.91 ± 1.09 µM/g in the bottom samples. Maximum concentration found was 8.52 µM/g (C6) in the surface and 4.19 µM/g (C3) in the bottom during Post-M season. Pre-M season showed a distinct variation in the surface-bottom distribution of Ni compared to other seasons (Fig.4.23).

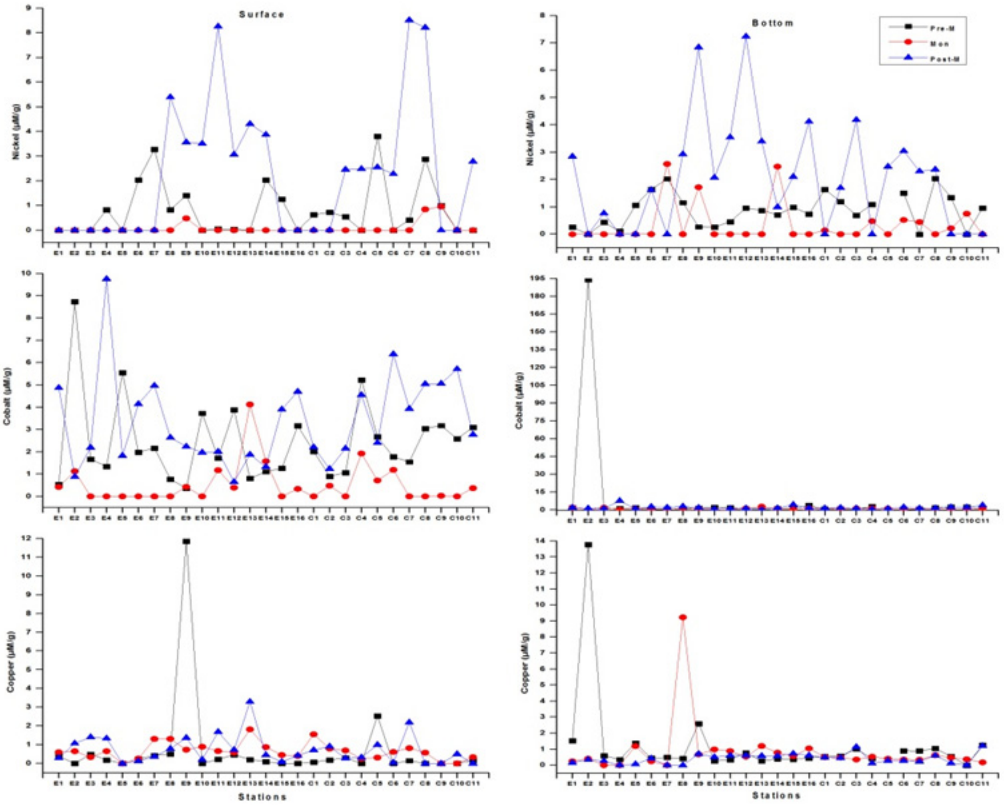

Figure 4.23 Spatial and temporal distribution of particulate Ni, Co and Cu

Cobalt

In the estuary, Co showed an annual average of 2.05 ± 2.17 µM/g in the surface and 5.41 ± 27.84 µM/g in the bottom particulate samples. Highest Co content found in the surface and bottom particulates were 9.76 µM/g (E4 during Post-M) and 194.08 µM/g (E2 during Pre-M) respectively. Depth profile was highly significant only during the Post-M season. Bottom sample in the station E2 was showing abnormally high values of Co (Fig.4.23). Higher values in the northern estuary which can be attributed to the influence of the industrial area of Cochin has been reported earlier.

Cobalt in the coastal particulates showed annual averages of 2.22 ± 1.85 µM/g in the surface particulates and 1.23 ± 0.88 µM/g in the bottom particulates. Highest concentrations found in the surface and bottom particulates were in C6 (6.39 µM/g) and C11 (3.86 µM/g) respectively during Post-M. Pre-M (p value – 0.001) and Post-M (p value – 0.004) seasons showed significant surface-bottom variations in the concentration of Co. Surface particulates were found to be having more cobalt compared to the bottom particulates in both the seasons.

Copper

Annual average of particulate Cu in the estuary was 0.84 ± 1.73 µM/g in the surface and 1.01 ± 2.31 µM/g in the bottom. Highest concentration of Cu was detected in stations E9 (11.85 µM/g) in the surface and E2 (13.77 µM/g) in the bottom during Pre-M (Fig. 4.23). Depth profile was significant (95% level) only during the Post-M season. Cu in the coastal particulate matter, showed an annual average of 0.47 ± 0.62 µM/g in the surface and 0.52 ± 0.34 µM/g in the bottom. Maximum concentrations of Cu in the surface and bottom particulates were 2.53 µM/g in C11 and 1.26 µM/g in C5 respectively during Pre-M season. In the coast, 99 % significant spatial variation in surface-bottom distribution of Cu was observed during Pre-M season and bottom particulates were found to be having more Cu compared to surface particulate matter.

Zinc

Annual average shown by the estuarine surface and bottom particulate Zn were 4.56 ± 11.62 µM/g in the surface and 7.18 ± 28.83 µM/g in the bottom particulates. Maximum particulate Zn concentrations found in the surface was in E4 (68.59 µM/g) during Post-M and that in the bottom was in

E2 (201.67 µM/g) during Pre-M. Surface to depth distribution was not significant in the case of Zn. Pre-M season was associated with lowest Zn content in the estuary (Fig. 4.24).

Zinc in the coastal particulates showed an annual average of 1.22 ± 1.85 µM/g in the surface and 3.02 ± 7.85 µM/g in the bottom particulates. Highest Zn content detected in C11 in the surface (8.92 µM/g) and C4 in the bottom (45.83 µM/g) during Pre-M season. Stations near the bar mouth exhibited higher concentrations irrespective of the seasons indicating a heavy estuarine input of Zinc to the coastal environment.

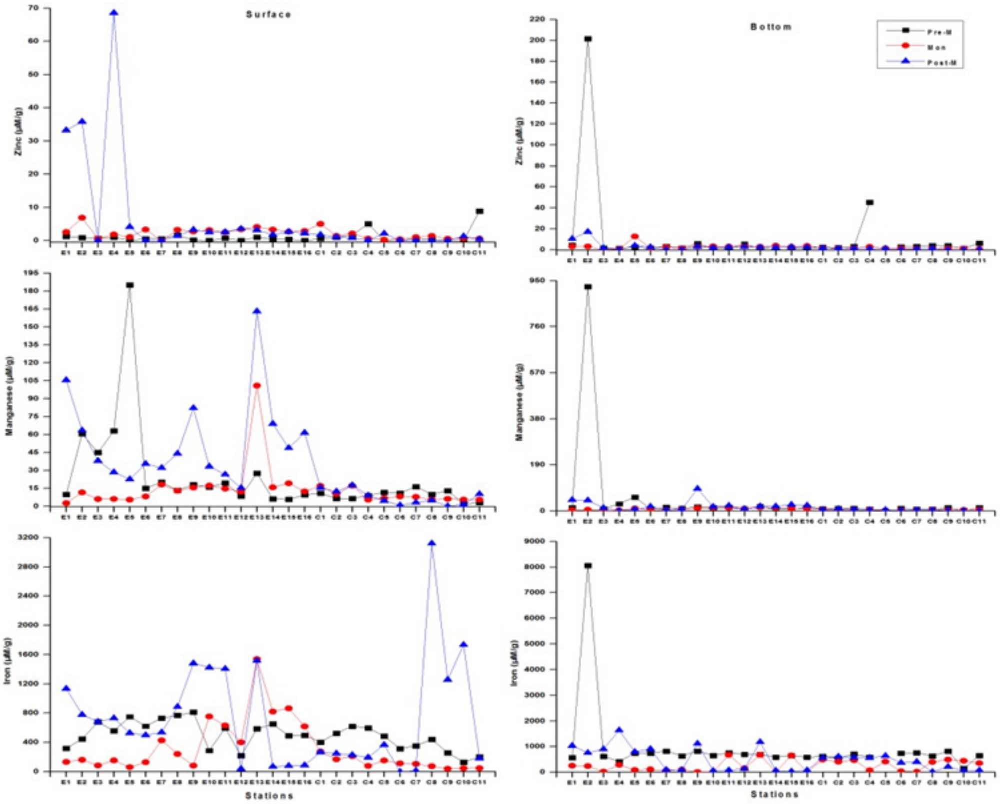

Figure 4.24 Spatial and temporal distribution of particulate Zn, Mn and Fe

Manganese

Particulate Mn in the estuary, showed an annual average of 34.85 ± 38.51 µM/g in the surface and 34.90 ± 132.15 µM/g in the bottom. Highest Mn concentrations were detected in stations E5 (185.06 µM/g) in the surface and E2 (924.91 µM/g) in the bottom during Pre-M. Significant variation in surface to bottom distribution was observed only in the Post-M season. In the coastal SPM, Mn showed an annual average of 8.33 ± 4.89 µM/g in the surface and 5.60 ± 3.57 µM/g in the bottom. Stations C3 (17.56 µM/g) in the surface during Post-M and C9 (14.21 µM/g) in the bottom during Pre-M were the stations detected with highest particulate Mn concentrations in the estuary. Significant variations were observed during Mon (99%) and Post-M (95%) in the surface to bottom distribution of Mn.

Particulate Mn content was lower in the coastal particulates compared to the estuary (Fig. 4.24). Coastal stations near the bar mouth were having more Mn concentrations compared to others during Mon and Post-M whereas during Pre-M, all the stations were more or less similar in Mn distribution except in station C9 which showed very lesser values compared to other stations. Surface particulates were found to be having more Mn in the Mon season which may be contributed by the increased run off during this season.

Iron

Iron in the estuarine particulates showed an annual average of 584.14 ± 409.58 µM/g in the surface and 633.70 ± 1161.59 µM/g in the bottom. Highest Mn concentrations recorded in the surface ad bottom particulate samples was 1538.65 µM/g in E13 during Mon and 8058.02 µM/g in E2 during Pre-M. Surface-bottom variation in the distribution of Fe was prominent during Mon (95% level). In the coast, particulate Fe showed annual average of 402.12 ±

601.47 µM/g in the surface and 435.60 ± 238.93 % in the bottom. In the surface, station C8 (3122.48 µM/g) during Post-M and in the bottom, C9 (816.80 µM/g) during Pre-M was detected with maximum particulate Fe concentrations.

Regarding the surface-bottom distribution, Pre-M and Mon seasons showed significant variations at 99% level. Bottom samples were observed to be with more Fe compared to the surface in both the seasons and this difference was more prominent during the Mon period (Fig. 4.24).

Bottom particulate in the station E2 showed abnormally high values of all the metals except Ni compared to other samples during Pre-M season. Compared to other stations, SPM was low in this station. Such a trend may be explained by the fact that when SPM concentrations are low, the particles tend to be of fine size with high surface area and be enriched in heavy metals (Balls, 1989; Turner *et al.,* 1992; Smith and Flegal, 1993; Benoit *et al.,* 1994). Similar inverse relationships have also been reported in many laboratory-based studies (Li *et al.,* 1984; Balistrieri and Murray, 1986; Higgo and Rees, 1986; Turner, 1996).

4.2.2.1 Spatial and Temporal Variations of Particulate Metals

Two-way ANOVA without replication was performed to examine the spatial and temporal variations in the distribution of particulate metals under study (Table 4.16).

Cd lacked significant temporal variability in its distribution in the entire study area. Still, Cd was distributed along the entire study area in the Pre-M season compared to other seasons; in these seasons, most of the stations were found to be below detectable level. Pb showed significant temporal variation both in the surface and bottom SPM in the coast, whereas, temporal variation was significant only in the estuarine surface particulates. Post-M season was found to be associated with more particulate lead concentration followed by Mon and Pre-M seasons. During the still periods (Post-M), particulate matter is constituted of fine particles and particle active metals like Pb is preferably found in association with these fine particles (Balls, 1989; Zhang *et al.,* 2002). Decrease during Pre-M can be attributed to the salinity induced desorption from the particulates (Bourg, 1987; Comber *et al.,* 1995).

Significant temporal variations (99% level) were observed for Cr both in the surface and bottom estuarine particulates. Seasonal variations significant at 99 and 95% levels were observed for Cr in the surface and bottom coastal particulate samples respectively. In the estuary, significant temporal variations (99% level) were observed for Ni both in the surface and bottom particulates. In contrast to the bottom coastal particulates, surface samples showed significant temporal variation of nickel. Post-M season was found to be associated with highest Ni content followed by Pre-M and Mon seasons. In the estuary, Co showed highly significant temporal variation (99% level) in the surface particulates and temporal variations were not significant in the bottom particulates. Temporal variations significant at 99 and 95 % levels were observed for Co in the surface and bottom coastal particulate samples respectively. Post-M season was found to be associated with highest Co content, followed by Pre-M and Mon seasons. Zn showed highly significant temporal variation (95% level) in the estuarine surface particulates only and temporal variations were not significant in the bottom particulates and in the coast. Mn showed highly significant temporal variation (95% level) in the estuarine surface particulates and in the coastal bottom samples (99% level) only. In the estuary, Post-M season was associated with higher Mn content, while in the coast, Pre-M season showed lowest Mn content. Temporal variations in the particulate Fe distribution were not significant in the estuary and Fe showed significant temporal variation (99% level) in the coastal bottom samples only. Cu lacked significant temporal variation in the entire study area. All the metals under study except Cd in the estuarine surface particulates were devoid of significant spatial variation in the study area.

Table 4.16 ANOVA Results of the particulate heavy metals in the Cochin Estuary and its adjacent coast

Estuary	Spatial (*df*=15)				Temporal (*df*=2)			
	Surface		Bottom		Surface		Bottom	
	F	P-value	F	P-value	F	P-value	F	P-value
Cd	3.51	0.002**	1.07	NS	1.14	NS	0.97	NS
Pb	0.78	NS	1.50	NS	35.31	0.000**	2.88	NS
Cr	1.08	NS	0.96	NS	6.90	0.003**	5.93	0.007**
Ni	0.89	NS	0.95	NS	5.90	0.007**	8.45	0.001**
Co	0.41	NS	0.97	NS	5.90	0.007**	0.99	NS
Cu	1.23	NS	0.82	NS	0.07	NS	0.95	NS
Zn	1.08	NS	1.24	NS	3.49	0.043*	0.94	NS
Mn	1.10	NS	1.06	NS	4.36	0.022*	1.09	NS
Fe	1.11	NS	1.09	NS	2.37	NS	2.82	NS
Coast	Spatial (*df*=10)				Temporal (*df*=2)			
Cd	0.62	NS	1.84	NS	2.05	NS	1.81	NS
Pb	1.69	NS	1.21	NS	38.21	0.000**	12.22	0.000**
Cr	0.75	NS	1.29	NS	10.59	0.000**	5.73	0.011*
Ni	1.48	NS	0.83	NS	5.68	0.011*	3.09	NS
Co	2.29	NS	0.41	NS	28.10	0.000**	5.09	0.017*
Cu	1.58	NS	1.99	NS	0.60	NS	3.14	NS
Zn	0.83	NS	1.13	NS	0.70	NS	2.36	NS
Mn	1.63	NS	1.10	NS	0.50	NS	12.68	0.000**
Fe	0.83	NS	0.86	NS	2.62	NS	6.27	0.009**

** Significant at the 0.01 level, * Significant at the 0.05 level, NS Not Significant

Significant seasonal variability in particulate concentrations could be explained in terms of change in SPM composition due to biological processes during summer months (Hatje *et al.,* 2001). When reduced river flows during Pre-M season increase the retention time of the upper estuary and higher temperatures increase the rate of bacterial activity / bioturbation (Collett, 1972; Aller, 1980; Griffiths, 1987; Webb and Metcalfe, 1987), the metal concentrations tend to be higher in the particulates. Due to the low fresh water discharge during Pre-M season and the processes of precipitation, adsorption and flocculation, the concentration of heavy metals in Cochin estuary were reported to be high compared to other seasons (Shibu, 1992). The river discharge is considerably reduced (2%) during Pre-M period, whereas during Post-M, the region receives approximately 12 % of the annual discharge (Srinivas *et al.,* 2003). Other physical disturbances like resuspension (Sanders, 1978; Duinker *et al.,* 1982; Byrd *et al.,* 1990) in the estuarine stations can also be operative in this season.

4.2.2.2 Correlation among the Particulate Metals and other Hydrographic Parameters

Pearson correlation analysis was performed to find out inter metallic relationships and the relationships of particulate metals with other hydrochemical parameters in the estuary (Tables 4.17 to 4.22) and coast (Tables 4.23 to 4.28).

Table 4.17 Pearson correlation matrix of particulate metals and hydrographic parameters in the surface waters of Cochin estuary during pre-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	-0.138	1												
Cr	-0.442	.522*	1											
Ni	-0.12	-0.141	0.133	1										
Co	.816**	-0.121	-0.222	-0.33	1									
Cu	-0.153	0.391	-0.087	0.188	-0.278	1								
Zn	0.098	-0.066	-0.193	0	-0.283	-0.227	1							
Mn	0.261	-0.164	-0.037	-0.264	.500*	-0.107	-0.168	1						
Fe	-0.204	0.015	0.062	0.469	-0.289	0.382	0.139	0.296	1					
Temp.	0.061	-0.147	-0.14	0.28	-0.062	-0.01	0.35	0.346	.556*	1				
pH	0.137	-0.084	-0.369	-0.42	0.002	-0.162	0.231	0.08	-0.435	-0.207	1			
DO	.577*	-0.07	-0.297	-0.396	.624**	-0.059	-0.044	0.18	-0.289	-0.182	0.063	1		
Salinity	-0.488	0.174	0.336	0.323	-.510*	-0.191	0.168	0.057	0.365	0.116	0.105	-.583*	1	
SPM	-0.496	-0.015	0.002	0.247	-.664**	-0.131	.591*	-0.282	0.289	0.2	0.05	-0.461	.677**	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.18 Pearson correlation matrix of particulate metals and hydrographic parameters in the bottom waters of Cochin estuary during pre-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	.999**	1												
Cr	.620*	.615*	1											
Ni	-0.365	-0.358	0.094	1										
Co	.999**	.999**	.614*	-0.362	1									
Cu	.981**	.981**	.590*	-0.395	.983**	1								
Zn	.999**	.999**	.614*	-0.356	.999**	.986**	1							
Mn	.999**	.998**	.615*	-0.358	.999**	.984**	.998**	1						
Fe	.998**	.998**	.636**	-0.328	.998**	.984**	.999**	.997**	1					
Temp.	0.245	0.264	-0.036	0.118	0.264	0.274	0.278	0.252	0.259	1				
pH	0.122	0.117	-0.388	-.550*	0.128	0.147	0.124	0.126	0.088	0.261	1			
DO	.791**	.795**	0.473	-0.381	.780**	.762**	.777**	.777**	.792**	0.016	-0.076	1		
Salinity	-.592*	-.592*	-.535*	0.18	-.583*	-.598*	-.584*	-.578*	-.601*	0.141	0.183	-.718**	1	
SPM	-0.431	-0.405	-0.252	0.445	-0.421	-0.453	-0.409	-0.428	-0.419	0.271	-0.201	-.498*	.549*	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.19 Pearson correlation matrix of particulate metals and hydrographic parameters in the surface waters of Cochin estuary during monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	0.168	1												
Cr	-0.013	.746**	1											
Ni	-0.111	-0.13	-0.207	1										
Co	0.036	-0.151	-0.345	-0.043	1									
Cu	-0.331	0.309	0.198	0.01	.611*	1								
Zn	-0.025	0.071	-0.365	-0.002	0.441	0.172	1							
Mn	-0.149	-0.163	-0.229	-0.022	.880**	.722**	0.253	1						
Fe	-0.129	-0.201	-0.438	-0.237	.731**	.594*	0.221	.811**	1					
Temp.	-0.085	0.122	0.004	-0.051	0.125	0.244	-0.006	0.216	0.204	1				
pH	.524*	0.14	0.351	-0.079	-0.252	-0.227	-0.237	-0.317	-.515*	0.168	1			
DO	.597*	0.161	0.228	-0.351	0.133	0.047	-0.003	0.044	0.006	-0.101	.623**	1		
Salinity	-0.221	-0.081	0.326	0.434	-0.381	-0.126	-0.25	-0.219	-.525*	-0.3	0.081	-0.285	1	
SPM	-0.131	-0.366	-.632**	.723**	-0.023	-0.193	0.162	-0.119	-0.079	-0.043	-0.299	-.585*	0.054	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.20 Pearson correlation matrix of particulate metals and hydrographic parameters in the bottom waters of Cochin estuary during monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	-0.334	1												
Cr	0.461	-0.306	1											
Ni	0.125	-0.369	-0.071	1										
Co	-0.103	-0.106	0.057	-0.151	1									
Cu	-0.253	-0.004	0.015	-0.147	0.269	1								
Zn	-0.094	0.171	-0.086	-0.011	-0.051	-0.057	1							
Mn	-.567*	0.464	-.856**	0.074	0.074	0.051	0.393	1						
Fe	-0.26	.676**	-0.238	-0.354	0.003	-0.084	-0.098	0.305	1					
Temp.	-.559*	0.301	-0.382	-0.296	-0.013	0.265	0.345	0.461	0.483	1				
pH	0.394	-0.234	0.406	-0.029	0.125	0.106	0.242	-0.356	-0.228	-0.435	1			
DO	-0.336	0.371	-0.21	-0.224	-0.041	0.006	.645**	.500*	0.161	0.396	0.072	1		
Salinity	.661**	-0.48	0.427	0.34	-0.014	-0.164	-0.416	-.622*	-0.343	-.789**	0.457	-.743**	1	
SPM	-0.349	-0.176	-.631**	0.135	-0.032	-0.211	0.306	0.487	-0.357	0.078	-0.127	0.108	-0.18	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.21 Pearson correlation matrix of particulate metals and hydrographic parameters in the surface waters of Cochin estuary during post-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	-0.064	1												
Cr	0.087	0.392	1											
Ni	-0.208	-.541*	-0.024	1										
Co	-0.191	.724**	.514*	-0.441	1									
Cu	-0.08	-0.049	0.079	0.447	-0.111	1								
Zn	0.308	.661**	0.372	-0.334	.629**	0.102	1							
Mn	0.105	-0.146	-0.05	0.1	-0.102	.576*	0.029	1						
Fe	-0.03	-0.026	-0.083	0.478	-0.088	.556*	0.095	0.417	1					
Temp.	-0.028	-0.135	0.152	-0.157	0.098	0.18	0.045	0.445	-0.152	1				
pH	0.055	0.354	-0.244	-.530*	0.132	-0.183	0.205	-0.285	-0.047	-0.341	1			
DO	0.126	0.094	-0.15	-0.271	-0.059	0.088	0.27	0.351	0.181	-0.058	.529*	1		
Salinity	-0.207	0.366	-0.261	-0.314	0.184	-0.429	-0.122	-0.405	-0.164	-.663**	.557*	0.04	1	
SPM	-0.221	-.660**	-0.329	.553*	-.555*	0.168	-0.373	-0.056	-0.11	0.288	-0.278	-0.112	-0.374	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.22 Pearson correlation matrix of particulate metals and hydrographic parameters in the bottom waters of Cochin estuary during post-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	-0.017	1												
Cr	.783**	-0.278	1											
Ni	0.229	-0.417	0.403	1										
Co	0.003	.574*	-0.142	-0.263	1									
Cu	-0.187	-.502*	0.073	.600*	-0.339	1								
Zn	0.039	0.206	0.163	-0.128	-0.23	0.005	1							
Mn	-0.177	0.054	0.122	0.457	-0.199	0.447	0.45	1						
Fe	-0.35	.508*	-.519*	-0.148	0.305	-0.29	0.2	0.245	1					
Temp.	-0.188	-0.32	-0.163	0.057	0.133	0.338	0.068	0.002	0.134	1				
pH	0.111	0.329	-0.206	-0.194	0.239	-.608*	-0.148	-0.208	0.492	0.219	1			
DO	0.324	-.524*	0.217	0.081	-0.176	0.116	0.07	-0.284	-0.37	0.339	-0.108	1		
Salinity	0.259	0.409	-0.12	-0.248	0.243	-.598*	-0.353	-0.145	0.465	-0.303	.632**	-0.279	1	
SPM	0.089	-.712**	0.098	0.461	-0.345	0.496	-0.118	-0.208	-0.438	0.309	-0.381	.558*	-.548*	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

In the estuary, temperature showed weak positive correlation with Fe in the surface particulates during Pre-M. Weak negative correlation was observed with Cd in the bottom during Mon season. During Pre-M, pH showed weak negative correlation with Ni in the bottom particulates. pH exhibited weak positive correlation with Cd and weak negative correlation with Fe in the surface during Mon. pH exhibited weak negative correlation with Ni in the surface and Cu in the bottom particulates during Post-M season. Dissolved oxygen exhibited weak and strong positive correlations with Cd and Co respectively in the surface particulates during Pre-M season. In the bottom, strong positive correlation observed for DO with all the metals except Cr and Ni suggested resuspension of the bottom sediments. During Mon, DO showed weak positive correlation with Cd in the surface; strong and weak positive correlations with Zn and Mn respectively in the bottom. During Post-M season, weak negative correlation was observed with Pb in the bottom.

Salinity showed weak negative correlation with Co in the surface particulates during Pre-M. In the bottom, salinity showed weak negative correlations with all the metals except Ni, suggesting salinity induced desorption of these metals from the particulates. During Mon, salinity exhibited weak negative correlation with Fe in the surface particulates; strong positive and weak negative correlations with Cd and Mn respectively in the bottom particulates. During Post-M, salinity showed weak negative correlation with Cu in the bottom particulates. During Pre-M, SPM exhibited strong negative and weak positive correlations with Co and Zn respectively in the surface particulates. SPM showed strong positive correlations with Ni in the surface particulates and strong negative correlations with Cr in the surface and bottom particulates during Mon season. SPM showed strong negative correlation with Pb in the surface and bottom particulates. Ni and Co showed weak positive and negative correlations with SPM in the surface.

During Pre-M, significant correlations were found for the metallic pairs Cd – Co, Pb – Cr and Co – Mn in the surface (Table 4.17). In the bottom particulates all the metals except Ni exhibited positive correlations with each other (Table 4.18). Strong inter-metallic correlations observed in the estuarine bottom particulates during Pre-M could be suggestive of the same source for these metals which can be the resuspension events in the estuary. All the correlations were very strong except the correlations found for Cr with metals Cd, Pb, Co, Cu, Zn and Mn which were weak. During Mon season, significant positive correlations were observed for the pairs Pb – Cr, Co – Cu, Co – Mn, Co – Fe, Cu – Mn, Cu – Fe and Mn – Fe in the surface (Table 4.19). In the bottom, negative correlations were shown by Cd – Mn, Cr – Mn and positive correlation was shown by Pb – Fe (Table 4.20). During Post-M season, the following metallic pairs exhibited significant positive correlations Pb – Co, Pb

– Zn, Cr- Co, Co – Zn, Cu – Mn and Cu – Fe in the surface. Negative correlation was observed between Pb and Ni in the surface (Table 4.21). In the bottom, Cd – Cr, Pb – Co, Pb – Fe and Ni – Cu showed significant positive correlations and negative correlations were shown by Pb – Cu and Cr – Fe (Table 4.22). Although not significant, majority of the metals (except Zn in the surface during Pre-M, Ni in the surface during Mon and Post-M) showed an inverse relationship with SPM concentration suggesting the particle concentration effect operating in the estuary.

In the coast, temperature showed significant positive correlation with Cr in the surface and Fe in the surface and bottom during Pre-M season. During Mon season, temperature showed strong negative correlations with Fe and weak negative correlations with Cu and Mn in the surface. Strong positive correlation was observed between temperature and Cr during this season. pH showed weak negative correlations with Fe in the surface particulates during Pre-M season. In the bottom, Cd was correlated positively to the pH during this season. pH of the bottom waters showed weak positive correlations with Co and Cu during Mon season. During Post-M, pH showed significant positive correlations with Pb and Fe and weak negative correlation with Mn in the surface. While in the bottom, Cr was the only metal which showed a significant positive correlation with pH. DO exhibited weak positive and negative correlations with Ni and Fe respectively in the surface particulates during Mon season. While in the bottom, it showed weak positive correlation with Co only. During Post-M, Co and Mn in the bottom particulates showed weak positive and negative correlations respectively with DO. Salinity exhibited strong negative correlation with Zn in the surface during Pre-M. Salinity exhibited weak negative correlations with Fe in the bottom. During Mon season, salinity showed weak positive correlation with Cr and strong negative correlations with Cu, Zn, Mn and Fe in the surface. In the bottom, salinity exhibited weak negative correlation with Fe. During Post-M, salinity of the bottom waters exhibited negative correlations with Zn and Mn. During Pre-M, SPM in the surface showed strong positive and negative correlations with Cr and Co respectively. Co showed strong negative correlation with SPM in the bottom particulates also. During Mon season, SPM in the bottom showed weak negative correlations with Cr and Mn and strong negative correlation with Fe. During Post-M season, SPM in the surface showed significant negative and positive correlations with Co and Zn respectively. However in the bottom, it showed weak negative correlation with Pb and strong positive correlation with Zn.

During Pre-M, weak positive correlations in the surface were shown by the pairs Cd – Pb and Cd – Co. Ni and Cu showed strong positive correlations in the surface (Table 4.23). In the bottom, Cr – Mn, Mn – Fe, Pb – Co, Cr – Cu and Fe – Cu showed positive correlations; Cu – Pb and Cu – Co showed negative correlations (Table 4.24). During Mon season, significant positive correlations were observed in the surface particulates for Cd – Mn, Cu – Zn, Cu –Mn, Cu – Fe, Zn – Mn, Zn – Fe, Mn – Fe and negative correlations observed for Cr – Cu, Cr – Zn, Cr – Mn and Cr – Fe (Table 4.25). In the bottom particulates, weak positive correlations was shown by the metallic pairs Cd – Cu and Pb – Mn (Table 4.26). Significant positive correlation was observed in the surface during Post-M season for Cr – Fe and negative correlations observed for Pb – Mn and Co – Mn (Table 4.27). Strong positive correlations were shown by Pb – Co, Zn –Mn and Mn – Fe in the bottom particulates. Pb – Zn, Pb – Mn, Co – Zn, Co – Mn and Co – Fe exhibited negative correlations in the bottom particulates (Table 4.28).

Table 4.23 Pearson correlation matrix of particulate metals and hydrographic parameters in the surface waters of Cochin coast during pre-monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	.679*	1												
Cr	-0.252	-0.151	1											
Ni	-0.104	0.203	0.168	1										
Co	.621*	0.183	-0.539	0.039	1									
Cu	0.02	0.118	0.072	.737**	-0.029	1								
Zn	0.319	-0.276	-0.098	-0.372	0.444	-0.158	1							
Mn	0.134	0.383	-0.147	0.308	-0.046	0.167	-0.458	1						
Fe	0.048	-0.256	0.596	0.277	-0.042	0.244	-0.041	0.206	1					
Temp.	0.246	-0.114	.709*	-0.035	0.016	-0.036	0.206	-0.112	.730*	1				
pH	-0.057	0.247	-0.494	0.083	0.2	-0.274	0.078	0.074	-.664*	-.728*	1			
DO	0.425	0.304	-0.254	-0.076	0.333	-0.155	0.216	-0.554	-0.345	-0.089	0.242	1		
Salinity	-0.336	0.011	0.265	0.014	-0.463	-0.195	-.779**	0.425	0.274	0.058	-0.218	-0.462	1	
SPM	-0.462	-0.395	.835**	-0.154	-.791**	-0.069	-0.198	-0.141	0.507	0.532	-.607*	-0.343	0.431	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.24 Pearson correlation matrix of particulate metals and hydrographic parameters in the bottom waters of Cochin coast during pre-monsoon (n=10)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	0.222	1												
Cr	0.063	-0.464	1											
Ni	0.08	-0.486	0.323	1										
Co	0.428	.754*	-0.631	0.009	1									
Cu	-0.245	-.639*	.730*	0.289	-.637*	1								
Zn	-0.284	0.485	-0.382	0.048	0.588	-0.215	1							
Mn	0.266	-0.479	.851**	0.435	-0.414	0.583	-0.185	1						
Fe	0.09	-0.619	0.548	0.4	-0.34	.678*	-0.012	.771**	1					
Temp.	0.039	-0.541	0.038	0.411	-0.088	0.302	0.211	0.382	.693*	1				
pH	.633*	0.241	0.45	-0.202	-0.036	0.061	-0.572	0.275	-0.146	-0.558	1			
DO	0.178	0.206	0.514	0.058	-0.093	-0.006	-0.21	0.416	-0.114	-0.617	.646*	1		
Salinity	0.068	0.425	-0.412	-0.545	0.132	-0.568	-0.359	-0.563	-.731*	-.721*	0.373	0.313	1	
SPM	-0.467	-0.569	0.525	-0.075	-.866**	0.479	-0.316	0.371	0.223	0.24	-0.114	-0.027	-0.213	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.25 Pearson correlation matrix of particulate metals and hydrographic parameters in the surface waters of Cochin coast during monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	0.246	1												
Cr	-0.233	0.125	1											
Ni	0.019	-0.005	0.266	1										
Co	-0.488	0.192	-0.054	-0.322	1									
Cu	0.352	-0.035	-.641*	-0.304	-0.214	1								
Zn	0.6	-0.111	-.685*	-0.117	-0.387	.849**	1							
Mn	.693*	0.325	-.655*	-0.31	-0.311	.753**	.812**	1						
Fe	0.504	0.12	-.768**	-0.417	-0.147	.836**	.791**	.908**	1					
Temp.	-0.111	-0.075	.860**	0.397	-0.174	-.677*	-0.524	-.624*	-.794**	1				
pH	0.137	-0.197	0.217	0.162	-0.274	-0.567	-0.264	-0.354	-0.506	0.422	1			
DO	-0.175	-0.197	0.522	.665*	-0.214	-0.479	-0.423	-0.55	-.692*	.731*	0.246	1		
Salinity	-0.536	-0.143	.717*	0.226	0.267	-.752**	-.814**	-.912**	-.806**	0.579	0.405	0.313	1	
SPM	-0.48	-0.331	-0.315	0.109	0.399	0.001	-0.152	-0.329	-0.177	-0.392	-0.014	0.064	0.128	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.26 Pearson correlation matrix of particulate metals and hydrographic parameters in the bottom waters of Cochin coast during monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	0.264	1												
Cr	-0.008	-0.359	1											
Ni	-0.446	-0.181	-0.061	1										
Co	-0.168	-0.099	-0.199	-0.337	1									
Cu	.707*	0.387	-0.396	-0.098	0.241	1								
Zn	-0.133	0.051	-0.458	0.248	0.462	0.478	1							
Mn	0.111	.619*	0.262	-0.2	-0.067	0.157	0.097	1						
Fe	0.437	0.399	0.308	-0.519	-0.073	0.151	-0.266	0.581	1					
Temp.	0.393	-0.121	.826**	0.028	-0.538	-0.056	-0.409	0.347	0.401	1				
pH	0.173	-0.164	-0.358	0.088	.657*	.615*	0.497	-0.262	-0.322	-0.345	1			
DO	0.414	0.109	-0.255	-0.596	.689*	0.596	0.331	0.211	0.296	-0.262	.628*	1		
Salinity	-0.267	-0.011	0.205	0.333	-0.048	-0.16	0.026	0.028	-.623*	0.118	0.076	-0.377	1	
SPM	-0.359	-0.286	-.611*	0.539	0.041	-0.021	0.347	-.686*	-.905**	-0.589	0.355	-0.237	0.301	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.27 Pearson correlation matrix of particulate metals and hydrographic parameters in the surface waters of Cochin coast during post-monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	0.468	1												
Cr	0.006	-0.125	1											
Ni	-0.289	-0.176	0.488	1										
Co	0.379	0.595	0.118	0.184	1									
Cu	-0.018	0.002	0.098	0.342	-0.315	1								
Zn	0.249	-0.353	-0.096	-0.48	-0.571	0.219	1							
Mn	-0.326	-.695*	-0.06	-0.201	-.791**	-0.025	0.35	1						
Fe	0.355	0.195	.723*	0.268	0.426	-0.361	-0.171	-0.352	1					
Temp.	0.056	0.198	-0.328	0.312	0.532	-0.213	-0.491	-0.351	0.071	1				
pH	0.418	.693*	0.536	0.393	0.545	0.159	-0.387	-.638*	.685*	0.134	1			
DO	0.5	0.368	0.166	-0.286	0.593	-0.577	0.054	-0.525	0.543	-0.092	0.298	1		
Salinity	0.071	0.362	0.349	0.066	0.05	0.253	0.143	-0.373	0.18	-0.6	0.436	0.414	1	
SPM	-0.126	-0.526	-0.048	-0.401	-.658*	0.323	.837**	0.554	-0.395	-0.485	-0.555	-0.273	-0.05	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 4.28 Pearson correlation matrix of particulate metals and hydrographic parameters in the bottom waters of Cochin coast during post-monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Temp.	pH	DO	Salinity	SPM
Cd	1													
Pb	-0.337	1												
Cr	-0.234	-0.18	1											
Ni	-0.134	-0.291	-0.062	1										
Co	-0.187	.833**	0.09	-0.296	1									
Cu	-0.01	0.546	-0.462	0.304	0.402	1								
Zn	0.531	-.653*	-0.316	0.382	-.689*	0.211	1							
Mn	0.412	-.622*	0.07	0.421	-.603*	0.082	.803**	1						
Fe	0.509	-0.47	-0.242	0.314	-.615*	-0.059	0.59	.756**	1					
Temp.	-0.238	-0.042	-0.114	0.579	-0.257	0.295	0.229	0.274	0.238	1				
pH	-0.204	0.087	.691*	-0.318	0.145	-0.373	-0.398	-0.337	-0.435	-0.149	1			
DO	0.258	0.458	0.022	-0.446	.610*	-0.113	-0.575	-.679*	-0.448	-0.518	0.321	1		
Salinity	-0.087	0.358	0.405	-0.529	0.521	-0.357	-.735**	-.673*	-0.537	-0.143	0.537	.659*	1	
SPM	0.019	-.686*	-0.21	0.528	-0.546	-0.056	.622*	0.355	0.086	0.16	-0.354	-0.471	-0.576	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

4.2.2.3 Principal Component Analysis

Transformation between dissolved and particulate forms is the main process in the mixing zone in estuaries. These transformations include adsorption/desorption of heavy metals on to/from the surfaces of the suspended particles. Another major process in which suspended particulate matter involved is the coagulation, flocculation and precipitation. Salinity of the system will influence the flocculation/aggregation of the suspended particulate matter, the higher the salinity, the greater will be the aggregation of suspended particles and bigger the flocs which will settle down faster to the bottom (Kranck, 1973 & 1979; Lick *et al.,* 1992). Settling of SPM to the bottom sediments plays a major role in removal of particulate metals in aquatic systems with longer residence times. Incorporation into organic material (biologically produced) in SPM and its decomposition also influence the heavy metal distribution.

PCA of particulate heavy metals and other physicochemical parameters was done to identify the major processes these metals undergo in the Cochin estuary and its adjacent coast. Varimax rotation was applied to identify the variables that are more significant to each factor based on the significance of their correlations and are expressed as factor loading (Buckley *et al.,* 1995; Davis, 2002). Parameters with factor loading > 0.50 and components with eigen values > 1 are considered for interpretation. The loadings of each variable, percentage variance accounted by each component and cumulative percentage variances in the estuarine and coastal area are given in Tables 4.29 & 4.30 respectively.

Table 4.29 Factor loadings showing eigen values of particulate metals and hydrographical parameters in the Cochin estuary

Variables	**Components**																
	Pre-monsoon						**Monsoon**						**Post-monsoon**				
Surface	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**
Cd	**0.851**	-0.045	0.139	0.141	-0.167	-0.114	-0.141	**0.847**	-0.064	-0.048	0.201	-0.017	0.047	-0.064	0.038	0.084	**0.967**
Pb	-0.034	-0.108	0.059	-0.074	**0.890**	0.332	-0.082	0.083	**0.912**	-0.078	0.249	0.131	**0.884**	-0.062	-0.184	0.169	-0.136
Cr	-0.316	0.261	-0.240	-0.029	**0.780**	-0.268	-0.138	0.090	**0.885**	-0.152	-0.377	-0.066	**0.646**	0.013	0.182	-0.485	0.143
Ni	-0.316	**0.778**	0.072	-0.011	-0.191	0.077	0.000	-0.081	-0.080	**0.952**	-0.022	-0.031	-0.488	**0.595**	-0.103	**-0.551**	-0.084
Co	**0.831**	-0.100	-0.268	0.253	-0.025	-0.292	**0.883**	0.098	-0.168	-0.009	0.295	0.018	**0.889**	-0.132	0.046	-0.047	-0.267
Cu	-0.040	0.112	-0.138	0.003	0.104	**0.964**	**0.830**	-0.179	0.413	0.037	0.007	0.128	0.004	**0.816**	0.288	-0.033	-0.084
Zn	-0.046	-0.083	**0.949**	0.009	-0.053	-0.099	0.232	-0.028	0.022	0.085	**0.831**	-0.097	**0.764**	0.114	0.116	0.148	0.283
Mn	0.192	-0.215	-0.247	**0.889**	-0.021	-0.138	**0.963**	-0.062	-0.108	-0.021	0.025	0.061	-0.024	**0.589**	**0.567**	0.269	0.077
Fe	-0.293	0.483	0.184	**0.626**	0.007	0.367	**0.787**	-0.196	-0.298	-0.322	0.193	0.156	0.018	**0.892**	-0.151	0.049	0.026
Temp	-0.018	0.347	0.429	**0.648**	-0.149	0.059	0.158	-0.016	0.084	0.010	-0.075	**0.941**	0.014	-0.103	**0.948**	-0.034	-0.103
pH	-0.076	**-0.861**	0.149	-0.046	-0.249	-0.040	-0.253	**0.805**	0.187	0.059	-0.305	0.186	0.176	-0.177	-0.400	**0.753**	-0.027
DO	**0.807**	-0.184	0.004	-0.052	-0.006	-0.002	0.154	**0.840**	0.137	-0.346	-0.024	-0.125	0.050	0.225	0.087	**0.819**	0.149
Salinity	**-0.786**	-0.020	0.182	0.271	0.189	-0.240	-0.185	-0.162	0.210	**0.502**	**-0.527**	-0.460	0.125	-0.286	**-0.766**	0.314	-0.288
SPM	**-0.671**	0.029	**0.628**	-0.034	-0.048	-0.087	-0.175	-0.274	-0.468	**0.706**	0.301	0.106	**-0.729**	0.004	0.307	-0.190	-0.195
% of Variance	**24.77**	**13.53**	**12.90**	**12.66**	**11.44**	**10.35**	**23.52**	**16.28**	**16.07**	**13.75**	**10.91**	**8.82**	**24.24**	**16.96**	**16.22**	**14.63**	**9.29**
Cumulative %	**24.77**	**38.30**	**51.19**	**63.85**	**75.29**	**85.64**	**23.52**	**39.80**	**55.86**	**69.61**	**80.52**	**89.34**	**24.24**	**41.20**	**57.42**	**72.04**	**81.34**
Bottom	**PC1**	**PC2**	**PC3**				**PC1**	**PC2**	**PC3**	**PC4**			**PC1**	**PC2**	**PC3**	**PC4**	**PC5**
Cd	**0.988**	0.103	-0.051				**-0.723**	-0.208	-0.123	-0.324			0.126	0.048	**0.952**	-0.038	-0.032
Pb	**0.991**	0.096	-0.030				0.273	**0.752**	0.185	-0.188			**0.512**	**-0.583**	-0.143	-0.258	0.314
Cr	**0.675**	**-0.512**	-0.186				**-0.882**	0.040	-0.055	0.132			-0.204	-0.013	**0.890**	0.193	0.108
Ni	-0.274	**-0.773**	0.353				0.107	**-0.597**	-0.166	-0.289			-0.167	0.157	0.283	**0.850**	-0.196
Co	**0.989**	0.107	-0.031				-0.011	-0.068	-0.034	**0.684**			0.493	-0.094	-0.132	-0.256	-0.060
Cu	**0.976**	0.141	-0.048				0.031	0.071	-0.009	0.821			**-0.561**	0.269	-0.188	**0.653**	-0.015
Zn	**0.991**	0.102	-0.018				0.083	-0.070	**0.912**	-0.074			-0.105	0.023	0.081	0.005	**0.969**
Mn	**0.987**	0.105	-0.038				**0.832**	0.089	0.349	-0.039			-0.039	-0.242	-0.088	**0.765**	0.499
Fe	**0.994**	0.064	-0.038				0.208	**0.848**	-0.093	-0.125			**0.718**	-0.115	-0.448	0.157	0.273
Temp	0.314	0.138	**0.819**				**0.548**	0.480	0.274	0.260			0.198	**0.828**	-0.280	0.153	0.145
pH	0.039	**0.909**	0.179				**-0.670**	-0.251	0.386	0.124			**0.886**	0.131	0.038	-0.117	-0.091
DO	**0.795**	0.018	-0.363				0.212	0.276	**0.842**	0.005			-0.213	**0.749**	0.344	-0.220	0.023
Salinity	**-0.621**	0.179	**0.547**				**-0.609**	-0.462	-0.493	-0.188			**0.749**	-0.363	0.165	-0.103	-0.312
SPM	-0.381	-0.311	**0.693**				**0.622**	**-0.578**	0.248	-0.122			**-0.519**	**0.651**	0.078	0.148	-0.268
% of Variance	**61.62**	**13.64**	**12.74**				**26.30**	**18.75**	**16.29**	**10.99**			**22.38**	**16.71**	**16.42**	**14.62**	**11.54**
Cumulative %	**61.62**	**75.25**	**87.99**				**26.30**	**45.05**	**61.34**	**72.33**			**22.38**	**39.08**	**55.51**	**70.13**	**81.67**

Table 4.30 Factor loadings showing eigen values of particulate metals and hydrographical parameters in the Cochin coast

Variables	**Components**														
	Pre-monsoon					**Monsoon**					**Post-monsoon**				
Surface	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC1**	**PC2**	**PC3**	**PC4**		**PC1**	**PC2**	**PC3**	**PC4**	**PC5**
Cd	0.163	**0.581**	-0.031	**0.767**	-0.083	0.415	**0.779**	-0.007	0.002		0.429	0.147	-0.105	-0.086	**0.813**
Pb	-0.183	-0.022	0.108	**0.926**	0.136	-0.051	0.249	-0.134	**0.815**		**0.904**	-0.134	0.130	-0.007	0.157
Cr	**0.755**	-0.485	-0.147	-0.095	0.101	**-0.834**	0.187	0.279	0.213		-0.057	**0.927**	0.272	0.031	-0.076
Ni	-0.002	-0.084	0.133	0.102	**0.925**	-0.134	0.015	**0.877**	-0.035		0.130	**0.591**	-0.203	0.435	**-0.537**
Co	-0.128	**0.873**	-0.005	0.259	0.011	-0.229	**-0.672**	-0.413	0.351		**0.799**	0.199	-0.255	-0.317	-0.032
Cu	0.116	0.061	0.029	-0.019	**0.923**	**0.901**	0.038	-0.100	0.077		0.004	0.007	0.208	**0.962**	0.096
Zn	0.124	**0.719**	-0.465	-0.251	-0.233	**0.883**	0.314	-0.022	-0.135		**-0.516**	-0.125	0.318	0.093	**0.717**
Mn	-0.066	-0.014	**0.891**	0.234	0.183	**0.824**	0.438	-0.231	0.223		**-0.886**	-0.118	-0.050	0.029	-0.026
Fe	**0.847**	0.054	0.288	-0.106	0.216	**0.879**	0.182	-0.354	0.150		0.268	**0.846**	-0.026	-0.367	0.142
Temp	**0.949**	0.088	-0.069	0.093	-0.094	**-0.774**	0.323	0.437	-0.027		0.385	-0.060	**-0.859**	-0.009	-0.149
pH	**-0.840**	0.075	-0.058	0.076	-0.039	**-0.504**	0.352	-0.050	**-0.651**		**0.728**	**0.591**	0.104	0.164	0.066
DO	-0.210	0.133	**-0.734**	0.497	-0.068	-0.426	-0.014	**0.818**	-0.106		0.433	0.193	0.283	**-0.720**	0.317
Salinity	0.142	**-0.646**	**0.620**	0.054	-0.185	**-0.880**	-0.243	0.027	-0.131		0.340	0.174	**0.893**	0.075	-0.004
SPM	**0.659**	**-0.642**	-0.059	-0.310	-0.146	0.116	**-0.835**	0.083	-0.330		**-0.715**	-0.190	0.246	0.230	0.440
% of Variance	**25.00**	**19.47**	**14.86**	**14.44**	**13.92**	**41.48**	**17.62**	**14.96**	**10.66**		**30.53**	**17.79**	**14.58**	**14.09**	**13.18**
Cumulative %	**25.00**	**44.47**	**59.34**	**73.77**	**87.70**	**41.48**	**59.10**	**74.07**	**84.72**		**30.53**	**48.33**	**62.91**	**77.00**	**90.19**
Bottom	**PC1**	**PC2**	**PC3**	**PC4**		**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC1**	**PC2**	**PC3**	**PC4**	
Cd	0.208	0.494	0.136	**0.807**		-0.068	0.178	-0.354	0.055	**0.888**	-0.012	**0.760**	-0.486	0.207	
Pb	-0.474	**0.736**	0.305	-0.176		-0.133	-0.318	-0.097	**0.845**	0.224	**0.851**	-0.445	-0.033	0.216	
Cr	**0.548**	**-0.538**	**0.600**	0.145		-0.133	**0.962**	-0.009	-0.029	-0.202	0.006	-0.059	0.091	**-0.891**	
Ni	**0.697**	0.056	-0.030	0.007		-0.243	-0.132	**0.796**	-0.113	-0.045	-0.278	0.063	**0.719**	0.224	
Co	-0.086	**0.986**	-0.087	-0.036		**0.931**	-0.134	-0.169	-0.065	-0.165	**0.733**	-0.482	-0.220	0.088	
Cu	**0.572**	**-0.618**	0.143	-0.062		0.380	-0.190	0.004	0.223	**0.862**	0.471	-0.033	0.391	**0.680**	
Zn	0.185	**0.573**	-0.111	**-0.770**		**0.595**	-0.376	0.364	0.200	0.135	**-0.514**	**0.637**	0.226	0.371	
Mn	**0.792**	-0.295	0.410	0.196		0.079	0.323	-0.072	**0.911**	0.000	-0.318	**0.790**	0.412	0.048	
Fe	**0.865**	-0.263	-0.094	0.075		-0.112	0.328	**-0.725**	0.490	0.156	-0.140	**0.871**	0.208	0.134	
Temp	**0.700**	-0.089	**-0.644**	-0.023		-0.373	**0.866**	0.049	0.096	0.272	0.068	0.081	**0.825**	0.029	
pH	-0.135	0.023	**0.696**	**0.657**		**0.762**	-0.176	0.202	-0.275	0.424	0.146	-0.225	-0.134	**-0.790**	
DO	-0.038	0.002	**0.937**	0.106		**0.761**	-0.068	-0.473	0.094	0.346	0.428	-0.258	**-0.734**	-0.062	
Salinity	**-0.877**	0.078	0.180	0.278		0.060	0.230	**0.790**	0.055	-0.147	0.439	-0.347	-0.412	**-0.541**	
SPM	0.078	**-0.880**	0.006	-0.161		0.027	**-0.640**	**0.561**	**-0.502**	-0.035	**-0.877**	-0.067	0.211	0.319	
% of Variance	**29.16**	**26.47**	**17.84**	**13.50**		**19.90**	**19.51**	**19.04**	**16.03**	**14.93**	**22.26**	**21.83**	**19.14**	**18.47**	
Cumulative %	**29.16**	**55.64**	**73.48**	**86.98**		**19.90**	**39.41**	**58.44**	**74.47**	**89.40**	**22.26**	**44.09**	**63.24**	**81.71**	

In the estuary, PCA rendered 6 principal components with 85.64 % cumulative variance for the surface particulate samples during Pre-M (Fig. 4.25). PC1 in the surface which explained 24.77 % of the cumulative variance was loaded positively with Cd, Co & DO. Salinity & SPM were loaded negatively in this component. This PC represented desorption process of Cd and Co from the SPM by the increased competition from seawater cations with the increase in salinity. PC2 which accounted for 13.53 % of the cumulative variance was characterised with positive and negative loadings of Ni & pH respectively. PC3 which was positively loaded with Zn and SPM explained 12.90 % of the total variance and stood for the process of adsorption of Zn on to the SPM. Mn, Fe and temperature were positively loaded in PC4 and this component explained 12.66 % of the cumulative variance. PC5 was loaded with Pb & Cr and it accounted for 11.44 % of the total variance. Cu stood alone in PC6 which explained 10.35 % of the cumulative variance.

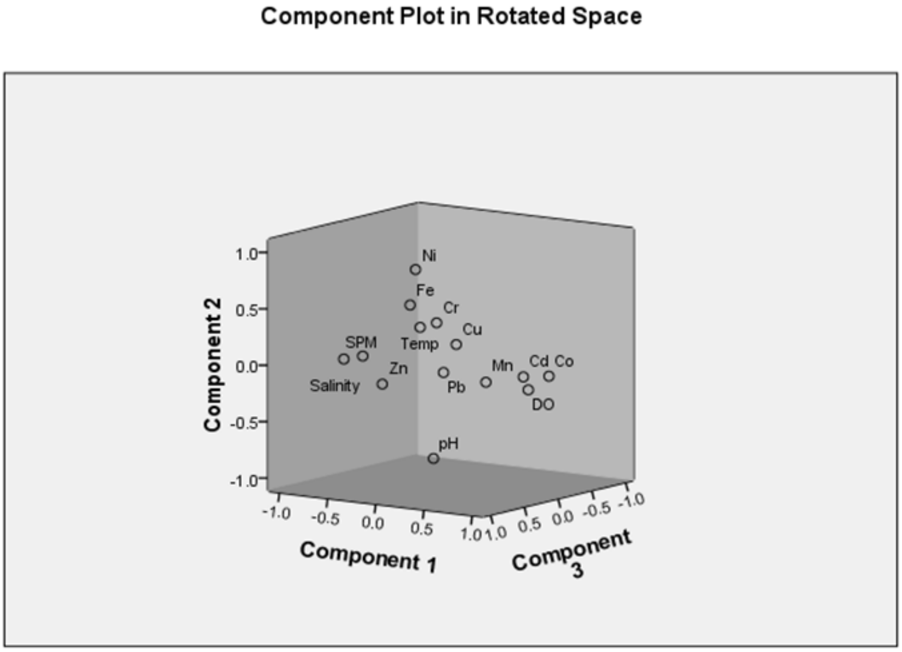

Figure 4.25 Ordination plot of principal components of SPM in the estuarine surface during pre-monsoon

During Pre-M season, bottom particulates exhibited three principal components with 87.99 % cumulative variance (Fig. 4.26). PC1 explained 61.62 % of the cumulative variance and it was characterised by high positive loadings of DO and all the metals except Ni; salinity also loaded negatively in this PC. This PC might be indicating the riverine addition of all the metals. PC2 which explained 13.64 % of the total variance was characterised by negative loading of Cr, Ni and positive loading of pH respectively. This PC stood for the pH induced desorption of these metals. PC3 which was loaded positively with temperature, salinity and SPM explained 12.74 % of cumulative variance. Loading of all the metals in PC1 (except Ni) with DO suggested a similar source which might be the physically disturbed sediments. However these associations were not seen in the surface particulates. Loadings of all the hydrographic parameters (except pH and DO) in PC3 suggested that the metal distribution in the bottom SPM was independent of these parameters.

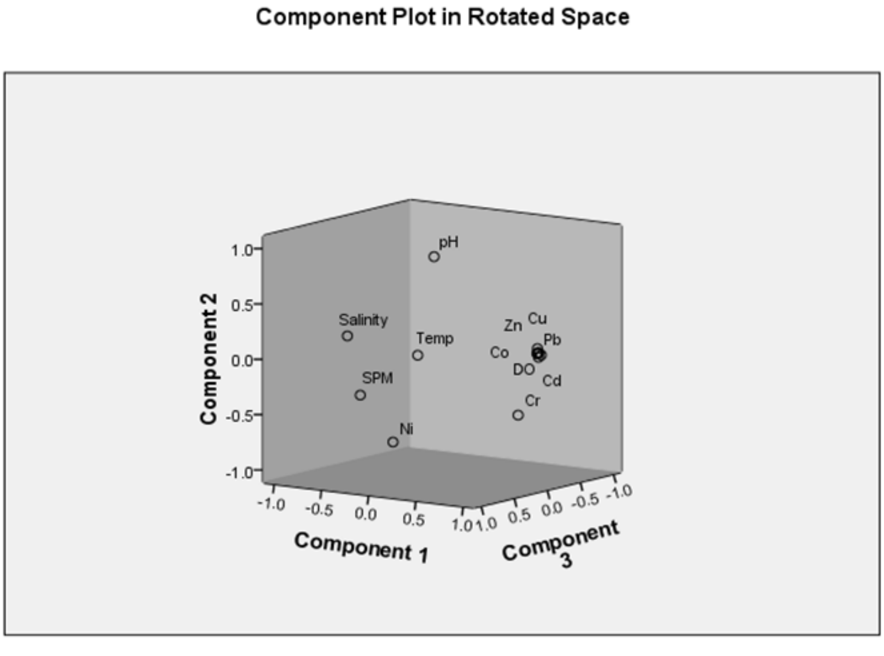

Figure 4.26 Ordination plot of principal components of SPM in the estuarine bottom during pre-monsoon

During Mon, surface particulate samples have got 6 principal components with 89.34 % total variance (Fig. 4.27). PC1 was characterised by high positive loadings of Co, Cu, Mn & Fe and explained 23.52 % of the total variance. PC1 suggested a common pathway for Cu and Co in the estuary which might be the adsorption on to the surface of freshly formed hydrated oxides of Fe and Mn which are known to have strong scavenging action for heavy metals (Jenne, 1968; Tessier *et al.,* 1979; Botte *et al.,* 2010; Sundaray *et al.,* 2011). PC2 which accounted for 16.28 % of the total variance was loaded positively with Cd, pH & DO. PC3 with 16.07 % of the total variance was characterised by positive loadings of Pb and Cr which could be considered as an anthropogenic component.

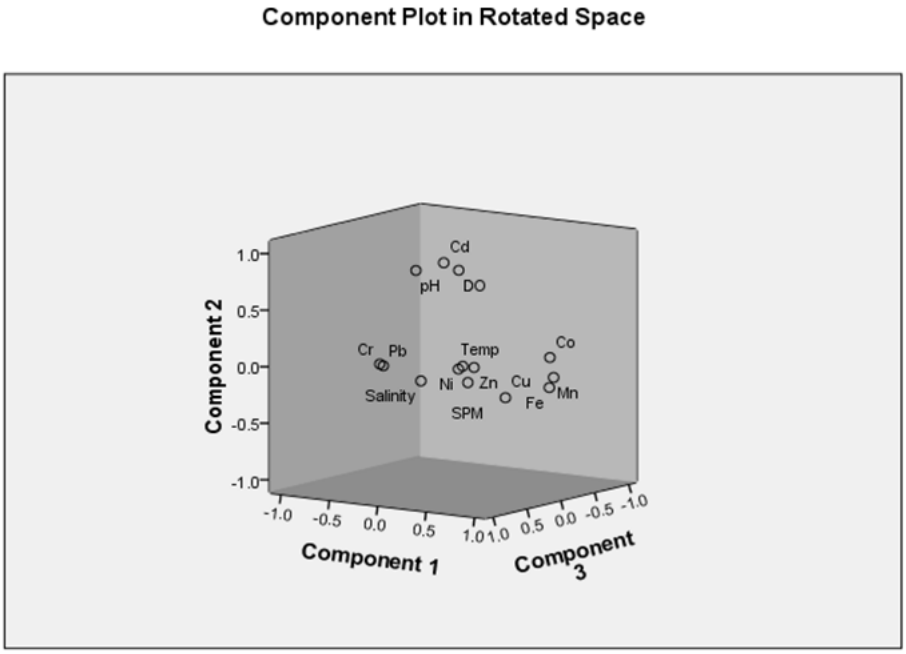

Figure 4.27 Ordination plot of principal components of SPM in the estuarine surface during monsoon

PC4 which explained 13.75 % of the total variance was characterised by high positive loadings of Ni and moderate positive loading of salinity & SPM. PC5 which explained 10.91 % of the cumulative variance was loaded positively with Zn and negatively with salinity. This component represented the industrial input of Zn from the catchment area (Shibu *et al.,* 1995, Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Paneer Selvam *et al.,* 2012, Deepulal *et. al.,* 2012; Shaiju, 2013; Bindu *et.al.,* 2015). PC6 was characterised by the positive loading of temperature alone and this component explained 8.82 % of the total variance.

Bottom samples have rendered 4 major components in PCA with 72.33 cumulative percent (Fig. 4.28). Cd, Cr, pH and salinity were loaded negatively; Mn, temperature and SPM were loaded positively in PC1 which explained 26.30 % of total variance. PC2 which explained 18.75 % of the total variance was characterised by positive loading of Pb & Fe and negative loading of Ni and SPM. This PC explained particle concentration effect for the particle reactive elements Pb and Fe. PC4 was characterised with positive loading of Zn & DO and it explained 16.29 % of the total variance. PC5 was loaded positively with Co and this PC explained 10.99 % of the total variance.

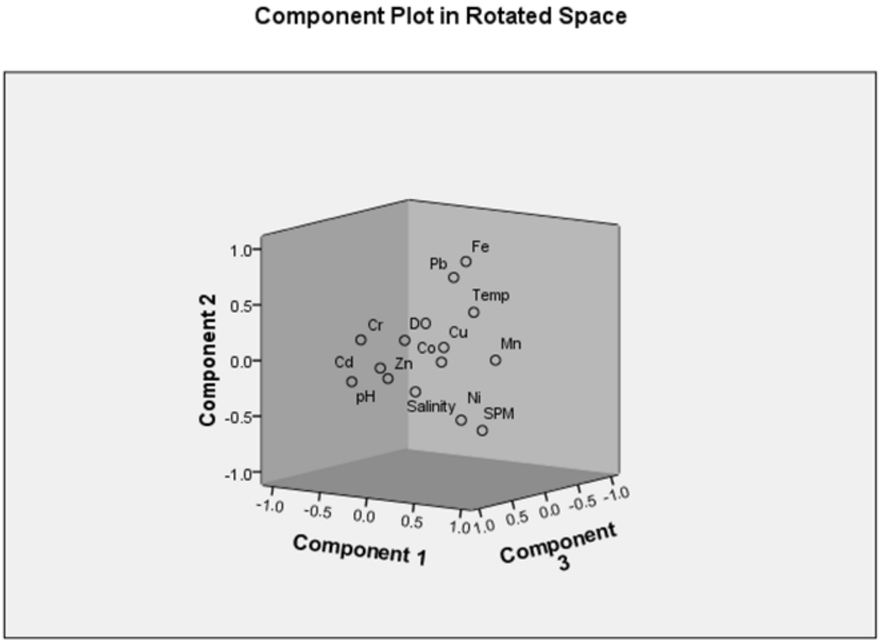

Figure 4.28 Ordination plot of principal components of SPM in the estuarine bottom during monsoon

Surface and bottom estuarine particulate samples rendered five principal components with 81.34 and 81.67 % of the total variance respectively, from PCA during Post-M season (Fig. 4.29 & 4.30). PC1 was loaded positively with Pb, Cr, Co, Zn and negatively with SPM which explained 24.24 % of the cumulative variance. This PC pointed to the particle concentration effect. PC2 which explained 16.96 % of the total variance was loaded positively with Ni, Cu, Mn & Fe. This component indicated the scavenging of Ni and Cu by the hydrated oxides of Fe and Mn. PC3 was loaded with Mn, temperature and negatively with salinity and this PC accounted for 16.22 % of the total variance. PC4 was characterised with negative loading of Ni and positive loadings of pH and DO and this component explained 14.63 % of the total variance. Cd stood alone in PC5 indicating its entirely different behaviour in the surface particulates and this PC explained 9.29 % of the cumulative variance. PC1 in the bottom, which accounted for 22.38 % of the cumulative variance, was characterised by positive loading of Pb, Fe, pH, salinity and negative loading of Cu and SPM. This PC might be representing the particle reactive nature of Pb and Fe. PC2 which explained 16.71 % of the cumulative variance was characterised by positive loadings of SPM, DO and temperature and Pb was loaded negatively in this PC. PC3 was loaded positively with Cd, Cr and this explained 16.42 % of the total variance. PC4 which accounted for 14.62 % of the total variance characterised by positive loading of Ni, Cu & Mn. This component pointed to the role of Mn oxy-hydroxides in the transport of the above metals. PC5 which explained 11.54 % of the cumulative variance was loaded by Zn only suggesting an entirely different pathway for this metal in the estuary during Post-M.

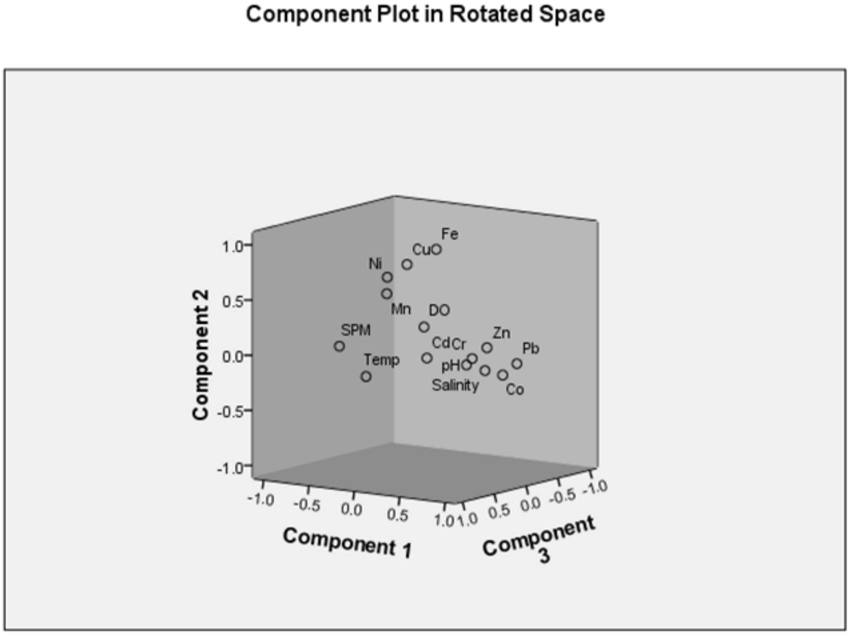

Figure 4.29 Ordination plot of principal components of SPM in the estuarine surface during post-monsoon

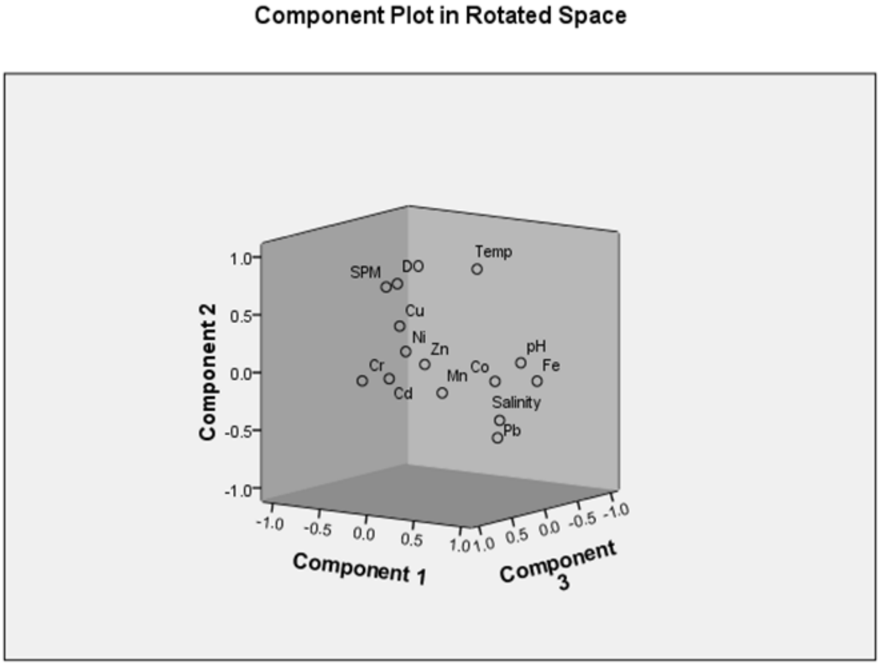

Figure 4.30 Ordination plot of principal components of SPM in the estuarine bottom during post-monsoon

In the coast, PCA rendered 5 principal components for the surface (Fig. 4.31) and 4 principal components for the bottom particulate samples (Fig. 4.32) during Pre-M; with 87.70 & 86.98 % cumulative variance respectively. PC1 in the surface was characterised with positive loading of Cr, Fe & SPM, temperature and negative loading of pH. This component explained 25 % of the total variance and suggested the role of Fe in the particulate Cr adsorption. PC2 with 19.47 % of the total variance was loaded positively with Cd, Co & Zn; negatively with SPM & salinity. This component could be considered as the anthropogenic one. Mn and salinity were loaded positively and DO was loaded negatively in PC3 which explained 14.86 % of the total variance. PC3 might be representing the formation of particulate Mn oxy-hydroxides with increase in salinity. PC4, which explained 14.44 % of the cumulative variance, was characterised by positive loading of Cd and Pb and this component can be considered as the one representing anthropogenic influence. PC5 which accounted for 13.92 % of the variance was characterised by high positive loading of Ni & Cu.

In the bottom particulates, PC1 was loaded with Cr, Ni, Cu, Mn, Fe, temperature (positive) and salinity (negative). PC1, which explained 29.16 % of the cumulative variance, could be considered as the one showing the scavenging action of Fe-Mn oxy-hydroxides (Moore, 1963; Potter *et al.,* 1963; Jenne, 1968; Grieve and Fletcher, 1977; Tessier *et al.,* 1979; Jayasree and Nair, 1995; Singh *et al.,* 1984; Kabata - Pendias, 2001; Dang *et al.,* 2015). PC2 was characterised by positive loading of Pb, Co & Zn; negative loading of Cr, Cu & SPM. PC2 accounted for 26.47 % of the cumulative variance. PC3 was loaded positively with Cr, pH and DO; negatively with temperature and this PC explained 17.84 % of the total variance. PC4 with 13.50 % of the total variance was characterised by positive loading of Cd and pH; negative loading of Zn.

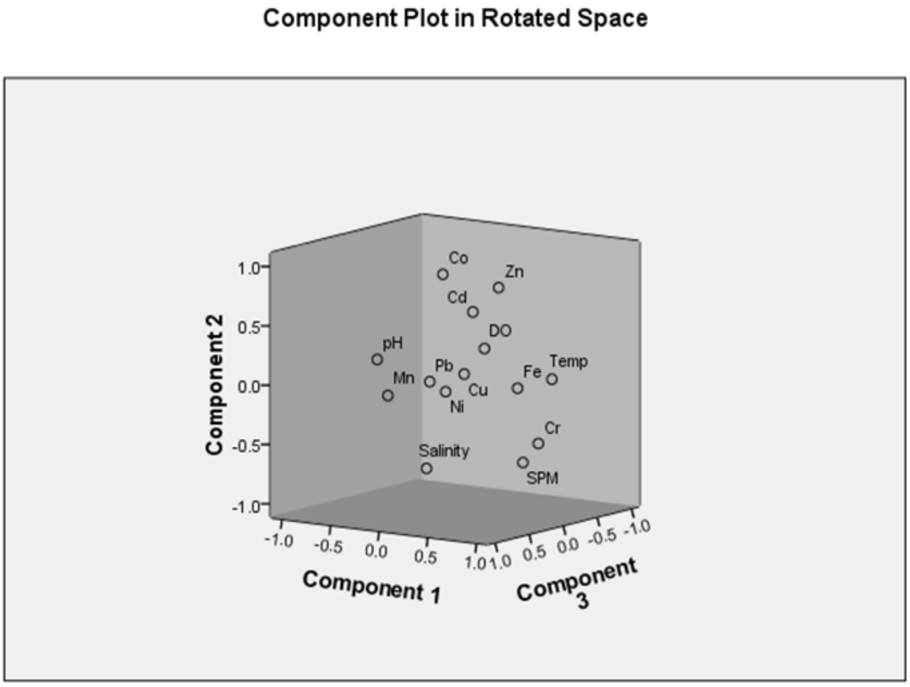

Figure 4.31 Ordination plot of principal components of SPM in the coastal surface during pre-monsoon

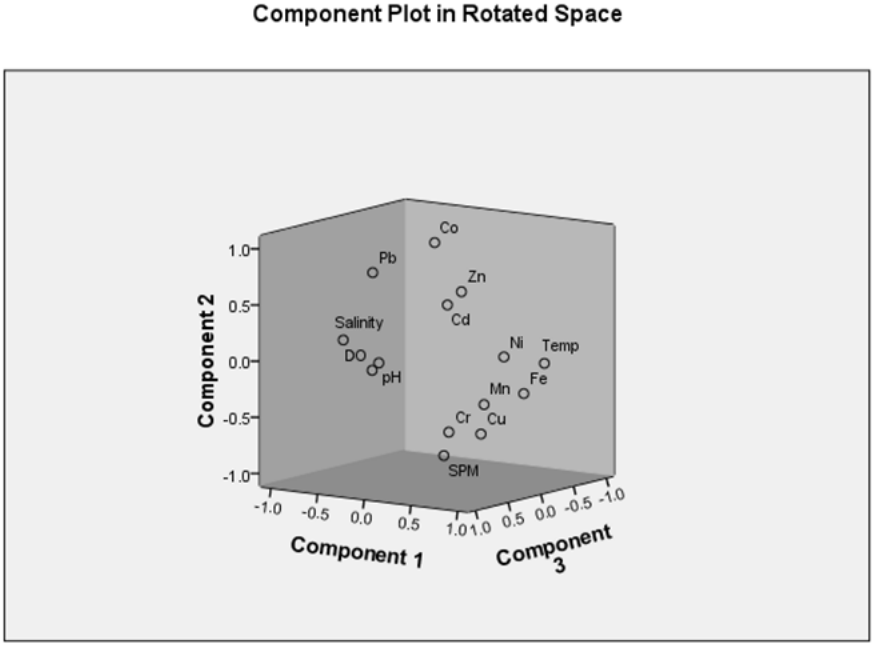

Figure 4.32 Ordination plot of principal components of SPM in the coastal bottom during pre-monsoon

During Mon season, 4 & 5 principal components in the surface and bottom respectively were obtained and they have 84.72 & 89.40 % cumulative percentage of variance respectively (Fig. 4.33 & 4.34). PC1 which accounted for 41.48 % of the total variance was characterised by positive loadings of Cu, Zn, Mn and Fe; negative loadings of Cr, pH, temperature and salinity. Cd (positive), Co & SPM (negative) were loaded in PC2 which explained 17.62 % of total variance and this component might be pointing to the competitive desorption of Co by the Cd ions. PC3 was characterised positive loadings of Ni & DO and it explained 14.96 % of the cumulative variance. PC4 was characterised by positive and negative loadings of Pb and pH respectively and this component explained 10.66 % of the total variance.

In the bottom, PC1 was characterised by positive loadings of Co, Zn, pH and DO and this PC explained 19.90 % of the cumulative variance. PC2, which explained 19.51 % of the total variance, was loaded positively with Cr and temperature; negatively with SPM. PC3 was characterised by positive loadings of Ni, SPM and salinity; negative loadings of Fe and this component explained 19.04 % of the total variance. Pb & Mn were loaded positively in PC4 which explained 16.03 % of the cumulative variance. PC5 was characterised by positive loading of Cd & Cu and explained 14.93 % of the cumulative variance.

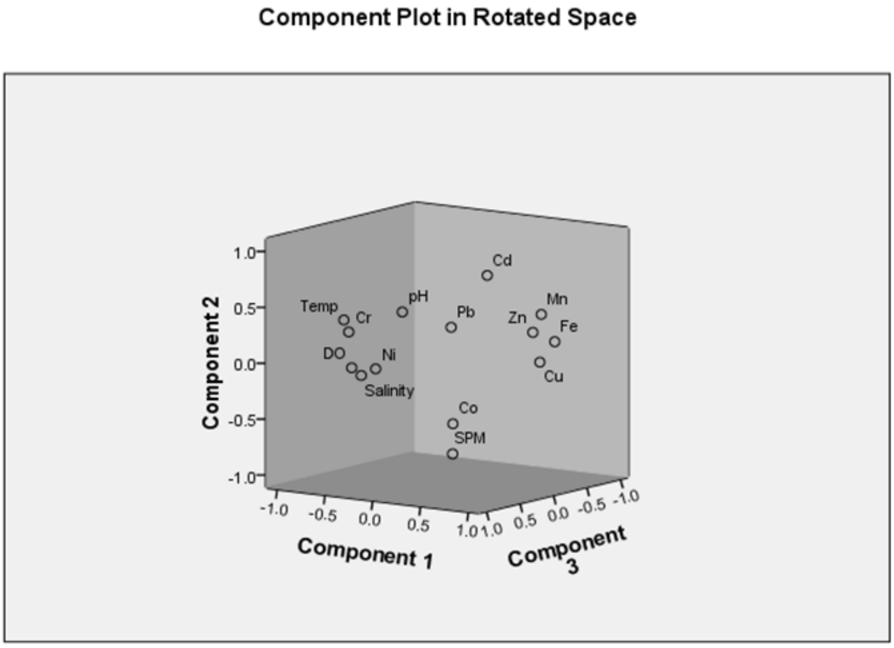

Figure 4.33 Ordination plot of principal components of SPM in the coastal surface during monsoon

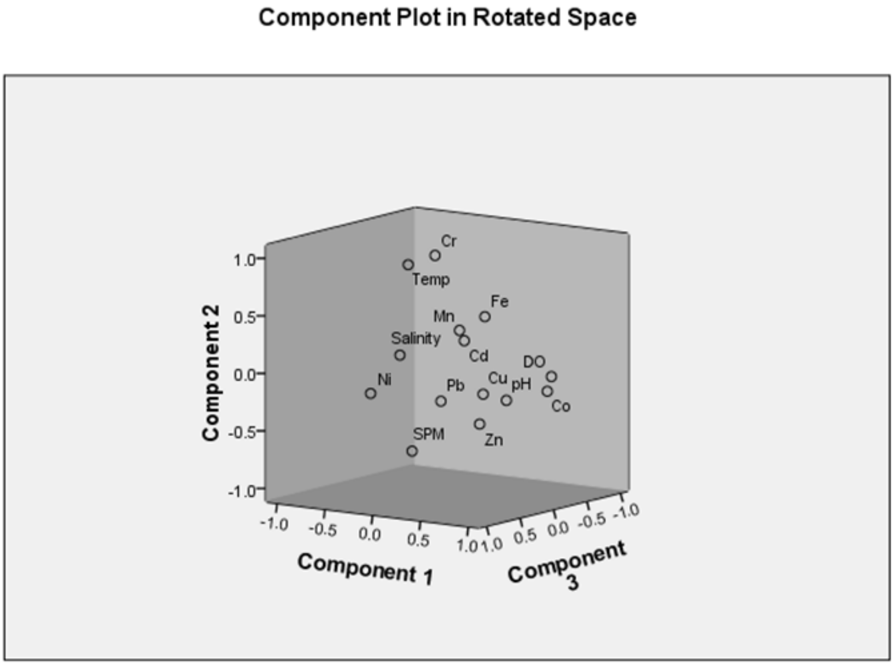

Figure 4.34 Ordination plot of principal components of SPM in the coastal bottom during monsoon

PCA rendered 5 principal components (90.10 % cumulative variance) for surface particulates during Post-M (Fig. 4.35). PC1 was loaded positively with Pb, Co, pH; negatively with Zn, Mn, SPM and explained 30.53 % of the total variance. PC2 which explained 17.79 % of the cumulative variance was characterised by positive loading of Cr, Ni, Fe and pH. Salinity and temperature were loaded positively and negatively in PC3 which explained 14.58 % of the total variance. PC4 which explained 14.09 % of the cumulative variance was characterised by positive and negative loadings of Cu and DO respectively. PC5 was characterised with positive loading of Cd, Zn and negative loading of Ni. This Pc explained 13.18 % of the cumulative variance and could be considered as the anthropogenic component.

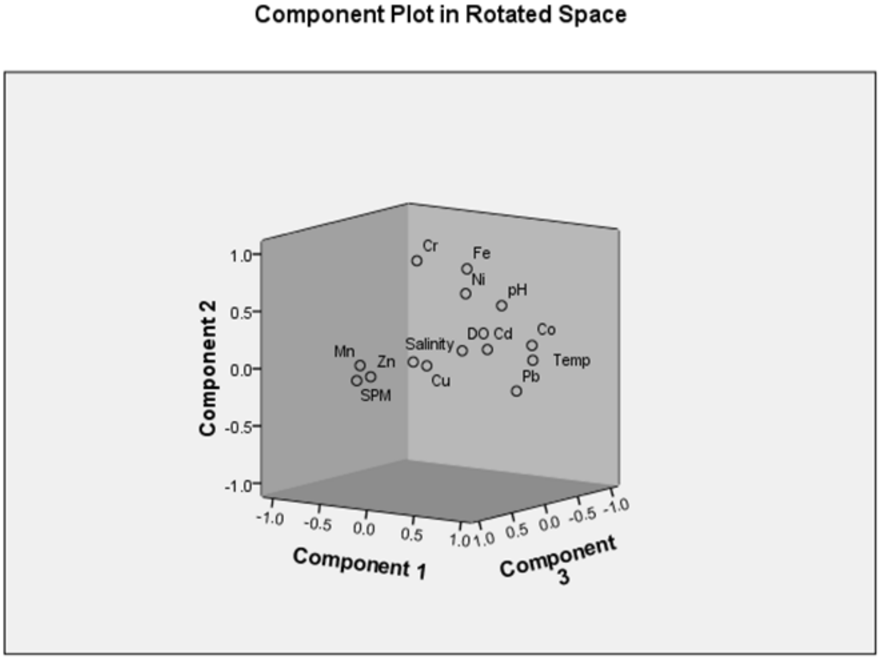

Figure 4.35 Ordination plot of principal components of SPM in the coastal surface during post-monsoon

In the bottom particulates, PC1 was loaded positively with Pb, Co; negatively with Zn and SPM and it explained 22.26 % of the total variance (Fig.

4.36). PC2 with 21.83 % variance was characterised by positive loading of Cd, Zn, Mn and Fe. PC3 was characterised by positive loading of Ni and temperature; negative loading of DO. This component explained 19.14 % of the cumulative variance. PC4, which explained 18.47 % of the total variance, was characterised by positive loading of Cu and negative loading of Cr, pH & salinity.

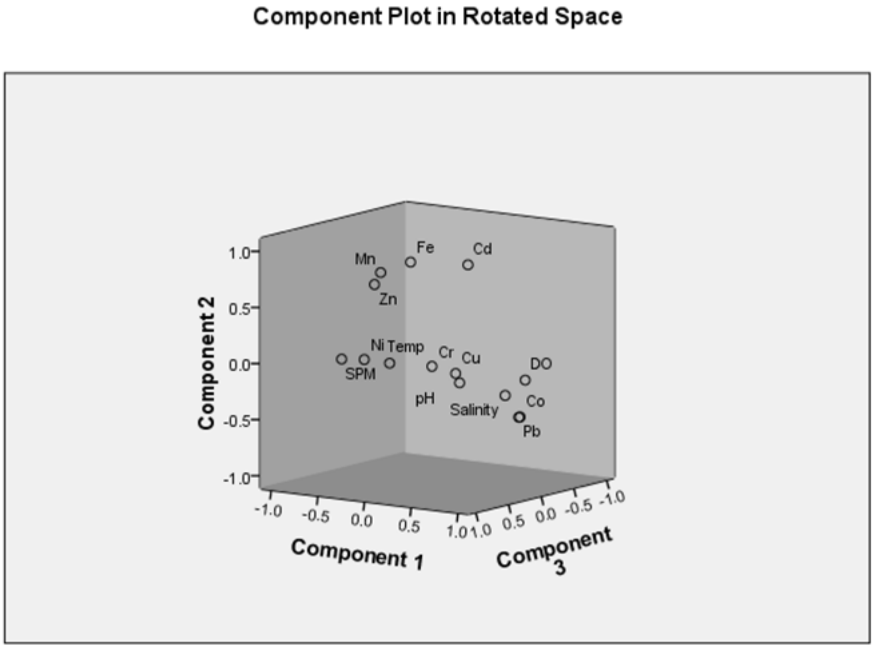

Figure 4.36 Ordination plot of principal components of SPM in the coastal bottom during post-monsoon

In the estuarine surface, salinity induced desorption of Cd and Co from SPM was the dominating process during Pre-M season. Scavenging of Co and Cu by the Fe-Mn oxy-hydroxides was the leading process during Mon and particle concentration of Pb, Cr, Co and Zn is dominating during Post-M season. Rest of the PCs in the surface has almost comparable % of variance. PC1 in the bottom during Pre-M was the only process with a very high percent of variance. Particle active behaviour of Pb and Fe dominated during Post-M.

Adsorption of Cr together with Fe on to SPM was the leading process in the coastal surface during Pre-M. Scavenging of metals by hydrous oxides of Fe and Mn and their adsorption on to SPM with decrease in salinity (PC1) and also the intermetallic competition for adsorption on to SPM (PC2) were the two processes dominating in the bottom during Pre-M. During Mon season, scavenging and adsorption of metals with decrease in salinity were dominating in the surface. Competition of Pb and Co with Zn and Mn for adsorption sites on SPM is the dominating process in the surface during Post-M season. All the processes in the bottom were of comparable percentage of variance during Mon and Post-M seasons

PCs which contribute highly to the cumulative percentage were PC1 in the estuarine bottom during Pre-M (61.62 % of variance) and PC1 in the coastal surface during Mon season (41.48 % of variance). As can be seen from the comparable % of variance of rest of the PCs, no major processes are operating regarding the particulate metals.

4.2.2.4 Cluster Analysis

Data were subjected to Hierarchical cluster analysis (distance cluster combine) and the dendrogram plots using average linkage between groups are shown in the Figures 4.37 - 4.42.

Two major clusters of stations were obtained in the estuary during Pre-M period (Fig. 4.37). First major cluster in the surface was formed by two sub clusters. E1, E6-E16 formed the first sub cluster with greater similarity. These stations were associated with lower Mn content. Stations E2, E3 & E4 constituted the second sub cluster and are characterised by higher levels of Mn. Second major cluster was a simplicifolious cluster formed by E5 and was characterised by highest Mn content, higher levels of metals Cd, Cr, Co & Fe and lower SPM content.

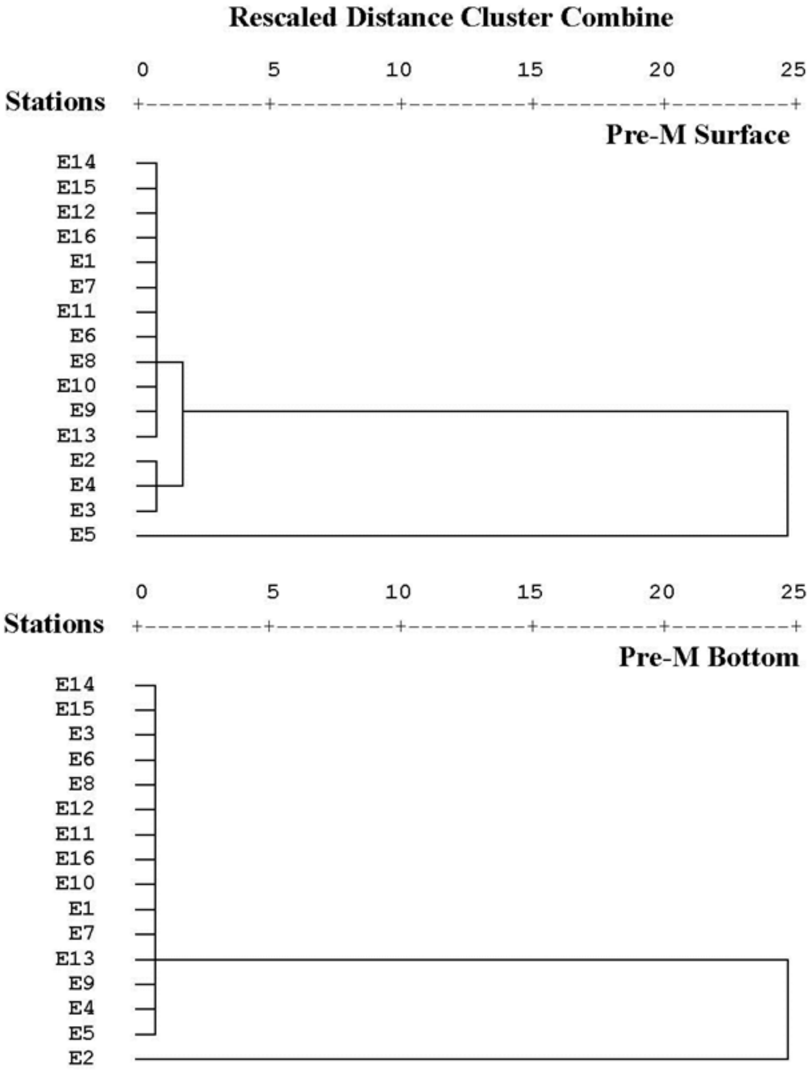

Figure 4.37 Dendrogram showing clusters of sampling locations in the estuary during pre-monsoon

First major cluster was constituted by the stations except E2 in the bottom (Fig. 4.37). E2 stood alone in the second major cluster indicating its greater dissimilarity from other sampling stations. E2 was associated with exceptionally high concentrations of all the metals except Ni and highest DO, lowest salinity and SPM compared to other stations. Source of this high metal content might be the riverine run off carrying industrial effluents along with. This area has been reported to have high influence of industrial area lying north of the estuary (Sankaranarayanan *et al.,* 1978; Paul and Pillai, 1983a; Nair *et al.,* 1990; Ouseph, 1992; Shibu *et al.,* 1990; Shibu *et al.,* 1995; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; SCMC, 2004; Martin *et al.,* 2008 & 2012; Deepulal *et al.,* 2012; Bindu *et al.,* 2015).

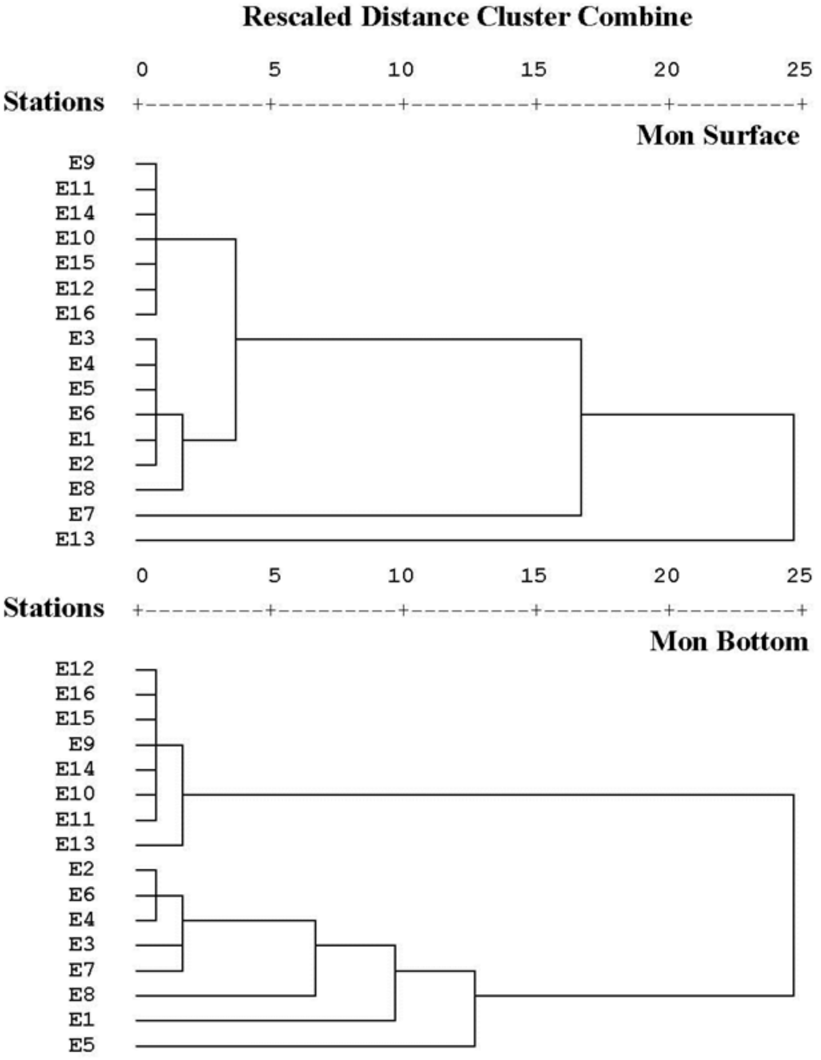

Figure 4.38 Dendrogram showing clusters of sampling locations in the estuary during monsoon

Three major clusters of stations were obtained in the surface during Mon (Fig. 4.38). Comparable concentrations of Cu, Zn and Mn; higher SPM content brought the stations E9-E12, E14-E16 together in the first sub cluster. Stations, E1-E6 were detected with lower concentrations of Mn, Fe and SPM compared to other stations which brought them together in second sub cluster. Lower Fe and SPM contents made station E8 show similarity to the above cluster. E7 and E13 formed simplicifolious second and third major clusters respectively suggesting their entirely different character compared to other stations. E7 showed highest levels of Pb & Cr and lowest SPM content. E13 was associated with highest concentrations of Cu, Co, Mn & Fe compared to other stations.

Two major clusters of stations were obtained in the bottom during Mon (Fig. 4.38). First major cluster was formed by the southern stations E9-E16 were associated with higher Mn, SPM and lower salinity compared to rest of the stations. Second major cluster formed by northern stations E1-E8, was divided in to 5 sub clusters, three of which were simplicifolious. Sub cluster constituted by stations E2, E4 and E6 were associated with comparable Mn and SPM contents. Comparable Cr, salinity, SPM and higher Cd contents made stations E3 and E7 cluster together. Simplicifolious clusters formed by E1 was characterised by highest content of Cr; E5 was characterised by highest content of Zn and E8 was characterised by highest content of Cu. These clusters were characterised by higher levels of metals and it can be attributed to the industrial effluents from the northern industrial area of Kochi. Thus clear segregation of anthropogenically influenced stations was found in the bottom during Mon season.

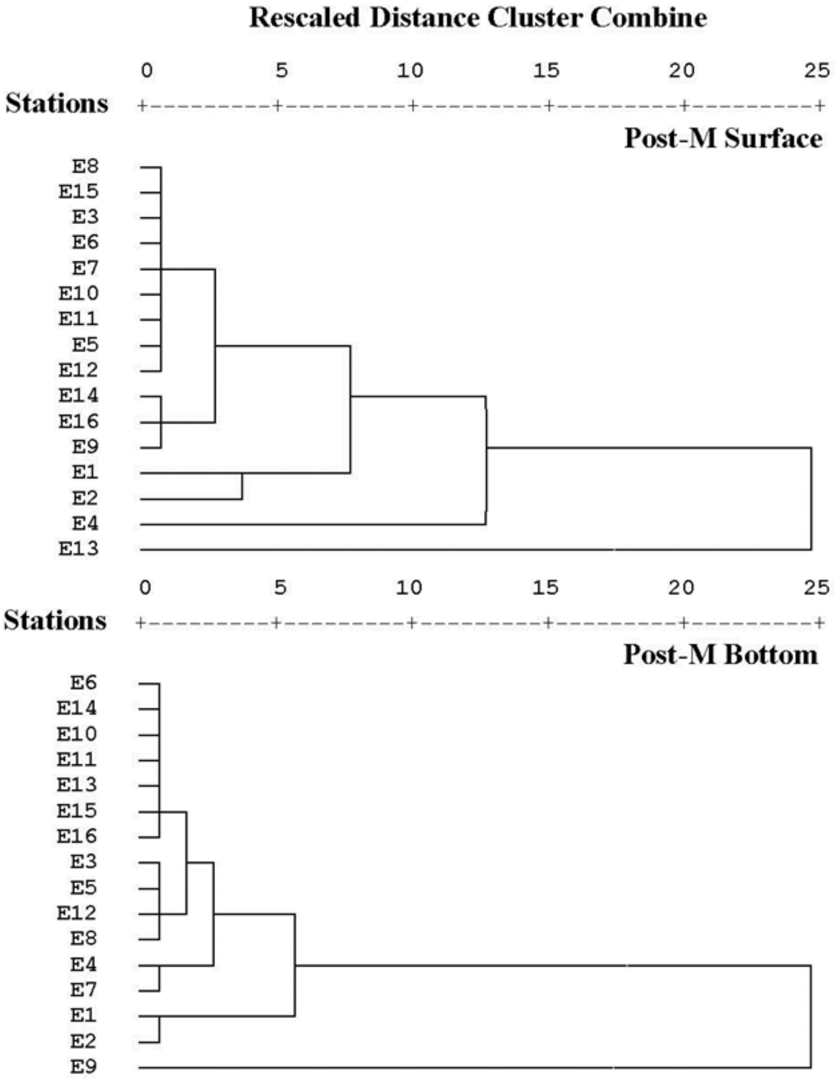

Figure 4.39 Dendrogram showing clusters of sampling locations in the estuary during post-monsoon

During Post-M, two clusters were obtained in the surface in which first one was more diffuse than the simplicifolious second cluster formed by E13 (Fig. 4.39). This station was characterised by highest concentration of Cu, Mn and Fe. First major cluster was again branched in to 4 sub clusters. E4 was detected with highest levels of Pb, Co & Zn; E1 and E2 were associated with higher levels of Zn compared to other stations which caused variance from other stations.

Like the surface, two clusters were obtained in the bottom also during Post-M, in which first one was more diffuse than the simplicifolious second cluster formed by E9, which was characterised by highest level of Mn (Fig. 4.39). First sub cluster constituted by E6, E10, E11, E13-E16 was characterised by similar concentrations of Cu, Zn and Mn which brought them together. Third sub cluster formed by stations E4 and E7 might be based on lower SPM, lower DO and similar distribution of Cd, Ni, Cu and Zn. E1 & E2 clustered together like in the surface and were characterised with highest level of Zn and higher levels of Pb, Mn and lower salinity and SPM compared to other stations.

In the coast, two major clusters were obtained for the surface SPM during Pre-M (Fig. 4.40). First cluster is again divided in to two sub clusters and the second one showed further branching. Highest SPM, comparable levels of Cr, Co and Mn brought stations C2 and C3 together in a sub cluster. Simplicifolious cluster formed by C10 was characterised by lowest concentrations of all the metals except Co. Stations C1, C5-C9 clustered together based on higher concentrations of Mn compared to other coastal stations. Comparable levels of Co and Mn brought stations C1 and C6 together in third sub cluster. Station C5 was characterised with highest Ni content; C7 with lowest DO and highest Mn contents; C9 with highest Cd, Pb and lowest SPM contents. Stations C4 and C11 constituted the second major cluster and they showed higher concentration of Cd and Zn compared to other stations in the coast. C4 was associated with highest Co content and C11 highest Zn content.

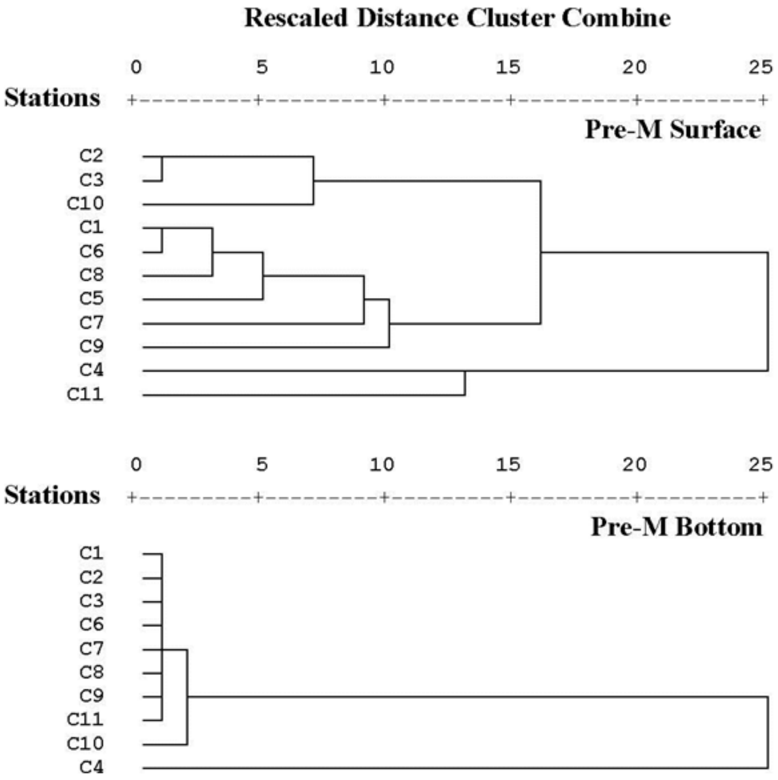

Figure 4.40 Dendrogram showing clusters of sampling locations in the coast during pre-monsoon

Two major clusters were obtained in the bottom during Pre-M (Fig. 4.40). Station C4 stood alone in the second major cluster and C4 showed variance from other stations with a very high level of Zn, which might have reached from the estuary as this stations is near the bar mouth. C10 showed dissimilarity from the first sub cluster in its lower levels of Mn, Fe, Zn, Cu, Ni, Cr and higher level of Pb in comparison with the stations C1-C3 and C6-C11. Unlike the surface stations, bottom stations showed well defined pattern of clustering, indicating more or less, an even distribution of metals in the bottom SPM.

Two major clusters were obtained for the surface stations during Mon (Fig. 4.41). First cluster was again clustered in to 4 and three of them were simplicifolious. First sub cluster formed by C5, C7, C8, C9 & C10 were characterised by comparable levels of Cr, Mn and SPM. C6 was associated with highest Pb content. Cluster formed by C11 was characterised with highest Cr and lowest Mn contents. C4 was associated with highest Co and highest SPM content. C3 showed higher levels of Pb, Cu, Zn and highest concentrations of Cd and Mn attributing to its dissimilarity with other stations. This station is near the bar mouth and it might be getting the metals from the estuary. C1 & C2 have similar and higher concentrations of Cu, Zn, Mn & Fe compared to rest of the stations which brought the stations cluster together.

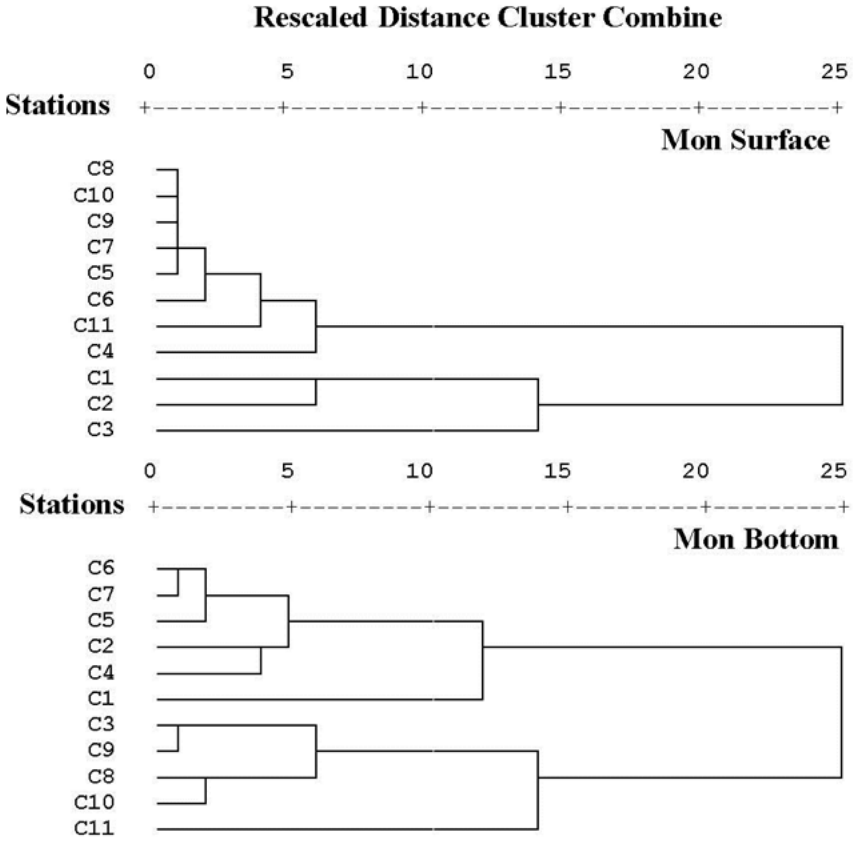

Figure 4.41 Dendrogram showing clusters of sampling locations in the coast during monsoon

Two major clusters were obtained for the bottom stations during Mon (Fig. 4.41). Sub cluster formed by C5, C6 and C7 was associated with higher

SPM content and comparable Cu concentrations. Cluster formed by C2 and C4 was characterised with similar distribution for Co, Cu and salinity. C1 formed simplicifolious cluster with highest concentrations of Pb, Mn and Fe. First sub cluster in second major cluster was constituted by stations C3 and C9 and were associated with comparable levels of Cr, Cu, Mn, Fe and SPM. Comparable levels of Zn, Fe, SPM and salinity brought stations C8 and C10 together in a sub cluster. Highest concentration of Cr and lowest concentrations of Cu & Zn compared to other stations brought C11 in the simplicifolious cluster.

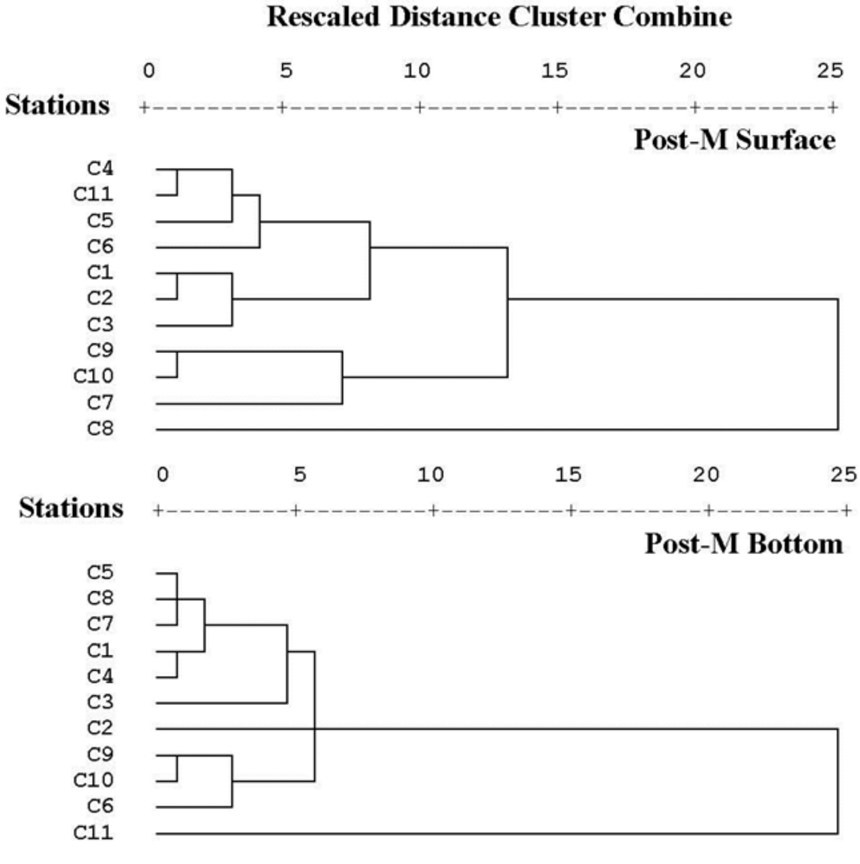

Figure 4.42 Dendrogram showing clusters of sampling locations in the coast during post-monsoon

During Post-M, sampling stations were grouped in to two clusters both in the surface and bottom, one of which was simplicifolious (Fig. 4.42). This season showed a diffuse clustering unlike Pre-M and Mon. In the surface, C8 formed a single membered major cluster with highest levels for Cr & Fe. First major cluster was again divided in to 3 sub clusters. C4 & C11 were found to be clustered together based on the similar concentrations of Pb, Ni, Mn & Fe. Stations C5 & C6 shown similarity to the above cluster with the comparable distribution for Ni. Sub cluster formed by C1, C2 & C3 was associated with higher levels of Mn in comparison with other stations. Sub cluster formed by C9, C10 & C7 were characterised with high levels of Pb and lower SPM content.

During Post-M, 4 sub clusters were found in the bottom (Fig. 4.42). Stations C5, C7 & C8 were clustered together based on the similar distribution of Cr, Ni and Co. C1 & C4 are characterised with similar concentrations of Fe. Simplicifolious cluster formed by C3 was characterised with highest content of Ni and higher levels of Cu, Zn, Fe and lowest DO. C2 was associated with highest Mn, higher Cd, Cr, Zn and Fe contents. Similar Pb, Co and salinity contents brought the stations C6, C9 & C10 together in a cluster. Second major cluster occupied by C11 is characterised with highest levels of Pb, Co and Cu.

4.3 Partition Coefficient

The simplest and most common method of estimating contaminant retardation is based on the partition (distribution) coefficient, Kd (Margaret and Bucher, 2012). Significance of metal partitioning lies in the fact that it determines whether an element is removed from the water column and accumulated in bottom sediments or it will be transported to an oceanic environment. Partitioning of metals between the SPM and the water was determined by the modification of the equation proposed by Ball (1988 & 1989) and Valenta *et al*. (1986), K_d = Conc. metal in SPM (mg/kg) / Conc. Metal in water (mg/l). Kd values of metals in the study area are given in the Tables 4.31 to 4.33 and that of the coast are given in the Tables 4.34 to 4.36.

In the estuary, Cd showed preference to the dissolved phase although partitioning among the two phases was more prominent during Pre-M. During this season, 63 and 88 % of the stations showed partitioning in the surface and bottom respectively. During Mon, Station E3 in the surface only detected with dissolved Cd. There was no partitioning of Cd during Mon season and Cd showed preference to the particulate phase. During Post-M, Cd showed preference to dissolved phase in the surface and particulate phase in the bottom. Preference of Cd to the dissolved phase during Pre-M and Post-M can be explained in terms of the salinity increase during these seasons. With the increase in salinity, the remobilization of free metal ions increased and the partition coefficient decreased. During Pre-M, Cd in the coastal area was partitioned between the dissolved and particulate compartments, except in the stations C7, C8 and C10 in the surface; C4 and C6 in the bottom, in which Cd remains in the dissolved form. During Mon, Cd was found to be below the detectable levels in stations C4-C6 and C11. Only 25 % of the surface stations were detected with dissolved and particulate Cd. In the bottom, Cd showed preference to the particulate phase. During Post-M, Cd remained in the dissolved form and there was no partitioning in the surface (exception C10). While in the bottom, stations C1 to C6 showed partitioning of Cd and in C7 to C10, Cd showed preference to dissolved phase. Cd in C11 was below the detectable levels. Cd showed preference to dissolved phase during Pre-M and Post-M seasons, while during Mon, particulate phase was preferred in the bottom.

Partitioning of Cd among the dissolved and particulate phases showed following trend in the study area, Pre-M > Post-M > Mon. In the estuary, partitioning was more pronounced in the bottom during Pre-M; surface during Post-M and there was no partitioning of Cd during the Mon season. While in the coast, partitioning was more pronounced in the bottom compared to the surface stations during the entire study period.

In the estuary, Pb showed preference to dissolved phase in the surface and bottom estuarine waters during Pre-M and this can be explained by the less efficient scavenging of Pb by particulate matter during this season. However, stations which showed partitioning among the dissolved and particulate phases were more in the bottom (56 %) compared to the surface (25 %). During Mon, Pb showed preference to the particulate phase and dissolved Pb was below the detectable levels in majority of the stations. Partitioning between the dissolved and particulate phases were similar both in the surface and bottom waters (44 % of the stations). During Post-M, Pb showed preference to the particulate phase. In the surface and bottom, 63 and 56 % of the stations respectively, exhibited partitioning among the two phases. In the coast, partitioning among the particulate and dissolved phases were more pronounced in the bottom compared to the surface stations. Pb showed preference to dissolved phase during Pre-M and in the surface during Mon; to particulate phase during Post-M and in the bottom during Mon. Higher dissolved Pb compared to the particulate fraction can be attributed to the increased river and land run off during Mon and the salinity induced desorption from particulates and sediments during Pre-M season (Elbaz-Poulichet *et al.,* 1986; Shibu, 1992). However, in the study period, Pb was found to be with more affinity to the particulate matter in the bottom. This can be attributed to the settling of SPM loaded with Pb in the bottom waters or the remobilisation from the bottom sediments due to activities like dredging (Luther *et al.,* 1986).

Table 4.31 Partition coefficients of metals in the estuary during pre-monsoon

Surface	Cd, L/kg (10^4)	Pb, L/kg (10^4)	Cr, L/kg (10^4)	Ni, L/kg (10^4)	Co, L/kg (10^4)	Cu, L/kg (10^4)	Zn, L/kg (10^4)	Mn, L/kg (10^4)	Fe, L/kg (10^4)
E1	0.53	0.00	0.95	0.00	5.00	0.93	0.90	108.39	0.00
E2	4.31	0.00	0.00	0.00	0.00	0.00	0.57	1904.76	0.00
E3	0.25	2.09	2.53	0.00	0.00	1.53	3.09	759.35	0.00
E4	0.00	0.00	1.97	0.59	158.76	0.78	4.81	4619.93	0.00
E5	0.84	0.00	2.98	0.00	0.00	0.00	0.00	2904.76	0.00
E6	0.39	0.00	1.70	1.40	0.00	0.67	0.62	236.99	53.12
E7	0.87	0.00	2.84	2.17	0.00	0.74	0.32	192.03	29.29
E8	0.00	1.32	2.82	0.54	0.00	1.55	0.35	161.69	197.29
E9	0.00	1.27	1.65	0.93	0.00	3.77	0.18	664.76	1211.43
E10	0.00	0.00	1.58	0.00	0.00	0.00	0.00	0.00	51.22
E11	0.00	0.00	2.49	0.04	21.37	0.71	2.83	172.35	132.23
E12	0.76	3.67	5.29	0.03	0.00	1.47	0.04	269.99	0.00
E13	0.00	0.00	2.58	0.00	0.00	0.73	4.07	1014.75	68.93
E14	0.05	0.00	2.79	1.55	0.00	0.37	1.18	68.33	2077.38
E15	0.92	0.00	1.14	0.87	5.23	0.00	1.69	54.70	0.00
E16	0.10	0.00	1.26	0.00	39.30	0.00	0.00	94.55	0.00
Bottom	**Cd, L/kg (10^4)**	**Pb, L/kg (10^4)**	**Cr, L/kg (10^4)**	**Ni, L/kg (10^4)**	**Co, L/kg (10^4)**	**Cu, L/kg (10^4)**	**Zn, L/kg (10^4)**	**Mn, L/kg (10^4)**	**Fe, L/kg (10^4)**
E1	0.27	0.00	1.09	0.20	0.00	2.77	1.04	160.38	0.00
E2	28.51	187.50	7.81	0.00	0.00	19.34	18.67	11955.88	90000.00
E3	0.04	0.00	3.34	0.31	0.00	1.62	3.15	181.82	0.00
E4	0.13	1.58	1.60	0.07	0.00	1.22	4.23	809.83	0.00
E5	0.77	0.00	3.69	0.85	0.00	3.42	3.62	1052.70	0.00
E6	0.00	5.77	3.44	1.10	0.00	1.27	1.86	102.54	38.99
E7	0.13	0.00	3.23	1.30	0.00	1.60	5.29	418.75	70.47
E8	0.00	2.82	3.08	0.76	0.00	1.55	4.62	214.16	58.17
E9	0.24	1.15	3.70	0.16	0.00	2.49	1.24	637.20	0.00
E10	0.49	1.11	2.11	0.17	0.00	1.04	2.92	120.77	177.88
E11	1.51	7.72	3.65	0.36	47.78	1.33	4.44	131.85	133.77
E12	0.26	2.56	4.43	0.62	0.00	1.43	1.29	147.96	0.00
E13	0.52	6.21	3.78	0.69	0.00	1.07	5.12	142.11	106.66
E14	0.42	0.00	2.81	0.54	0.00	1.13	3.60	41.70	1195.39
E15	0.03	0.00	3.50	0.63	0.00	1.19	3.27	59.87	0.00
E16	0.27	0.00	4.54	0.52	0.00	1.81	2.55	228.41	0.00

Table 4.32 Partition coefficients of metals in the estuary during monsoon

Surface	Cd, L/kg (10^4)	Pb, L/kg (10^4)	Cr, L/kg (10^4)	Ni, L/kg (10^4)	Co, L/kg (10^4)	Cu, L/kg (10^4)	Zn, L/kg (10^4)	Mn, L/kg (10^4)	Fe, L/kg (10^4)
E1	0.00	3.67	0.00	0.00	2.66	1.68	1.45	25.47	98.18
E2	0.00	19.79	0.00	0.00	2.67	1.85	1.26	282.41	47.09
E3	0.00	0.00	0.00	0.00	0.00	1.24	0.61	146.86	123.09
E4	0.00	0.00	0.00	0.00	0.00	2.08	4.24	83.85	109.70
E5	0.00	0.00	0.00	0.00	0.00	0.00	1.41	44.97	31.32
E6	0.00	0.00	0.00	0.00	0.00	0.83	6.52	4.88	88.75
E7	0.00	0.00	0.00	0.00	0.00	6.67	0.00	16.39	322.11
E8	0.00	19.44	0.00	0.00	0.00	4.17	0.00	17.17	447.66
E9	0.00	2.50	0.00	0.00	1.07	2.35	3.69	24.88	126.93
E10	0.00	3.25	0.00	0.00	0.00	4.55	0.00	55.01	788.23
E11	0.00	0.00	0.00	0.00	0.00	2.41	1.09	0.00	497.71
E12	0.00	48.90	0.00	0.00	7.15	2.93	0.00	0.00	778.78
E13	0.00	0.00	0.00	0.00	0.00	11.57	0.00	0.00	2231.84
E14	0.00	3.49	0.00	0.00	8.64	3.69	0.00	0.00	740.62
E15	0.00	0.00	0.00	0.00	0.00	1.93	0.00	0.00	799.46
E16	0.00	0.00	0.00	0.00	0.93	1.44	0.00	0.00	396.81
Bottom	**Cd, L/kg (10^4)**	**Pb, L/kg (10^4)**	**Cr, L/kg (10^4)**	**Ni, L/kg (10^4)**	**Co, L/kg (10^4)**	**Cu, L/kg (10^4)**	**Zn, L/kg (10^4)**	**Mn, L/kg (10^4)**	**Fe, L/kg (10^4)**
E1	0.00	7.67	0.00	0.00	6.89	0.88	1.30	22.88	266.23
E2	0.00	0.00	0.00	0.00	0.05	3.47	74.34	92.55	144.17
E3	0.00	0.00	0.00	0.00	4.39	0.00	0.00	11.54	22.60
E4	0.00	24.39	0.00	0.00	0.00	0.00	0.00	21.54	294.44
E5	0.00	24.24	0.00	0.00	6.17	3.79	2.57	6.26	9.13
E6	0.00	0.00	0.00	0.00	3.75	0.89	4.00	5.60	113.74
E7	0.00	0.00	0.00	11.39	0.00	0.00	5.54	2.87	55.48
E8	0.00	0.00	0.00	0.00	21.99	33.54	5.24	8.91	92.24
E9	0.00	0.00	0.00	0.00	5.07	2.15	4.95	16.92	7.80
E10	0.00	2.04	0.00	0.00	0.00	5.01	0.00	97.11	11.72
E11	0.00	12.81	0.00	0.00	0.00	3.20	0.00	0.00	811.27
E12	0.00	0.00	0.00	0.00	5.14	1.50	2.07	0.00	196.60
E13	0.00	14.63	0.00	0.00	8.31	5.08	8.64	0.00	957.09
E14	0.00	5.70	0.00	0.00	0.00	2.85	6.78	0.00	17.30
E15	0.00	0.00	0.00	0.00	0.00	1.58	4.16	0.00	365.32
E16	0.00	0.00	0.00	0.00	5.80	3.35	12.09	720.98	1.69

Strong adsorption onto clays, Al, Fe and Mn oxy-hydroxides (Marshall and Fairbridge, 1999), co-precipitation with carbonates (Salomons and Förstner, 1984) and formation of insoluble hydroxides (Stumm and Morgan, 1996) were reported to reduce the dissolved Pb fraction in the surface waters. In aquatic environments, Pb has been reported to complex with dissolved organic carbon, thus decreasing its bioavailability (Paquin *et al.,* 2002, Nolan *et al.,* 2003). However, preference to the dissolved phase during Pre-M season may be attributed to the salinity induced desorption from particulates and sediments and this has been reported in many previous studies in Cochin estuary (Shibu, 1992; Unnikrishnan and Nair, 2004). Lead initially adsorbed onto particles in the upper estuary can subsequently be released back to the dissolved phase at higher salinities (Elbaz-Poulichet *et al.,* 1986). Partitioning of Pb among the dissolved and particulate phases showed following trend in the entire study area, Post-M > Mon > Pre-M.

Cr showed preference to the particulate phase in the entire study area. Partitioning was strong only during Pre-M. There was no partitioning of Cr during Mon and Post-M (except E5 in the surface; C5 in the surface and bottom) as the dissolved phases were below the detectable levels in the estuary and coastal waters.

Although Nickel was partitioned between the two phases during Pre-M (56 % in surface & 94 % in bottom) followed by Post-M (50 % in surface & 75 % in bottom) seasons, it showed preference to the dissolved phase. Partitioning was more prominent in the bottom estuarine stations compared to the surface. Ni showed no partitioning in the estuary during Mon season and both the dissolved and particulate Ni was below the detectable limits in many of the stations during this season. In the coast also partitioning followed a trend, Pre-M > Post-M > Mon. Ni showed affinity to the dissolved phase compared to the particulate phase during the study period. Unlike the estuarine stations, Ni was partitioned between the two phases during Mon season. Partitioning was more pronounced in the bottom during Pre-M (63 % in surface & 80 % in bottom) and Mon (18 % in surface & 45 % in bottom), whereas during Post-M, more surface stations exhibited partitioning among two phases (64 % in surface & 55 % in bottom). The partitioning behaviour of Ni was characterized by the preference of Ni to the dissolved phase and this behaviour could be attributed to the formation of chloride and sulfate complexes of Ni at higher salinities leading to a depletion of Ni in the particulate phase. Considerable portion of Ni ions has been reported to exist in sea water as complexes with chloride and sulfate ions (Nriagu, 1980).

Table 4.33 Partition coefficients of metals in the estuary during post-monsoon

Surface	**Cd, L/kg (10^4)**	**Pb, L/kg (10^4)**	**Cr, L/kg (10^4)**	**Ni, L/kg (10^4)**	**Co, L/kg (10^4)**	**Cu, L/kg (10^4)**	**Zn, L/kg (10^4)**	**Mn, L/kg (10^4)**	**Fe, L/kg (10^4)**
E1	2.53	0.00	0.00	0.00	15.53	3.55	4.89	2108.55	2670.86
E2	6.22	12.99	0.00	0.00	8.31	10.10	2.52	1549.78	0.00
E3	0.00	0.00	0.00	0.00	11.51	71.43	0.00	697.92	0.00
E4	0.00	142.86	0.00	0.00	42.59	28.33	93.93	298.10	0.00
E5	0.00	60.39	0.00	0.00	2.35	0.00	2.45	995.12	0.00
E6	0.00	0.00	0.00	0.00	4.59	6.67	0.00	339.61	0.00
E7	0.00	29.02	0.00	0.00	8.81	3.02	0.00	504.46	0.00
E8	0.00	0.00	0.00	8.92	10.55	5.26	4.53	421.74	1166.67
E9	0.00	47.03	0.00	26.20	4.93	6.96	15.70	1290.15	682.97
E10	0.00	153.51	0.00	6.65	33.21	1.39	21.11	318.08	374.07
E11	0.00	32.83	0.00	11.54	11.30	14.31	0.00	216.61	10481.48
E12	0.00	0.00	0.00	4.48	6.45	8.85	0.00	187.65	0.00
E13	0.00	64.58	0.00	6.03	3.70	9.31	104.69	2756.25	11295.83
E14	25.30	13.47	0.00	4.57	4.41	8.18	0.00	632.66	0.00
E15	0.00	0.00	0.00	0.00	5.20	1.49	0.00	1339.29	72.30
E16	0.00	28.47	0.00	0.00	9.73	6.81	0.00	1039.60	211.86
Bottom	**Cd, L/kg (10^4)**	**Pb, L/kg (10^4)**	**Cr, L/kg (10^4)**	**Ni, L/kg (10^4)**	**Co, L/kg (10^4)**	**Cu, L/kg (10^4)**	**Zn, L/kg (10^4)**	**Mn, L/kg (10^4)**	**Fe, L/kg (10^4)**
E1	0.00	14.00	0.00	7.60	0.00	3.38	2.90	2014.86	0.00
E2	1.83	99.21	0.00	0.00	7.01	3.36	3.95	696.71	0.00
E3	0.00	0.00	0.00	1.31	2.25	5.15	10.21	557.32	0.00
E4	0.00	0.00	0.00	0.00	17.06	0.00	0.00	3.07	0.00
E5	0.00	0.00	68.03	0.00	1.29	1.73	1.81	61.36	0.00
E6	0.00	0.00	0.00	2.49	7.29	7.21	9.28	269.90	0.00
E7	0.00	17.09	0.00	0.00	3.94	0.00	0.00	49.89	114.59
E8	0.00	0.00	0.00	10.59	6.99	0.00	0.00	135.30	110.65
E9	0.00	131.15	0.00	16.07	3.90	12.02	0.00	3362.02	0.00
E10	0.00	12.28	0.00	2.66	1.68	6.89	489.08	140.44	0.00
E11	0.00	12.49	0.00	4.06	6.04	6.24	71.82	370.58	0.00
E12	0.00	45.65	0.00	9.66	58.99	5.89	0.00	136.24	0.00
E13	0.00	0.00	0.00	2.83	0.00	5.96	45.42	181.07	323.59
E14	0.37	0.00	0.00	1.45	2.79	5.29	0.00	237.39	15.54
E15	0.00	15.80	0.00	2.11	8.85	20.59	0.00	577.41	47.54
E16	0.00	112.45	0.00	4.44	3.87	7.46	59.04	1667.34	38.72

Co showed the following trend in partitioning Post-M > Mon > Pre-M in the study area. During Pre-M, Co showed affinity to the particulate phase. Only 31 % of the estuarine stations showed partitioning between the two phases and partitioning was absent in the bottom waters. During Mon, Co showed preference to the dissolved phase and 31 and 56 % of the surface and bottom stations respectively exhibited partitioning. During Post-M, all the stations in the surface and stations except E1 and E13 in the bottom exhibited partitioning between dissolved and particulate phases. In the coast, Co showed preference to the particulate phase in all the seasons except in the surface during Mon. Partitioning was more pronounced in the bottom during Mon and Post-M, whereas it reversed during Pre-M.

Although Cu was partitioned between the dissolved and particulate phases in majority of the estuarine stations, it showed preference to the dissolved phase. This can be attributed to complexing by dissolved organic Cu-complexing ligands. During Pre-M, Cu was partitioned in all the bottom stations and in 69 % of the surface stations. During Mon and Post-M, 94 and 81 % of the surface and bottom stations respectively exhibited partitioning between the dissolved and particulate phases. In the coast, partitioning was pronounced in the bottom stations in the study period. Partitioning was higher during Mon followed by Post-M and Pre-M seasons. Dissolved phase of Cu dominated in the coastal waters also. Preference of Cu to the dissolved phase can be attributed to the availability of dissolved organic matter to which copper is known to be mainly associated with in estuarine waters (Donat *et al.,* 1994; Baeyens *et al.,* 1998; Shank *et al.,* 2004). Speciation of dissolved Cu in natural waters is dominated by interactions with dissolved organic matter (DOM), and the formation of relatively stable Cu-DOM complexes. These complexes are assumed not to be bioavailable (Sunda and Guillard, 1976) and therefore it is unlikely that Cu poses any ecological risk.

Table 4.34 Partition coefficients of metals in the coast during pre-monsoon

Surface	Cd, L/kg (10^4)	Pb, L/kg (10^4)	Cr, L/kg (10^4)	Ni, L/kg (10^4)	Co, L/kg (10^4)	Cu, L/kg (10^4)	Zn, L/kg (10^4)	Mn, L/kg (10^4)	Fe, L/kg (10^4)
C1	0.11	0.00	0.00	1.40	68.05	0.34	0.74	400.88	1504.39
C2	0.51	0.00	46.26	1.64	35.51	0.58	2.26	71.03	0.00
C3	1.31	0.00	16.32	0.57	10.52	0.54	1.51	63.28	235.31
C4	3.32	0.00	1.50	0.00	0.00	0.00	8.10	35.98	208.88
C5	1.13	0.00	2.60	3.65	0.00	9.44	0.00	364.20	3621.40
C6	1.18	2.65	0.58	0.00	0.00	0.00	0.00	1196.30	1172.84
C7	0.00	0.00	0.66	0.37	0.00	0.65	3.34	402.36	0.00
C8	0.00	0.00	2.87	2.93	0.00	0.00	0.93	240.28	0.00
C9	2.01	33.09	1.49	0.83	0.00	0.00	0.00	262.03	0.00
C10	0.00	0.00	0.22	0.00	0.00	0.00	0.00	49.15	491.45
C11	0.91	0.00	1.24	0.00	0.00	0.56	5.57	32.25	0.00
Bottom	**Cd, L/kg (10^4)**	**Pb, L/kg (10^4)**	**Cr, L/kg (10^4)**	**Ni, L/kg (10^4)**	**Co, L/kg (10^4)**	**Cu, L/kg (10^4)**	**Zn, L/kg (10^4)**	**Mn, L/kg (10^4)**	**Fe, L/kg (10^4)**
C1	0.61	0.00	0.00	3.15	5.46	2.47	4.83	141.14	0.00
C2	0.91	0.00	24.35	1.64	11.28	1.78	4.19	151.29	0.00
C3	0.27	10.35	75.68	0.92	0.00	2.52	7.49	491.07	426.91
C4	0.00	36.12	4.29	1.29	0.00	0.33	1.32	482.76	0.00
C6	0.00	0.00	12.00	1.17	0.00	1.48	2.21	77.72	0.00
C7	0.28	0.00	5.31	0.00	0.00	2.46	4.77	153.61	0.00
C8	0.66	0.00	5.90	1.67	0.00	2.78	4.71	0.00	1427.97
C9	2.26	20.47	7.88	1.29	0.00	1.87	7.17	208.19	6081.87
C10	0.58	7.91	1.14	0.00	0.00	0.00	2.92	30.83	459.48
C11	0.407	10.694	13.573	0.630	0.000	4.061	5.434	195.95	1624.92

Partitioning of Zn was higher during Pre-M followed by Mon and Post-M seasons. Industries lying to the northern side of the Cochin estuary were reported as the source of Zn and the low flow conditions during Pre-M could be attributed to the high amount of Zn both in the dissolved and particulate phases. Zn preferred particulate phase during Mon and Post-M seasons. Preference to the dissolved phase during Pre-M can be attributed to the desorption of Zn from sediment particles at higher salinity (Ackroyd *et al.,* 1986; Dehairs *et al.,* 1989); the remobilisation processes of recently deposited biogenic particulates (Kremling *et al.,* 1997), anthropogenic inputs (Sankaranarayanan *et al.,* 1978; Paul and Pillai, 1983a; Nair *et al.,* 1990; Ouseph, 1992; Shibu *et al.,* 1990; Shibu *et al.,*1995; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,*2006; SCMC, 2004; Martin *et al.,* 2008; Deepulal *et al.,* 2012) and also association of zinc with organic matter (Paul and Pillai, 1983b). During Pre-M, Zn was partitioned between the dissolved and particulate phases in all the bottom coastal stations. Only 64 % of the surface stations exhibited partitioning and Zn showed preference to dissolved phase in the surface waters. Although Zn preferred particulate phase during Mon, partitioning was more pronounced compared to other seasons. In the study area, partitioning of Zn was lower during Post-M season.

During Pre-M, Mn was partitioned between the dissolved and particulate phases in all the estuarine stations in the surface (except E10) and bottom. During Mon, Mn preferred to attach to the particulate phase endorsing its particle reactive nature (Balls, 1989; Vignati, 2004) and partitioning was less compared to other two seasons. During Post-M, Mn was partitioned between the dissolved and particulate phases in all the stations. In the coast, Mn in the surface water was partitioned between the dissolved and particulate phases irrespective of the seasons. In the bottom, all the stations exhibited partitioning during Mon. While, stations C8 and C10 in the bottom were devoid of partitioning during Pre-M and Post-M seasons respectively. The resuspension of fine grained particles, from the bottom sediments of the comparatively shallow water column, which are highly enriched with manganese, is a major reason for the increased concentration of Mn in the particulate phase.

In the estuary, Fe was partitioned between the dissolved and particulate phases during Mon. 50 % of the stations during Pre-M; 50 % and 38 % of the stations in the surface and bottom respectively during Post-M, exhibited partitioning. Partitioning followed the trend Mon > Pre-M > Post-M in the estuary. Partitioning of Fe in the coastal area was prominent during the Mon season, both in the surface (Except in C3) and bottom. While during Pre-M and Post-M, approximately 50 % of the stations only exhibited partitioning. Fe showed preference to particulate phase in the study area indicating its particle reactive nature (Balls, 1989; Vignati, 2004).

Table 4.35 Partition coefficients of metals in the coast during monsoon

Surface	Cd, L/kg (10^4)	Pb, L/kg (10^4)	Cr, L/kg (10^4)	Ni, L/kg (10^4)	Co, L/kg (10^4)	Cu, L/kg (10^4)	Zn, L/kg (10^4)	Mn, L/kg (10^4)	Fe, L/kg (10^4)
C1	8.60	0.00	0.00	0.00	0.00	0.92	3.57	414.46	866.31
C2	0.00	0.00	0.00	0.00	3.08	2.88	3.30	124.16	155.95
C3	0.00	0.00	0.00	0.00	0.00	1.97	3.32	270.54	0.00
C4	0.00	1.20	0.00	0.00	18.16	1.10	1.46	133.77	72.07
C5	0.00	0.00	0.00	0.00	0.00	1.14	0.75	40.00	154.26
C6	0.00	0.00	0.00	0.00	16.54	5.21	0.00	69.11	230.79
C7	0.00	0.00	0.00	0.00	0.00	2.60	2.38	122.52	53.18
C8	0.00	0.00	0.00	1.28	0.00	2.10	1.93	23.03	6.12
C9	0.00	3.76	0.00	1.34	0.09	0.00	8.85	36.78	22.80
C10	0.00	0.00	0.00	0.00	0.00	0.00	6.47	68.68	39.98
C11	0.00	0.00	0.00	0.00	0.00	1.46	4.27	62.79	44.96
Bottom	**Cd, L/kg (10^4)**	**Pb, L/kg (10^4)**	**Cr, L/kg (10^4)**	**Ni, L/kg (10^4)**	**Co, L/kg (10^4)**	**Cu, L/kg (10^4)**	**Zn, L/kg (10^4)**	**Mn, L/kg (10^4)**	**Fe, L/kg (10^4)**
C1	2.32	5.73	0.00	0.28	0.60	2.55	3.02	51.26	627.30
C2	1.95	2.68	0.00	0.00	11.54	4.12	0.62	109.57	898.69
C3	0.00	1.20	0.00	0.00	0.00	1.29	1.90	32.46	763.05
C4	0.00	2.98	0.00	0.00	6.08	1.94	1.89	61.42	58.57
C5	0.00	3.01	0.00	0.00	22.45	2.06	1.24	30.47	280.38
C6	0.00	4.69	0.00	0.58	1.61	1.50	92.62	29.13	42.38
C7	0.00	3.60	0.00	0.00	6.06	1.23	0.00	22.55	8.14
C8	0.00	5.32	0.00	0.00	0.00	2.66	27.30	57.93	311.56
C9	0.00	0.00	0.00	0.52	0.02	2.97	0.00	1.88	53.29
C10	0.00	0.00	0.00	1.52	1.12	1.89	55.97	203.77	511.01
C11	0.00	1.78	0.00	0.00	0.72	0.51	0.19	68.21	354.34

Spatial and Temporal Variations

In the estuary, significant temporal variations were shown by the metals Pb (p value = 0.004), Cr (p value = 1.3×10^{-10}), Ni (p value = 0.01), Cu (p value = 0.014) and Mn (p value = 0.012) in the surface; Ni (p value = 0.006) in the bottom. Significant temporal variations shown by majority of the metals under study indicated that their distribution coefficient (K_d) in the estuary mainly depend on the suspended particulate matter distribution. General increases in the suspended matter during the seasons of high seasonal variations were reported in Cochin estuarine system (Rama Raju *et al.,* 1979) and seasonal or short term fluctuations were reported to cause variation in the particulate heavy metals concentrations in this estuary (Sankaranarayanan *et al.,* 1998). Phytoplankton blooms during the non-monsoon months may also indirectly affect heavy metal concentrations by increasing the pH, which favour sorption onto suspended matter.

Although SPM and particulate Zn concentrations exhibited temporal variation significant at 95 % confidence levels in the surface, lack of seasonality in K_d values suggested that the above seasonal fluctuations were of minor importance in the partitioning of zinc. Zn was always detected in high concentrations in the estuarine area irrespective of the seasons which might be attributed to the industries lying north to the Cochin estuary (Sankaranarayanan *et al.,* 1978; Paul and Pillai, 1983a; Nair *et al.,* 1990; Ouseph, 1992; Shibu *et al.,* 1990; Shibu *et al.,*1995; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; SCMC, 2004; Martin *et al.,* 2008; Deepulal *et al.,* 2012; Bindu *et al.,* 2015).

In the coast, partitioning among the dissolved and particulate phases showed significant temporal variations in the case of Pb (p value = 0.0002), Ni (p value = 0.015) and Cu (p value = 0.027) in the surface; Ni (p value = 0.047) and Cu (p value = 0.032) in the bottom. Nickel was the only metal which showed significant temporal variation in partitioning in the study area both in the surface and bottom. Spatial variation in the partitioning of metals under study was not significant in the study area.

Table 4.36 Partition coefficients of metals in the coast during post-monsoon

Surface	Cd, L/kg (10^4)	Pb, L/kg (10^4)	Cr, L/kg (10^4)	Ni, L/kg (10^4)	Co, L/kg (10^4)	Cu, L/kg (10^4)	Zn, L/kg (10^4)	Mn, L/kg (10^4)	Fe, L/kg (10^4)
C1	0.00	0.00	0.00	0.00	0.00	5.88	2.00	561.84	141.70
C2	0.00	40.38	0.00	0.00	0.00	19.23	0.00	390.11	0.00
C3	0.00	0.00	0.00	3.08	0.00	2.34	5.27	482.42	178.30
C4	0.00	19.36	0.00	3.39	0.00	3.62	0.63	221.19	0.00
C5	0.00	12.73	1020.00	2.15	0.00	16.89	0.00	255.00	355.27
C6	0.00	49.48	0.00	2.41	10.91	0.57	0.28	15.07	0.00
C7	0.00	27.49	0.00	9.76	5.69	39.76	0.00	45.36	0.00
C8	0.00	9.10	0.00	5.13	13.38	0.00	0.00	180.56	116250.00
C9	0.00	55.56	0.00	0.00	9.86	0.00	0.00	11.36	0.00
C10	22.28	37.80	0.00	0.00	58.54	12.87	14.64	19.14	64554.46
C11	0.00	0.00	0.00	6.61	10.91	0.00	0.00	225.93	0.00
Bottom	**Cd, L/kg (10^4)**	**Pb, L/kg (10^4)**	**Cr, L/kg (10^4)**	**Ni, L/kg (10^4)**	**Co, L/kg (10^4)**	**Cu, L/kg (10^4)**	**Zn, L/kg (10^4)**	**Mn, L/kg (10^4)**	**Fe, L/kg (10^4)**
C1	53.85	11.06	0.00	0.00	0.00	7.69	23.08	110.38	1041.99
C2	0.63	6.97	0.00	3.40	0.00	3.77	4.73	69.59	666.01
C3	0.10	47.62	0.00	3.92	37.34	24.17	0.00	26.29	0.00
C4	0.31	0.00	0.00	0.00	2.48	1.38	0.00	31.30	0.00
C5	2.12	7.63	57.11	3.42	2.44	0.00	0.00	1026.53	83.20
C6	0.76	87.45	0.00	3.29	7.44	14.45	5.49	15.89	0.00
C7	0.00	32.26	0.00	1.85	3.62	4.58	6.42	58.56	833.66
C8	0.00	3.23	0.00	2.40	2.95	13.85	0.00	32.84	0.00
C9	0.00	18.33	0.00	0.00	9.36	1.96	0.00	48.96	505.26
C10	0.00	5.97	0.00	0.00	7.58	0.00	9.43	14.68	415.09
C11	0.00	423.08	0.00	0.00	9.58	51.28	0.00	0.00	0.00

Parametric Relationship with Salinity, DO, pH and SPM

Kd is not a true equilibrium coefficient, but is an empirical term, which depends on factors such as pH, temperature, redox condition, solution composition, and concentration of colloids in the 'dissolved' phase, metal speciation and heterogeneity of the particle surfaces (Hatje *et al.,* 2003a). The resuspension by storm action, pH variation and the change in salinity favour the increase of metals in the solution (Kayode *et al.,* 2009). The distributions of partition coefficients in energetic, tidally influenced systems are controlled principally by variations in the salinity and the particle concentration (Turner, 1996).

In the estuary, variation of partition coefficient of all the metals with salinity was found to be scattered. This result suggested that the distribution of particulate metals in the Cochin Estuary was not dominated by a simple mixing of the riverine and marine particles and this estuarine mixing was reported to be interrupted when these chemical components are involved in estuarine reactions or are added to the estuary (Regnier and Wollast 1993; Benoit *et al.,* 1994) by anthropogenic means. The absence of a more general dependence of partitioning of heavy metals and salinity may be explained by the restricted salinity range observed in the present study area (20-35), and the widespread anthropogenic sources of metals to the estuary. Variations in partitioning coefficients were reported to be not affected by differences in salinity and pH in areas of salinity greater than 20 (Balls, 1989; Hatje *et al.,* 2003b). In the coast also, partitioning coefficients of all the metals under study was found to be scattered; the more significant relation was with Mn in the surface during Mon (r^2 value = 0.79, n=11).

Partitioning coefficients were not correlated to pH in the study area. In the estuary, dissolved oxygen was correlated positively (n=16) to partitioning coefficients of Fe ($r^2 = 0.61$), Cd ($r^2 = 0.63$), Pb ($r^2 = 0.64$), Zn ($r^2 = 0.62$), Mn ($r^2 = 0.59$), Cu ($r^2 = 0.56$) in the bottom during Pre-M. This suggested the precipitation of Fe and Mn hydrous oxides and scavenging of other metals. In the coast, DO did not correlate to the partitioning coefficients of any of the metals. SPM in the estuary was not correlated to partitioning coefficients of any of the metals under study. However in the coast, it was correlated (n=11) to the Kds of Cr ($r^2 = 0.51$) during Pre-M and Mn ($r^2 = 0.56$) during Post-M in the surface.

4.4 Conclusions

During Pre-M season, the entire estuary is heavily contaminated with respect to the dissolved metals Cd, Pb, Cr, Ni and Co compared to the coast. Except the high concentration found in some stations, Cu, Zn, Mn and Fe were found to be almost comparable in both the provinces. During Mon, Cd was detected only in the estuarine stations near the barmouth and northern and central coastal stations. Dissolved Pb and Ni were found to be higher in coastal environment. Estuary and coast were associated with almost comparable Co, Cu and Fe contents. Dissolved Zn was found higher in northern estuary and Mn was higher in central estuary during Mon season. During Post-M, northern estuarine and central coastal stations were contaminated more with respect to dissolved Cd. Pb and Ni were found to be higher in coastal waters, while Co, Cu and Zn were higher in estuary. Dissolved Mn was higher in the surface estuarine stations and the bottom coastal stations. Fe was detected in higher levels in the southern estuarine stations and coastal stations north and south of the bar mouth.

Particulate Cd was detected exceptionally high in E2 and it was comparable in rest of the coastal and estuarine stations during Pre-M and Post-M. During Mon, highest concentrations were detected in surface coastal stations near the bar mouth. This can be attributed to the seaward retrieval of saline front (where precipitation of Cd occurs) due to the increased monsoonal surface runoff. Particulate Pb was higher in the estuary than the coast during Post-M and it was comparable during Mon and Pre-M seasons. Cr was found to be almost comparable during Pre-M and Post-M seasons, whereas it was higher in estuary during Mon season. Ni was found higher in central estuarine and coastal stations. Except in some stations, particulate Co and Cu were almost comparable in the estuary and coast. Zn, Mn and Fe were detected higher in the estuary compared to the coast.

Kd values of elements like Fe, Mn, Pb and Co was infinitely large in many of the stations because the dissolved phase concentrations were not in a detectable range in these stations against the high concentrations found in the suspended particulate matter endorsing their particle reactive nature. Particle-less reactive metals like Cd, Ni, Cu, Zn and Cr were also associated with high Kd values indicating their geochemical behaviour also controlled by SPM. High Kd values indicate affinity of an element to be associated, and transported with the particulate phase in an aquatic system and so Kds are significant in pollution assessment. High partition coefficients observed for all the metals indicated that these metal ions tend to be bound to SPM. Hence dissolved metal, the bio available fraction, was lower and their geochemical behaviour was strongly controlled by SPM in the study area. Hence the fate of these metals in this study area was to adsorb on to the SPM and finally sink to the bottom sediments for the burial unless and until they are disturbed by the resuspension processes which bring them back to the cycle.

The measurements of pollutants in the water column are not conclusive due to the fluctuations in water discharge and low residence time of these pollutants. The same holds true for the suspended matter also. However, pollutants have a longer residence time in the sediments and it serves as the ultimate sink for these pollutants. Hence sediment analysis can serve as a useful indicator of heavy metal pollution.

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Chapter 5

SEDIMENTARY HEAVY METALS

Contents

5.1 Introduction

Sediments get into the hydrosphere from the atmosphere, rivers and streams, glacial activities and ground water. At the reduced flow rates and low velocities, suspended particulates settle down and get incorporated into the bottom sediments. Hence, the chemical composition of the sediments reflects that of the overlying water column (Salomons and Forstner, 1984). Lake sediments provide a useful archive of information on changing lacustrine and watershed ecology (Cohen, 2003). While reflecting the current quality status of an aquatic environment, sediments also give vital information on the transport and fate of the pollutants. Sediment analysis plays significant role within the framework of environmental surveys in those cases in which water column analysis is not sufficient to trace a short-term or past pollution (Meiggs, 1980). Estuarine sediments is a fundamental step in the pathway of contaminants to the oceans as these estuaries filter the fluvially fluxed metals derived from both natural and anthropogenic sources (Larrose *et al.,* 2010). Sediments are heterogeneous assemblages of various sorbent phases like organic matter as well as oxide, sulfide, carbonate and alumino-silicate minerals, whose relative abundance is controlled by pH, redox conditions and the depositional environment. Hence, the sediment matrix comprises varieties of coexisting phases which adsorb the heavy metals. The capability of the sediment to concentrate even the trace levels of majority of the metals render them useful indicators for monitoring purposes and for source identification of pollutants of an the aquatic system.

Heavy metals are considered as main anthropogenic pollutant in the coastal and marine environments (Ruilian *et al.,* 2008) and they have shown to be significantly hazardous in aquatic environments, even at very low concentrations (Nriagu and Pacyna, 1988; Salomons and Stigliani, 1995). They are of high ecological significance since they are not removed from water as a result of self-purification but accumulate in reservoirs and enter the food chain (Loska and Wiechula, 2003). Due to their particle reactivity, heavy metals tend to accumulate in sediments (Forstner and Wittman, 1983). The toxic metals in water and sediments will be incorporated into the aquatic food webs (Chapman *et al.,* 1998), and bio-magnified (Wang, 2002; Viana *et al.,* 2005) and can contribute to the degradation of aquatic ecosystems by reducing the species abundance and diversity (Hosono *et al.,* 2011). Aquatic sediments represent one of the ultimate sinks for the heavy metals released into the environment (Gibbs, 1972; Bettinetti *et al.,* 2003; Hollert *et al.,* 2003) and these metals accumulate in sediments through complex physical/chemical adsorption mechanisms, depending on the nature of the sediment matrix. Behaviour of heavy metals in the coastal sediments is mostly correlated to their capacity for complexation with dissolved/colloidal/ particulate organic matter phases. Under varying environmental conditions, these sediment bound heavy metals may be remobilized within the sedimentary compartment as well as the water column via biological and chemical agents and thenceforth enter the food chain. Thus, sediments represent not only a repository of metals but also a source which transfer them to the water column and biota (Adams *et al.,* 1992; Nipper, 1997; Prica *et al.,* 2008; Rigaud *et al.,* 2013; Oursel *et al.,* 2014; Superville *et al.,* 2014), increasing risks for aquatic ecosystems. Sediments may carry heavy metals up to five orders of magnitude above the overlying water (Bryan and Langston, 1992). Estuaries, which form the part of coastal systems, are also a major reservoir of naturally and anthropogenically derived heavy metals (Bryan *et al.,* 1985; Langston, 1982) and spatial variation of metals in the surface sediments of urbanized estuaries is often attributed to the mixing of the sediments of different origins and to the pollution sources (Forstner, 1981).

The measurement of heavy metal concentrations and their distribution in marine environments leads to a better understanding of the behaviour of metals and is also important in detecting the pollution sources (Unnikrishnan and Nair, 2004). Heavy metals like Cd, Zn, Cr, Ni etc. are used in pollution assessments in marine systems as they are mainly associated with anthropogenic activities (Burton *et al.,* 2004; Munuz *et al.,* 2004). Since sediments often constitute the ultimate depository for heavy metals released into aquatic systems, their analysis offers significant advantages over the water analysis in the monitoring of metal contamination in estuaries, assuming that the metals are not substantially mobilized after the deposition (Forstner and Wittman, 1983; Luoma, 1990; Belzile *et al.,* 2004). Hence, the metal concentrations and its distribution patterns in sediments provide the best information on the spatial extent, the magnitude of anthropogenic contributions and may be useful indicators of contaminant related biological stress in estuarine ecosystems (Birch and Olmos, 2008).

Higher concentrations of particulate Fe, Mn, Cu and Zn have been reported in the Cochin estuary (Sankaranarayan and Stephen, 1978).

Dominance of particulate metals over the dissolved phase with increasing salinity, due to precipitation, adsorption and flocculation processes have been reported (Shibu, 1992). The meandering flow in the perennially-undulating water bodies or null zones of Cochin estuary induces faster coagulation or co-precipitation of dissolved metals as colloids in association with the hydrous iron oxides by ion-exchange processes under the fluctuating salinity due to the estuarine mixing (Balachandran *et al.,* 2005). The weak flushing in the null zones with relatively long water residence times has resulted in the entrapment of fine colloidal particles with the heavy metals which settle to the bottom increasing the sediment metal concentrations in Cochin estuary (Nair *et al.,* 1993; Balachandran *et al.,* 2006). Chronological enrichment of metals in the sediments of the north-west Cochin estuary showed a 3-fold enrichment for Fe, Cu and Pb, 10-fold enrichment for Cd and 25-fold enrichment for Zn, placing northern part of the Cochin estuary among the most impacted in the world (Balachandran *et al.,* 2005).

In spite of the numerous industries and the consequent discharges of wastewater effluents into Cochin estuary and hence the nearby coast, limited studies have been carried out so far on assessing their impacts and the extent to which these sediments have been contaminated by metal rich waste discharges (Martin *et al.,* 2012; Robin *et al.,* 2012). Although separate studies on the heavy metal distributions in water, suspended particulates and sediments of the Cochin estuarine system and the adjacent coast are available, combined study are rarely reported (Shajan, 2001; Balachandran *et al.,* 2005; Balachandran, 2006). There is an increasing need to assess the distributions of heavy metals in the surface sediments, which serve as an important sink and source, to understand the overall status of heavy metal pollution and the associated ecological risks. In this context, a detailed study of the biogeochemical cycles of heavy metals in Cochin estuary and its adjacent coast with emphasis on the driving processes is aimed at. This chapter deals with the evaluation of the spatial and seasonal variations of nine heavy metals (Cd, Pb, Cr, Ni, Co, Cu, Zn, Mn and Fe) in the sediments of Cochin estuarine and its adjacent coastal systems. Possible sources and similarity in behaviour of heavy metals were identified from the correlation matrix (Pearson correlation) between metals; metals and other sedimentary parameters. Global average shale value was used to assess the localized enrichment on a global perspective although it ignores natural geochemical variability. It cannot take in to account of the natural anomalous concentrations above the shale value and so this comparison may lead to false anomalies being recognised in those area (Covelli and Fontolan, 1997; Abrahim and Parker, 2008). Considering the above things, metal contents were compared with average shale values in order just to assess the enrichment in the study area. Statistical analysis like PCA and CA were also employed to find out the possible sources, transport and fate of the above said metals and to classify the stations based on the metal distribution.

5.2 Results & Discussions

Concentrations of the metals analysed in the sediments of the estuary and its adjacent coast are given in the appendix 23 to 25. Comparing the metal data with average shale, enable us to have an idea about the enrichment of these metals is whether through natural or anthropogenic sources. Heavy metal concentrations were compared with shale average values reported by Wedephol (1995).

5.2.1 Metal Distribution

Cadmium

Annual average of Cd content in the estuarine sediments was 2.16 ± 1.92 mg/kg (Fig. 5.1). Highest value (9.39 mg/kg) was reported in the station E1 during Pre-M. Station E5 also showed higher Cd content compared to other stations as this station might be accumulating the metals received from the northern industries, because of the weak flow in this null zone. Same observation was reported previously by Deepulal *et al.* (2012). Higher values reported in the northern stations could be attributed to the industrial area lying north to the Cochin estuary. Lowest value (0.02 mg/kg) was reported in E3 during Post-M.

Cadmium in the coastal sediments showed an annual average of 1.90 ± 0.74 mg/kg (Fig. 5.1). Highest and lowest values were recorded in C5 (3.15 mg/kg) and C4 (0.29 mg/kg) respectively during Pre-M. Stations C3 and C4 were associated with lower values during the study period as the periodic dredging occurring in the shipping channel and high energy condition prevailing in the bar mouth prevent accumulation of estuarine derived metals in this region. Stations, C5-C8 shown higher Cd concentrations compared to other coastal stations which might have been retrieved from the dredge spoil which is discharged at about 12 m depth each on the south and north of the navigational channel (Balachandran, 2001).

During Pre-M and Mon seasons, Cd concentration in the estuarine and coastal sediments was above the world shale average value (0.1 mg/kg) indicating enrichment of Cd in the study area. Stations except E3, E11, E14 and E16 were above the average shale value indicating higher degree of Cd enrichment during Post-M also.

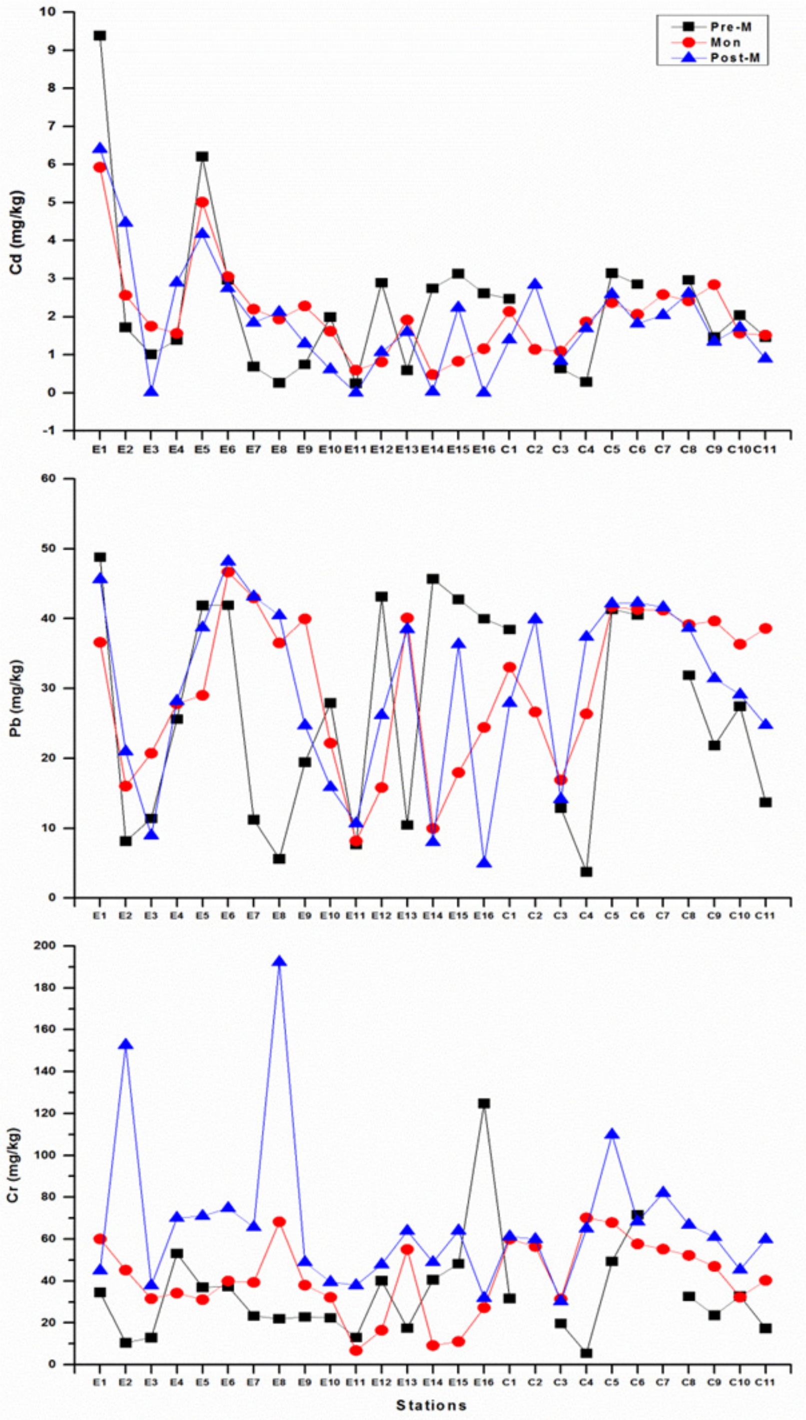


Figure 5.1 Spatial and temporal distributions of cadmium, lead and chromium in the sediments of Cochin estuary and its adjacent coast

Lead

In the estuarine sediments, Pb showed an annual average of 27.21 ± 14.12 mg/kg (Fig. 5.1). Highest value was found in station E1 (48.80 mg/kg) during Pre-M and the lowest was recorded in E16 (4.97 mg/kg) during Post-M. Station E6 was associated with highest Pb content during Mon and Post-M seasons.

Lead showed an annual average of 31.69 ± 10.62 mg/kg in the coastal sediments (Fig. 5.1). Highest Pb content was detected in station C6 (42.29 mg/kg) during Post-M. Higher Pb content was detected in station C5 during Pre-M & Mon seasons. Lowest values was observed in station C4 (3.75 mg/kg) during Pre-M. Station C3 which lies in the navigational channel was associated with lower Pb content during the study period. Higher values were found in the stations just south of the bar mouth which could be retrieved from the dredge spoil.

During Pre-M, some northern (E2 & E3) and central (E7 & E8) estuarine stations were below the shale average for Pb (14.8 mg/kg), thus Pb contamination in the central estuarine stations was less during this season. However, during Mon and Post-M seasons, northern and central estuarine stations were above the world shale average and hence enriched with Pb compared to the southern stations. Pb content of the estuarine station E11 was below the shale average for Pb during the entire study period. Compared to the estuary, coastal sediments were more polluted with Pb as majority of the stations were above the world shale average for Pb. Station C3 which is lying in the navigational channel, was associated with lower Pb content during Pre-M and Post-M seasons. During Pre-M season, stations C4 and C11 were also below the shale average, indicating less enrichment during Pre-M season in comparison with other seasons. All the coastal stations and northern and central estuarine stations were above the average shale value for Pb.

Chromium

Annual average of Cr in the estuarine sediments was 45.85 ± 34.62 mg/kg (Fig. 5.1). Lowest value was detected in E11 (6.86 mg/kg) during Mon and the highest was in E8 (192.36 mg/kg) during Post-M season. Compared to rest of the stations, higher values were observed in stations E2 and E8 during Post-M and in E16 during Pre-M seasons.

Cr in the coastal sediments showed an annual average of 50.51 ± 21.68 mg/kg (Fig. 5.1). Highest value (109.88 mg/kg) was found in station C5 during Post-M season. Lowest value was found in C4 (5.50 mg/kg) during Pre-M season. Station C3 and southern end stations were found to be associated with lower Cr content compared to the stations just north and south of the bar mouth.

Cr content in majority of the sediments was below the world shale average (126 mg/kg) and hence it can be said that Cr is not enriched in the study area. During Post-M, estuarine stations E2 and E8 only showed higher Cr content than the average shale value.

Nickel

In the estuarine sediments, annual average of Ni was 109.81 ± 49.51 mg/kg (Fig. 5.2). Highest Ni content during the study period was found in E6 (208.83 mg/kg; Pre-M) and the lowest was found in E16 (11.92 mg/kg; Post-M). Seasonal highest values were reported in E6 during Pre-M and Mon; in E8 during Post-M seasons. Lowest concentration was found in station E2 during Pre-M, E11 during Mon and E16 during Post-M seasons.

Annual average of Ni in the coastal sediments was 100.83 ± 32.88 mg/kg (Fig. 5.2). Highest Ni content was detected inC7 (145.48 mg/kg) during Mon and the lowest was in C4 (24.86 mg/kg) during Pre-M season. Station C6 during Pre-M and C7 during Mon and Post-M seasons were associated with highest value of Ni. Higher values of Ni were found in the central stations (C4-C9) compared to the rest of the stations. Lowest value found for Ni was in station C4 during Pre-M and C3 during Mon and Post-M. Ni content in the sediments of estuary and coast were comparable during Mon. But during Pre-M and Post-M seasons, estuarine stations were found to be associated with higher Ni content compared to the coastal stations.

Majority of the estuarine and coastal stations (except E2, C3 and C4) during Pre-M was above the world shale average for Ni (56 mg/kg). During Mon, all the coastal stations were enriched with Ni. Estuarine area also showed Ni concentration above the shale average during this season, except in station E11. Estuarine stations E3, E10-E12, E14, E16 and coastal station C3 were associated with lower Ni contents than the shale value. Ni content in the southern estuarine stations was below the shale average during Post-M season and central estuary was more enriched with Ni compared to the southern estuary.

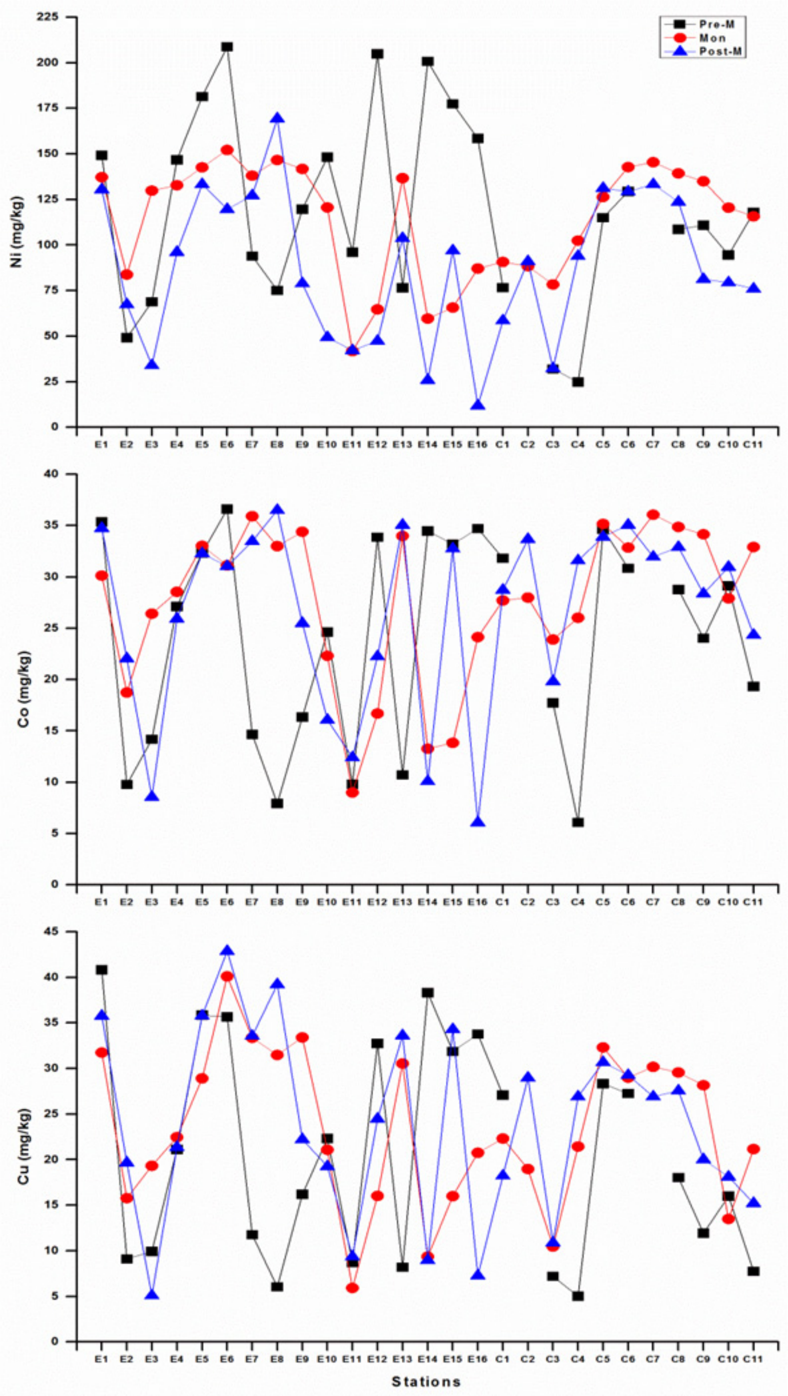


Figure 5.2 Spatial and temporal distributions of nickel, cobalt and copper in the sediments of Cochin estuary and its adjacent coast

Cobalt

Cobalt in the estuarine sediments showed an annual average of 24.27 ± 9.95 mg/kg (Fig. 5.2). Highest and lowest values were recorded in E6 (36.60 mg/kg) and E16 (6.08 mg/kg) respectively. Seasonal highest of Co was detected in stations E6, E7 and E8; lowest were detected in E8, E11 and E16 during Pre-M, Mon and Post-M seasons respectively.

In the coastal sediments, Co showed an annual average of 28.82 ± 6.47 mg/kg (Fig. 5.2). Highest and lowest Co contents during the study period were detected in stations C7 (36.07 mg/kg) and C4 (6.07 mg/kg) respectively. Stations C5, C7 and C6 were found to be associated with highest Co content during Pre-M, Mon and Post-M seasons respectively. Lowest Co concentration was found in stations C4 during Pre-M and C3 during Mon and Post-M seasons.

Southern estuarine stations (E12 - E16) were associated with lower Co concentrations compared to the world average shale value reported for Co (24 mg/kg). Compared to the southern estuarine stations, northern and central estuary was more enriched with Co. Unlike the Mon and Post-M seasons, central estuarine stations E7, E8 and E9 were less enriched with Co during Pre-M season. Stations E2 and E11 were always below the average shale value. Majority of the coastal stations were associated with Co content above the world average shale value. C4 and C11 during Pre-M season and C3 during the entire study period was associated with lower Co concentration indicating enrichment of Co compared to the average shale value.

Copper

Annual average of Cu in the estuarine sediments was 23.58 ± 11.41 mg/kg (Fig. 5.2). Post-Mon season was associated with the highest (42.88

mg/kg) and lowest (5.10 mg/kg) Cu content in the estuary during the entire study period. Highest Cu content was observed in stations E1 during Pre-M; E6 during Mon and Post-M seasons. Lowest values were reported for E8 during Pre-M; E11 during Mon and E3 during Post-M seasons. Northern station E1 and central stations (E5-E9) and southern stations beyond E11 were associated with higher Cu levels.

Copper in the coastal sediments showed an annual average of 21.25 ± 8.02 mg/kg (Fig. 5.2). Maximum of 32.32 mg/kg (C5 during Mon) and a minimum of 5.02 mg/kg (C4 during Pre-M) of Cu was detected in the estuary during the entire study period. Station C5 was associated with highest content of Cu during the entire study period. Stations lying south (C5 - C8) to the bar mouth region were found to be associated with higher Cu content. Lowest Cu content was detected in stations C4 during Pre-M; C3 during Mon and Post-M seasons.

Majority of the stations were below the average shale value reported for Cu (25 mg/kg) indicating lesser degree of enrichment of Cu in the estuary and its adjacent coast. Estuarine stations detected with Cu content higher than the average shale value were E1, E5, E6, E12, E14, E15 & E16 during Pre-M; E1, E5, E6, E7, E8, E9 & E13 during Mon and E1, E5, E6, E7, E8, E13 & E15 during Post-M seasons. Coastal stations C1, C5 & C6 during Pre-M; C5, C6, C7, C8 & C9 during Mon and C2, C4, C5, C6, C7 & C8 during Post-M seasons were found to be with Cu content higher than the average shale value.

Zinc

Zinc in the estuarine sediments showed an annual average of 198.29 ± 291.07 mg/kg (Fig. 5.3). Maximum of 1229.83 mg/kg of Zn was detected in E1 during Pre-M. Minimum concentration detected was 7.28 mg/kg in E16 during Post-Mon. Highest Zn content was found in station E1 during Pre-M & Mon seasons, while during Post-M season stations E5 was found to be with highest Zn content. Abnormally high concentrations of Zn found in stations E1 and E5 compared to the rest of the stations suggested the huge input of Zn from the northern industrial belt and it was supported by the previous studies also (Shibu *et al.,* 1995, Shajan, 2001; SCMC, 2004; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Paneer Selvam *et al.,* 2012, Deepulal *et. al.,* 2012; Shaiju, 2013; Bindu *et al.,* 2015). Stations E8, E11 and E16 were associated with lowest Zn concentration during Pre-M, Mon and Post-M seasons respectively.

Annual average of Zn in the coastal sediments was 69.36 ± 24.76 mg/kg (Fig .5.3). Maximum concentration of Zn detected in the coast was 114.39 mg/kg and the lowest detected was 9.62 mg/kg. Highest value for Zn was reported in station C5 during the entire study period and lowest value was found in C4 during Pre-M and C3 during Mon and Post-M seasons. Central stations (C5-C9) lying south to the bar mouth showed higher Zn content compared to rest of the stations in the coast.

During Pre-M season, estuarine stations except E3, E7-E9, E11 and E13 were associated with Zn concentrations above the world shale average (65 mg/kg). Stations E11, E12, E14 and E15 during Mon; E3, E9-E11, E14 and E16 during Post-M were detected with Zn content lower than the shale value. It is clear that the northern and first few central stations were above the average shale value pointing to the addition of Zn from the industrial area north to the Cochin estuary. During Pre-M season, coastal stations C1, C5, C6 and C8 were found to be with higher Zn content than the average shale value. Zn concentrations were below the average shale value in the stations C2, C3 and C10during Mon and C1, C3, C10 and C11 during Post-M seasons.

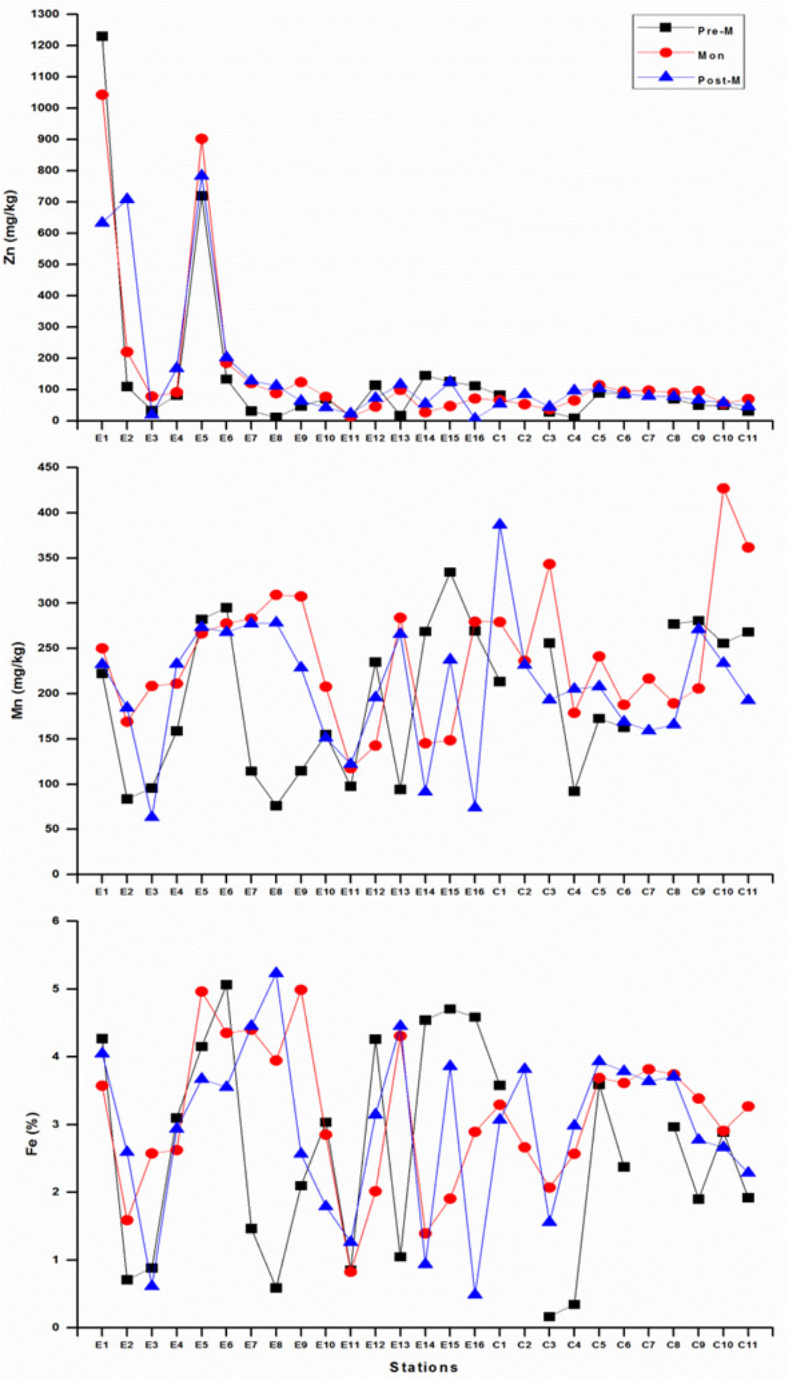


Figure 5.3 Spatial and temporal distributions of zinc, manganese and iron in the sediments of Cochin estuary and its adjacent coast

Manganese

Manganese in the estuarine sediments showed an annual average of 201.78 ± 77.82 mg/kg (Fig. 5.3). Maximum and minimum concentration of Mn recorded in the estuary was 334.49 mg/kg (E15) and 63.46 mg/kg (E3) respectively. Station E15 was associated with highest Mn content during Pre-M season and station E8 was associated with highest Mn content during Mon and Post-M seasons. Lowest concentrations were detected in E8 during Pre-M; E11 during Mon and E3 during Post-M seasons.

Annual average of Mn in the coastal sediments was 234.34 ± 72.01 mg/kg (Fig. 5.3). Highest Mn content was found in C10 (427.04 mg/kg) during Mon and lowest was detected in C4 (92.20 mg/kg) during Pre-M season. Highest Mn concentrations were detected in stations C9, C10 and C1 during Pre-M, Mon and Post-M seasons respectively. Lowest values were found in C4 during Pre-M and Mon seasons; in C7 during Post-M season.

Mn content of all the sediments in the study area was well below the value reported for world average shale (716 mg/kg). Thus it can be said that the study area is not enriched with respect to Mn and the origin of Mn in the study area is mainly from the natural weathering sources.

Iron

Annual average of Fe in the estuarine sediments was 2.92 ± 1.48 % (Fig. 5.3). Post-M season was associated with the maximum (5.23 %) and minimum (0.49 %) concentration of Fe detected in the estuary. Fe content was found to be highest in the central estuarine stations (E6, E9 and E8 during Pre-M, Mon and Post-M seasons respectively) around the Wellingdon Island. Lowest concentrations were reported in stations E8, E11 and E16 in the consecutive seasons.

Iron in the coastal sediments showed an annual average of 2.87 ± 0.96 % (Fig. 5.3). Maximum and minimum levels of Fe found in the coast were 3.93 % (C5 during Post-M) and 0.16 % (C3 during Pre-M) respectively. Lowest Fe concentrations were detected in C3 during the study period. Highest values were found in station C5 during Pre-M and Post-M seasons and in C7 during Mon season.

Estuarine stations except E6, E14, E15 & E16 during Pre-M; E5, E6, E7 & E9 during Mon and E7, E8 & E13 during Post-M seasons were associated with Fe content lower than the world average shale value for Fe (4.32 %). Northern stations were associated with lower Fe content than the average shale and some middle and southern stations were detected with Fe content higher than the average shale. It can be said that the Cochin estuarine system is not enriched with respect to Fe. Fe content of all the coastal stations was below the average shale and hence the coastal area is not enriched with respect to Fe. Thus it can be understood that the origin of Fe in this area is predominantly natural.

5.2.2 Statistical Analyses

5.2.2.1 Spatial and Temporal Variations of Metals

Two-way ANOVA without replication was performed to examine the spatial and temporal variations in the distribution of metals in the study area Table 5.1.

In the estuary, significant spatial variation was shown by the metals Zn, Cd (99 % confidence levels) and Cu (95 % confidence level) only. Cd and Zn were found to be higher in the northern estuarine stations compared to the rest of the stations indicating the influence of industrial effluents in their distribution (Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Deepulal *et* *al.,* 2012; Martin *et al.,* 2102; Shaiju, 2013; Bindu *et al.,* 2015). While northern station (E1), central stations (E5-E9) and southern stations beyond E11 were associated with higher Cu concentrations. These areas were influenced by industries, shipyard and boat building activities respectively. In the coast, significant spatial variations were observed in the distribution of all the metals under study except Mn. Cr and Ni were the only metals which showed significant temporal variations in the estuary. However, all the metals except Cd and Mn showed significant temporal variations in the coast.

Table 5.1 ANOVA results of the sedimentary heavy metals in the Cochin estuary and its adjacent coast

	Parameters	**Spatial (*df*=15)**		**Temporal (*df*=2)**			**Spatial (*df*=8)**		**Temporal (*df*=2)**	
		F	***P-value***	***F***	***P-value***		***F***	***P-value***	***F***	***P-value***
Estuary	**Cd**	8.08	0.000**	0.73	NS	**Coast**	4.29	0.006**	0.99	NS
	Pb	1.86	NS	0.01	NS		4.59	0.005**	3.76	0.046*
	Cr	0.98	NS	6.15	0.006**		3.49	0.016*	12.03	0.001**
	Ni	1.27	NS	5.51	0.009**		7.24	0.000**	6.59	0.008**
	Co	1.33	NS	0.15	NS		3.02	0.028*	3.64	0.049*
	Cu	2.12	0.039*	0.15	NS		5.5	0.002**	4.38	0.030*
	Zn	15.56	0.000**	0.09	NS		4.28	0.006**	3.65	0.049*
	Mn	1.28	NS	1.47	NS		1.87	NS	1.44	NS
	Fe	1.45	NS	0.15	NS		5.91	0.001**	7.66	0.005**

** Significant at the 0.01 level * Significant at the 0.05 level NS Not Significant

Cd lacked significant temporal variations both in the estuary and coast, whereas significant spatial variations were observed during the study period. This could be cementing the influence of point sources of Cd operating irrespective of the seasons in the estuary. Significant spatial and temporal variations were observed for Pb in the coast. Mon and Post-M seasons were associated with higher Pb content and Pre-M season with lower content. Stations lying just north and south to the bar mouth were found to be associated with higher Pb content compared to the bar mouth and southern coastal stations. This higher concentration could be attributed the dredge spoil which is discharged in this area (Balachandran, 2001) and the input from the estuary.

Cr showed spatial variation significant at 95 % confidence level in the coast and temporal variations significant at 99 % confidence level in the estuary and coast. Post-M season was found to be associated with higher Cr content in the study area followed by Mon and Pre-M seasons. Ni exhibited spatial (coast) and temporal (estuary and coast) variations significant at 99 % confidence levels. In the estuary, Pre-M season was found to be associated with higher Ni content followed by Mon and Post-M seasons. Whereas, in the coast, Mon season was associated with higher Ni content compared to other seasons. In the coastal area, significant spatial and temporal variability (95 % confidence level) was observed in the case of Co distribution. Mon and Post-M seasons were found to be associated with higher Co content compared to Pre-M season. Cu exhibited significant spatial variability in the estuary and coast and temporal variability in the coast. In the coast, Pre-M season was found to be with lower Cu content compared to Mon and Post-M seasons. In the study area, spatial variation observed in the case of Zn was highly significant (99 % confidence level), while the temporal variation was significant only in the coast (95 % confidence level). Highest concentrations were associated with Mon season followed by Post-M and Pre-M seasons. In the estuary, significant temporal and spatial variations were not observed in the case of Fe. While, significant spatial and temporal (99 % confidence level) variations were observed for Fe in the coastal sediments. Mon seasons was found to be associated with higher Fe content followed by Post-M and then Pre-M seasons.

Mn lacked significant temporal and spatial variability in its distribution in the study area which pointed to the absence of huge anthropogenic addition of Mn to the study area unlike the other metals.

5.2.2.2 Correlation among the Metals and Geochemical Features

Correlation matrices obtained from the Pearson correlation analysis of metals and other sedimentary parameters in the study area are represented in Tables 5.2 to 5.7.

In the estuary, sand showed significant negative correlation with all the metals except Zn during Pre-M and Mon; Zn and Cr during Post-M season. In the coast, Sand showed negative correlations with all the metals except Ni and Mn during Pre-M; Cr and Mn during Mon and Mn during Post-M. According to Valdes *et al.* (2010) coarse sand grains have low tendency of to retain heavy metals. Mn showed weak positive correlation with sand ($r^2 = 0.616$, $p < 0.05$) during Mon season and this can be most probably attributed to Mn oxide coatings on the sand grains (Shrader *et al.,* 1977; Rubio *et al.,* 2000). Association of Mn with sand fraction can also be supported by the significant negative correlation shown by Mn and clay ($r^2 = -0.613$, $p < 0.05$). This also suggested an entirely different dynamics of Mn from that of other metals in the coastal system as all other metals preferred the finer fractions of the sediments and TOM. Absence of significant correlation among Cd and TOM indicated its reduced affinity towards the organic fraction inside the estuary (Balachandran *et al.,* 2005) and its dispersion is probably driven by anthropogenic inputs. According to Zhuang and Gao (2014), concentration of Cd is not influenced by the sediment grain size and the amount of organic matter, probably because it is a typical anthropogenic element.

Table 5.2 Pearson correlation matrix of sedimentary parameters in Cochin estuary during pre-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Sand	Silt	Clay	pH	Eh	TC	TP	TN	TS	TOM
Cd	1																		
Pb	.750**	1																	
Cr	0.224	.551*	1																
Ni	.503*	.920**	0.491	1															
Co	.683**	.983**	.619*	.932**	1														
Cu	.774**	.993**	.556*	.908**	.978**	1													
Zn	.955**	.548*	0.073	0.284	0.469	.584*	1												
Mn	.601*	.930**	.596*	.900**	.932**	.922**	0.37	1											
Fe	.638**	.978**	.623**	.950**	.989**	.970**	0.415	.957**	1										
Sand	-.694**	-.984**	-.613*	-.930**	-.980**	-.982**	-0.485	-.956**	-.985**	1									
Silt	.668**	.962**	.629**	.914**	.955**	.964**	0.461	.963**	.960**	-.985**	1								
Clay	.699**	.973**	.571*	.914**	.973**	.966**	0.495	.912**	.977**	-.979**	.930**	1							
pH	-.504*	-0.363	0.022	-0.218	-0.308	-0.366	-.535*	-0.221	-0.309	0.328	-0.246	-0.412	1						
Eh	-0.134	-0.011	-0.043	0.089	-0.009	0.015	-0.09	-0.058	-0.037	0.053	0.005	-0.119	0.021	1					
TC	.681**	.978**	.613*	.925**	.993**	.975**	0.469	.935**	.979**	-.972**	.961**	.949**	-0.286	0.039	1				
TP	0.469	.806**	.732**	.732**	.842**	.796**	0.256	.831**	.836**	-.820**	.844**	.762**	-0.181	0.122	.853**				
TN	.687**	.973**	.600*	.915**	.984**	.973**	0.473	.959**	.983**	-.975**	.957**	.959**	-0.296	0.027	.983**	1	1		
TS	.647**	.959**	.565*	.922**	.943**	.952**	0.436	.893**	.935**	-.960**	.960**	.924**	-0.198	0.032	.941**	.767**	.923**	1	
TOM	0.398	.849**	.509*	.929**	.867**	.834**	0.154	.933**	.900**	-.893**	.912**	.837**	-0.126	0.031	.880**	.785**	.886**	.871**	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 5.3 Pearson correlation matrix of sedimentary parameters in Cochin estuary during monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Sand	Silt	Clay	pH	Eh	TC	TP	TN	TS	TOM
Cd	1																		
Pb	.527*	1																	
Cr	.583*	.727**	1																
Ni	.618*	.877**	.770**	1															
Co	.579*	.917**	.765**	.950**	1														
Cu	.615*	.982**	.734**	.907**	.922**	1													
Zn	.941**	0.278	0.37	0.38	0.357	0.372	1												
Mn	0.478	.894**	.738**	.854**	.931**	.894**	0.265	1											
Fe	.591*	.906**	.623**	.878**	.937**	.932**	0.4	.918**	1										
Sand	-.501*	-.974**	-.738**	-.909**	-.953**	-.964**	-0.249	-.944**	-.948**	1									
Silt	.557*	.876**	.639**	.867**	.883**	.911**	0.33	.914**	.939**	-.935**	1								
Clay	0.367	.938**	.737**	.822**	.888**	.881**	0.124	.837**	.819**	-.924**	.728**	1							
pH	-0.211	-0.238	-0.325	-0.372	-0.314	-0.189	-0.089	-0.136	-0.078	0.234	-0.098	-0.347	1						
Eh	0.079	0.073	-0.069	0.079	-0.014	0.124	0.001	0.045	-0.004	-0.057	0.199	-0.104	-0.122	1					
TC	0.13	.509*	0.243	0.418	0.496	.497*	-0.021	.577*	.584*	-.594*	.681**	0.414	-0.022	0.007	1				
TP	0.35	.910**	.740**	.832**	.912**	.865**	0.104	.853**	.840**	-.932**	.772**	.968**	-0.343	-0.005	0.436	1			
TN	0.438	.960**	.641**	.836**	.851**	.939**	0.187	.852**	.827**	-.927**	.828**	.898**	-0.308	0.186	0.464	.855**	1		
TS	0.425	.968**	.681**	.854**	.864**	.959**	0.152	.871**	.869**	-.960**	.892**	.893**	-0.185	0.199	.584*	.882**	.954**	1	
TOM	0.317	0.408	0.328	0.408	0.495	0.41	0.251	.536*	.576*	-.508*	.620*	0.313	0.053	0.102	.691**	0.418	0.236	0.406	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

In the estuary, silt and clay exhibited significant positive correlations with all the metals except Zn during Pre-M. During Mon season, silt showed significant positive correlations with all the metals except Zn and the exceptions were Cd and Zn in the case of clay during this season. Silt and clay showed significant positive correlations with all the metals except Cr and Zn during Post-M. TOM showed significant positive correlations with all the metals except Cd and Zn during Pre-M and Cr and Zn during Post-M. However during monsoon, TOM showed significant correlations with Mn ($r^2 = 0.536$, $p < 0.05$) and Fe ($r^2 = 0.576$, $p < 0.05$) only. TS and TN exhibited strong positive correlations with the metals except Zn during Pre-M, Cd and Zn during Mon and Cr and Zn during Post-M. TP showed significant positive correlations with all the metals except Cd and Zn. Lack of significant correlations for Zn suggested that textural features and organic fractions did not have an important role in its dynamics in the estuary. Cr also lacked significant correlations with the sedimentary parameters other than TP during Post-M and this indicated that Cr did not have textural control over its distribution during Post-M season.

In the coast, all the metals except Ni & Mn were positively correlated to silt, clay and TOM during Pre-M which pointed to their role in metal transport during Pre-M period. During Mon season, silt lacked significant correlations with all the metals under study, while the correlations observed suggested that clay and TOM might be the host phases for all the metals except Cr and Mn. Mn showed weak negative correlation with clay ($r^2 = -0.613$, $p < 0.05$) and TOM ($r^2 = -0.648$, $p < 0.05$) during this season. Silt exhibited significant positive correlations with all the metals except Cr, Ni and

Mn during Post-M. Clay and TOM showed significant positive correlations with all the metals except Mn during this season. Strong association of these metals with silt, clay and TOM implied that these metals could be accumulated either by clay minerals that adsorb these heavy metals directly or by organic matter, which is mounted on the clay surface (Wang and Chen, 2000). In the coast, significant positive correlations were observed for TS with all the metals except Cr, Ni and Mn during Pre-M, Cr and Mn during Mon and Post-M seasons. All the metals except Ni and Mn exhibited significant positive correlations with TN and TP during Pre-M. TN exhibited strong positive correlations with all the metals except Cr and Mn during Mon. TP showed significant positive correlations with all the metals except Mn during Mon. TP and TN showed significant positive correlations with all the metals except Mn during Post-M. Mn showed significant negative correlations with TP during Mon and Post-M. All these suggested the origin/behaviour of Mn was entirely different from that of other metals in the coastal sedimentary environment.

It is reported that organic matter content and grain size are important controlling factors influencing the abundance of heavy metals in sediments (Samuel and Phillips, 1988; Garcia *et al.,* 1999; Rubio *et al.,* 2000; Aloupi and Angelidis, 2001; Liaghati *et al.,* 2003; Ray *et al.,* 2006; Bhattacharyya and Gupta, 2008). The strong relationships of Fe and Mn with TOM, silt and clay in the estuary during all seasons suggested their presence as a constituent of clay minerals and on coatings on the surface of clay particles. But during Mon, weak association of the above metals with TOM and non-association of all other metals under study with TOM indicated the significant role of hydrous Fe-Mn oxides and mud (silt & clay) might be playing in controlling the distribution of heavy metals in the estuary. Whereas in the coast, weak association of metals with Mn and silt indicated hydrous Fe oxides, clay minerals and TOM might be the major hosting phases for heavy metals during Mon season.

In the estuary, only significant correlations observed for pH during the study period were with Cd and Zn during Pre-M season. In the coast, pH exhibited significant negative correlations with all the metals except Mn during Pre-M and Post-M, while none of them were significant during Mon season. In the estuary, all the metals except Cd, Cr and Zn showed significant negative correlations with Eh during Post-M season. Whereas, during Pre-M and Mon seasons Eh lacked significant correlations with any of the metals in the estuarine environment. But in the coast, significant correlations were shown by Co and Fe during Pre-M and Pb, Ni, Co and Fe during Mon.

Inter-metallic Correlations

During Pre-M, strong positive correlation in the estuary was shown by the following metallic pairs Cd-Pb, Cd-Co, Cd-Cu, Cd-Zn, Cd-Fe, Pb-Ni, Pb-Co, Pb- Cu, Pb-Mn, Pb-Fe, Cr-Fe, Ni-Co, Ni-Cu, Ni-Mn, Ni-Fe, Co-Cu, Co-Mn, Co-Fe, Cu-Mn, Cu-Fe and Mn-Fe. Weak positive correlations were exhibited by the metallic pairs Cd-Ni, Cd-Mn, Pb-Zn, Pb-Cr, Cr-Co, Cr-Cu, Cr-Mn and Cu-Zn. In the coast, all the metals except Mn, Ni and Cr exhibited significant correlations. Ni was correlated to Cd, Co and Fe only. Cr showed strong positive correlations with Cd, Pb, Cu, Zn and weak positive correlations with Co.

Table 5.4 Pearson correlation matrix of sedimentary parameters in Cochin estuary during post-monsoon (n=16)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Sand	Silt	Clay	pH	Eh	TC	TP	TN	TS	TOM
Cd	1																		
Pb	.680**	1																	
Cr	0.365	0.353	1																
Ni	.660**	.920**	.557*	1															
Co	.670**	.962**	0.451	.935**	1														
Cu	.631**	.975**	0.419	.908**	.952**	1													
Zn	.876**	0.411	0.327	0.434	0.413	0.391	1												
Mn	.606*	.937**	0.442	.909**	.970**	.938**	0.378	1											
Fe	.593*	.933**	.527*	.921**	.978**	.935**	0.337	.948**	1										
Sand	-.596*	-.977**	-0.333	-.919**	-.967**	-.971**	-0.343	-.942**	-.938**	1									
Silt	.528*	.918**	0.294	.852**	.881**	.932**	0.283	.841**	.837**	-.960**	1								
Clay	.610*	.924**	0.342	.885**	.955**	.891**	0.38	.955**	.950**	-.916**	.768**	1							
pH	-0.225	-0.084	-0.246	-0.099	-0.072	-0.121	-0.173	-0.09	-0.044	0.063	-0.1	-0.001	1						
Eh	-0.353	-.595*	-0.322	-.618*	-.685**	-.676**	-0.274	-.774**	-.705**	.648**	-.520*	-.741**	-0.021	1					
TC	.544*	.966**	0.374	.894**	.951**	.967**	0.307	.928**	.934**	-.985**	.956**	.887**	-0.023	-.603*	1				
TP	0.472	.749**	.669**	.850**	.833**	.740**	0.259	.781**	.890**	-.734**	.604*	.817**	0.077	-.544*	.753**	1			
TN	.515*	.959**	0.388	.894**	.953**	.967**	0.256	.927**	.946**	-.983**	.950**	.893**	-0.008	-.636**	.991**	.773**	1		
TS	.600*	.930**	0.292	.838**	.882**	.942**	0.409	.874**	.823**	-.950**	.971**	.785**	-0.084	-.559*	.956**	.575*	.935**	1	
TOM	.558*	.975**	0.367	.904**	.943**	.975**	0.311	.916**	.928**	-.989**	.965**	.883**	-0.054	-.598*	.993**	.738**	.991**	.955**	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 5.5 Pearson correlation matrix of sedimentary parameters in Cochin coast during pre-monsoon (n=9)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Sand	Silt	Clay	pH	Eh	TC	TP	TN	TS	TOM
Cd	1																		
Pb	.948**	1																	
Cr	.803**	.858**	1																
Ni	.761*	0.651	0.657	1															
Co	.926**	.957**	.775*	.711*	1														
Cu	.898**	.977**	.845**	0.552	.887**	1													
Zn	.945**	.992**	.849**	0.658	.938**	.973**	1												
Mn	0.115	0.038	-0.129	0.34	0.288	-0.155	0.034	1											
Fe	.905**	.871**	0.573	.693*	.896**	.833**	.850**	0.176	1										
Sand	-.901**	-.967**	-.887**	-0.623	-.921**	-.967**	-.957**	0.031	-.811**	1									
Silt	.865**	.875**	.721*	0.528	.923**	.798*	.849**	0.323	.769*	-.868**	1								
Clay	.791*	.885**	.868**	0.595	.782*	.939**	.888**	-0.269	.720*	-.941**	0.649	1							
pH	-.805**	-.899**	-.821**	-.695*	-.918**	-.823**	-.895**	-0.275	-.715*	.839**	-.784*	-.752*	1						
Eh	-0.591	-0.654	-0.543	-0.665	-.772*	-0.603	-0.631	-0.392	-.679*	.735*	-0.664	-.674*	.687*	1					
TC	.871**	.854**	.757*	.768*	.827**	.856**	.854**	0.011	.850**	-.907**	.722*	.898**	-.685*	-.792*	1				
TP	.854**	.920**	.916**	0.576	.834**	.943**	.911**	-0.24	.719*	-.944**	.753*	.934**	-.793*	-0.568	.809**	1			
TN	.861**	.943**	.837**	0.457	.840**	.981**	.926**	-0.228	.790*	-.958**	.803**	.920**	-.743*	-0.564	.834**	.928**	1		
TS	.777*	.884**	0.597	0.467	.846**	.910**	.893**	-0.017	.851**	-.861**	.700*	.843**	-.766*	-.678*	.794*	.790*	.854**	1	
TOM	.869**	.942**	.893**	0.537	.826**	.982**	.941**	-0.278	.753*	-.956**	.745*	.957**	-.776*	-0.54	.839**	.977**	.974**	.842**	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

During Mon season, all the metals in the estuarine sediments (except Zn) showed significant positive correlations with each other. During this season, Zn showed strong positive correlation with Cd ($r^2 = 0.941$, $p < 0.01$) only suggesting their similar origin which was entirely different from that of other metals under study. In the coastal sediments, all the metals except Mn and Cr showed significant positive correlations with other metals under study. Cr exhibited weaker positive correlation with Cu while, Mn showed strong and weak negative correlations with Cr and Cu respectively.

During Post-M, highly significant positive correlations observed in the estuary were Cd-Pb, Cd-Ni, Cd-Co, Cd-Cu, Cd-Zn, Pb-Ni, Pb-Co, Pb-Cu, Pb-Mn, Pb-Fe, Ni-Co, Ni-Cu, Ni-Mn, Ni-Fe, Co-Cu, Co-Mn, Co-Fe and Mn-Fe (99 % confidence levels) and weaker positive correlations were shown by the pairs Cd-Mn, Cd-Fe, Cr-Ni, Cr-Fe (95 % confidence levels). In the coast, all the metals except Mn exhibited significant positive correlations with each other.

Significant correlations among the metals observed in the study area suggested similar fate/transport of these metals. Absence of significant correlations with other metals during the study period indicated the origin/behaviour of Mn and Zn was entirely different from that of other metals in the coastal and estuarine environments respectively. Anthropogenic association of Cd with Zn predominated the granulometric association with clay in the transport of Cd in the estuary. This weak or little affinity towards clay fraction showed that the clay minerals are not a major adsorbent of Cd and this was reported in previous studies in Cochin estuary (Balachandran *et al.,* 2005; Shaiju, 2013) and other estuarine systems (Davies Colley *et al.,* 1984).

In the estuary, Zn was positively correlated with Cd only during entire study period. Pb and Cu also showed correlation with Zn (0.05 levels) during Pre-M. This association could be attributed to the anthropogenic influence by the industrial area in the Cochin estuary (Shibu *et al.,* 1995; CPCB, 1996; Shajan, 2001; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Deepulal *et al.,* 2012; Martin *et al.,* 2012; Bindu *et al.,* 2015). Whereas in the coastal environment, Zn showed strong positive correlations with geochemical parameters and all the metals except Ni & Mn during Pre-M; Cr & Mn during Mon and Mn during Post-M seasons.

Highly significant Fe-Mn relationship observed in the estuarine sediments revealed the formation of stable hydrous Fe-Mn oxide geochemical phases and significant correlation of Fe and Mn with all other metals indicated their adsorption and incorporation into the sediment matrix in the estuarine environment. Mn and Fe showed similar relationships with geochemical features and all metals except Zn (Pre-M); Zn& Cd (Mon); Zn & Cr (Post-M) in the estuary. Non association of Zn with other metals indicated entirely different transport for Zn in the estuary, whereas, all other metals were part of the hydrous Fe/Mn oxide scavenging as can be seen from their significant correlations with Fe and Mn. From the correlation analysis, it could be understood that a considerable fraction of the heavy metals were adsorbed onto hydrous Fe-Mn oxides (Moore, 1963; Potter *et al.,* 1963; Jenne, 1968; Tessier *et al.,* 1979; Botte *et al.,* 2010; Sundaray *et al.,* 2011) along with other geochemical phases in the estuarine sediments.

Fe-Mn correlations observed were not significant in the coastal sediments during Pre-M and Post-M seasons. Fe & Mn were assumed to have entirely different origin or transport pathway in the coastal area as can be seen from the negative correlation during Mon season. Also the non-association of metals with Mn during the entire study period indicated that the hydrous Fe oxides might be the potential scavengers of these metals in the coastal environment. Moreover, low concentrations of Mn detected in the coastal area also point to the insignificant role of manganese as a metal scavenger in the coastal environment. Also, the solubility of manganese was reported to be high in anaerobic conditions at pH above 6 (Kabata-Penidas, 2001; McBride, 1994).

Table 5.6 Pearson correlation matrix of sedimentary parameters in Cochin coast during monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Sand	Silt	Clay	pH	Eh	TC	TP	TN	TS	TOM
Cd	1																		
Pb	.730*	1																	
Cr	0.422	0.223	1																
Ni	.749**	.886**	0.143	1															
Co	.752**	.898**	0.241	.877**	1														
Cu	.848**	.785**	.642*	.764**	.875**	1													
Zn	.858**	.849**	0.525	.824**	.902**	.963**	1												
Mn	-0.575	-0.217	-.767**	-0.37	-0.393	-.723*	-0.573	1											
Fe	.800**	.941**	0.361	.845**	.925**	.890**	.893**	-0.394	1										
Sand	-.723*	-.763**	-0.395	-.767**	-.929**	-.928**	-.896**	.616*	-.866**	1									
Silt	0.19	0.25	-0.077	0.194	0.444	0.323	0.245	-0.251	0.302	-0.57	1								
Clay	.771**	.790**	0.509	.821**	.895**	.952**	.950**	-.613*	.888**	-.918**	0.198	1							
pH	-0.115	-0.335	-0.053	-0.298	-0.374	-0.32	-0.356	0.003	-0.466	0.416	-0.108	-0.444	1						
Eh	-0.423	-.785**	0.12	-.651*	-.659*	-0.42	-0.545	-0.168	-.697*	0.474	-0.222	-0.458	0.596	1					
TC	.891**	.873**	0.449	.895**	.920**	.956**	.951**	-.631*	.916**	-.913**	0.34	.926**	-0.241	-0.518	1				
TP	.814**	.734*	.659*	.715*	.824**	.973**	.960**	-.695*	.854**	-.888**	0.226	.950**	-0.457	-0.46	.902**	1			
TN	.786**	.851**	0.399	.830**	.919**	.929**	.930**	-0.514	.944**	-.928**	0.274	.974**	-0.462	-0.53	.931**	.910**	1		
TS	.748**	.787**	0.418	.651*	.890**	.888**	.860**	-0.523	.850**	-.918**	.607*	.802**	-0.258	-0.535	.873**	.836**	.839**	1	
TOM	.803**	.712*	0.272	.840**	.797**	.814**	.747**	-.648*	.809**	-.841**	0.458	.783**	-0.222	-0.379	.896**	.724*	.818**	.721*	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

Table 5.7 Pearson correlation matrix of sedimentary parameters in Cochin coast during post-monsoon (n=11)

	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe	Sand	Silt	Clay	pH	Eh	TC	TP	TN	TS	TOM
Cd	1																		
Pb	.816**	1																	
Cr	0.584	.762**	1																
Ni	.709*	.922**	.796**	1															
Co	.832**	.951**	.643*	.834**	1														
Cu	.862**	.977**	.746**	.883**	.927**	1													
Zn	.754**	.885**	.746**	.779**	.823**	.940**	1												
Mn	-0.221	-0.284	-0.15	-0.512	-0.141	-0.315	-0.305	1											
Fe	.877**	.953**	.757**	.861**	.938**	.944**	.803**	-0.134	1										
Sand	-.809**	-.987**	-.737**	-.896**	-.957**	-.960**	-.863**	0.225	-.944**	1									
Silt	.699*	.803**	0.587	0.57	.766**	.794**	.712*	0.138	.809**	-.848**	1								
Clay	.707*	.905**	.686*	.960**	.888**	.869**	.783**	-0.487	.829**	-.887**	0.507	1							
pH	-.645*	-.809**	-.705*	-.806**	-.843**	-.798**	-.790**	0.343	-.734*	.804**	-0.498	-.874**	1						
Eh	0.04	0.214	-0.017	0.163	0.282	0.254	0.189	-0.025	0.278	-0.167	0.049	0.228	-0.205	1					
TC	.785**	.918**	.691*	.967**	.877**	.893**	.800**	-0.547	.845**	-.902**	0.562	.977**	-.845**	0.123	1				
TP	.711*	.870**	.710*	.967**	.778**	.843**	.738**	-.644*	.790**	-.856**	0.535	.926**	-.800**	0.071	.968**	1			
TN	.781**	.900**	.769**	.955**	.847**	.886**	.824**	-0.532	.832**	-.888**	0.576	.942**	-.879**	0.07	.980**	.968**	1		
TS	.603*	.825**	0.595	.676*	.747**	.845**	.898**	-0.244	.681*	-.849**	.811**	.674*	-.671*	0.023	.704*	.674*	.713*	1	
TOM	.779**	.919**	.668*	.965**	.860**	.900**	.799**	-0.587	.843**	-.903**	0.585	.958**	-.814**	0.15	.993**	.979**	.973**	.721*	1

** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed)

5.2.2.3 Principal Component Analysis

Statistical procedures can be used for making inferences on the important pathways of elemental deposition (Isaac *et al.,* 2005). Multivariate statistical tools like PCA can be effectively used to detect the hidden structure of sediment sources, to distinguish natural and anthropogenic origin of metal-polluted samples (Spencer, 2002; Landajo *et al.,* 2004), to determine pollution distribution (Ausili *et al.,* 1998), to identify the geochemical parameters influencing their distribution (Loska and Wiechula, 2003) and to get signatures of major redox sensitive geochemical and biochemical processes acting along the salinity gradients of the estuary. Principal Components (PCs) provide information on the most meaningful parameters, which describe whole data set affording data reduction with minimum loss of original information (Vega *et al.,* 1998; Helena *et al.,* 2000).

Heavy metal behaviour in natural systems is dependent on environmental conditions which in turn influence its chemical speciation and affinity towards the carrier phases (Bruland and Lohan, 2003). Changing redox states and different biogeochemical processes like sorption, precipitation, dissolution, advection, diffusion and bioturbation which are influenced by early diagenesis control heavy metals mobility in sediments. The organic matter (OM), being the driving force of early diagenesis (Rullkotter, 2002), has been reported to strongly affect the chemical speciation of heavy metals (Luther III *et al.,* 2001; Louis *et al.,* 2009; Dang *et al.,* 2014).

The sedimentary distribution of certain elements like Fe, Mn, Cu and S provide information about the occurrence of oxidised forms of metals such as oxides and hydroxides of Fe and Mn and the conversion of these species to more reduced form such as sulphides (Canfield *et al.,* 1993; Kuzyk *et al.,* 2011). Therefore, these elements have potential to be used as qualitative

Table 5.8 Principal components showing loadings of each parameter during the study period

Variables	**Pre-monsoon**		**Monsoon**			**Post-monsoon**		
Estuary	**PC1**	**PC2**	**PC1**	**PC2**		**PC1**	**PC2**	**PC3**
Cd	0.340	**0.931**	0.286	**0.942**		0.405	0.185	**0.868**
Pb	**0.858**	**0.500**	**0.937**	0.275		**0.922**	0.212	0.289
Cr	**0.729**	-0.089	**0.656**	0.461		0.126	**0.906**	0.196
Ni	**0.912**	0.246	**0.835**	0.425		**0.801**	0.454	0.289
Co	**0.902**	0.410	**0.894**	0.367		**0.882**	0.353	0.270
Cu	**0.841**	**0.532**	**0.904**	0.375		**0.916**	0.250	0.251
Zn	0.083	**0.980**	0.018	**0.970**		0.129	0.131	**0.965**
Mn	**0.916**	0.304	**0.913**	0.252		**0.872**	0.339	0.230
Fe	**0.926**	0.355	**0.883**	0.359		**0.850**	0.466	0.175
TC	**0.901**	0.405	**0.666**	-0.163		**0.954**	0.224	0.148
TN	**0.898**	0.410	**0.907**	0.192		**0.954**	0.264	0.103
TS	**0.875**	0.389	**0.957**	0.147		**0.925**	0.054	0.282
TP	**0.872**	0.143	**0.926**	0.121		**0.608**	**0.733**	0.084
TOM	**0.939**	0.099	**0.906**	0.105		**0.956**	0.208	0.160
Sand	**-0.901**	-0.422	**-0.969**	-0.239		**-0.959**	-0.188	-0.201
Silt	**0.906**	0.384	**0.890**	0.296		**0.945**	0.076	0.158
Clay	**0.860**	0.451	**0.913**	0.142		**0.844**	0.323	0.234
% of Variance	69.630	22.690	69.070	17.900		66.300	14.660	13.970
Cumulative %	69.630	92.320	69.070	86.970		66.300	80.960	94.930
Coast	**PC1**	**PC2**	**PC1**	**PC2**	**PC3**	**PC1**	**PC2**	
Cd	**0.867**	0.423	**0.777**	0.395	0.083	**0.787**	0.334	
Pb	**0.943**	0.302	**0.955**	0.017	0.091	**0.885**	0.447	
Cr	**0.881**	0.094	0.149	**0.933**	-0.123	**0.707**	0.344	
Ni	**0.542**	**0.605**	**0.935**	0.052	0.070	**0.672**	**0.707**	
Co	**0.832**	**0.529**	**0.915**	0.140	0.320	**0.888**	0.347	
Cu	**0.986**	0.111	**0.786**	**0.576**	0.212	**0.882**	0.435	
Zn	**0.939**	0.293	**0.869**	0.432	0.111	**0.822**	0.385	
Mn	-0.272	**0.933**	-0.227	**-0.886**	-0.251	0.147	**-0.929**	
Fe	**0.773**	0.481	**0.931**	0.206	0.161	**0.906**	0.321	
TC	**0.860**	0.307	**0.882**	0.384	0.223	**0.669**	**0.730**	
TN	**0.976**	0.012	**0.899**	0.321	0.161	**0.677**	**0.711**	
TS	**0.858**	0.204	**0.725**	0.346	**0.502**	**0.803**	0.268	
TP	**0.972**	0.024	**0.760**	**0.601**	0.114	**0.588**	**0.790**	
TOM	**0.998**	-0.010	**0.746**	0.295	0.384	**0.662**	**0.740**	
Sand	**-0.962**	-0.220	**-0.774**	-0.373	-0.475	**-0.908**	-0.393	
Silt	**0.745**	**0.513**	0.144	-0.005	**0.982**	**0.942**	-0.074	
Clay	**0.967**	-0.013	**0.854**	0.448	0.093	**0.655**	**0.704**	
% of Variance	74.780	15.140	59.620	20.920	11.590	58.310	31.110	
Cumulative %	74.780	89.920	59.620	80.540	92.130	58.310	89.420	

indicators of various biogeochemical processes. PCA of heavy metals and other geochemical parameters was done to identify the major geochemical processes acting in the Cochin estuary and its adjacent coast. Varimax rotation was applied to identify the variables that are more significant to each factor based on the significance of their correlations and are expressed as factor loading (Buckley *et al.,* 1995; Davis, 2002). Parameters with factor loading > 0.50 and components with eigen values > 1 are considered for interpretation. The loadings of each variable, percentage variance accounted by each component and cumulative percentage variances are given in Table 5.8.

For the estuarine samples, PCA yielded two principal components with eigenvalue > 1, explaining 92.32 and 86.97 % of the total variance during Pre-M and Mon seasons respectively. During Post-M season, PCA yielded three principal components which explained 94.93 % of the total variance in the estuary.

During Pre-M, PC1 which accounted for 69.63 % of the total variance was characterised by high positive loading of Pb, Cr, Ni, Co, Cu, Mn, Fe, TC, TN, TS, TP, TOM, silt and clay. Sand showed high negative loading in PC1. PC1 represented the different physical and chemical processes acting on the sediment surface. The physical adsorption of heavy metals with clay minerals and organic matter and the subsequent sinking to the surface sediments is a significant geochemical process in the aquatic environment. Association of Fe and Mn in this component could lead light to the heavy metal scavenging of Fe-Mn oxy hydroxides and incorporation in to the surface sediments. Fe-Mn oxides either in bulk phases or as coatings of mineral particles were reported to readily adsorb heavy metals and organic matter was reported to flocculate the metals and they consequently sink to the sediments (Sholkovitz, 1976; Tessier *et al.,* 1980; Tessier *et al.,* 1985; Scholkovitz and Copland, 1981; Salomons and Forstner, 1984; Rubio *et al.,* 2000; Ibhadon *et al.,* 2004; Dang *et al.,* 2015). As this component was loaded with the usual indicators (TOM, TN and TS) of microbially mediated diagenetic process, it could be indicative of the early diagenetic processes acting in the surface sediments. The organic matter, being the driving force of early diagenesis (Rullkotter, 2002), is known to strongly impact chemical speciation of heavy metals by complexation mechanism (Luther III *et al.,* 2001; Louis *et al.,* 2009; Dang *et al.,* 2014). PC2 with 22.69 % of the total variance was characterised with high positive loadings of Cd & Zn; moderate positive loading of Pb & Cu. The above association could be considered as anthropogenic. It was reported in the Cochin estuary by many previous researchers (Balachandran *et al.,* 2005; Deepulal *et al.,* 2012; Shaiju, 2013) also. Although Pb and Cu were loaded in both the components indicating their complex behaviour during this season, PC1 has the high loading, which suggested the main process involved is similar to the metals other than Zn and Cd. It can be found from the ordination plot (Fig. 5.4) also that Cd and Zn behaves separately from other metals under study. Cr also shows a difference from the rest of the metals.

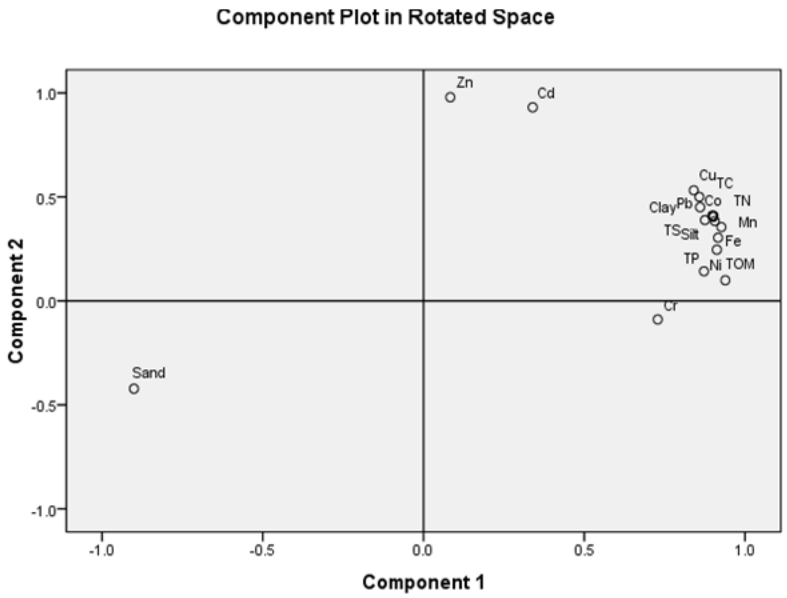


Figure 5.4 Ordination plot of principal components of estuarine sediments during Pre-Monsoon

PC1 in Mon, which accounted for 69.07 % of the cumulative variance was characterised by high positive loading of geochemical parameters and all the metals except Cd, Zn. Sand was loaded negatively in this component. This association can be considered as the adsorption of the metals by the organic matter, mud fractions and Fe-Mn oxyhydroxides. PC2 which explained 17.90 % of the cumulative variance was characterised by high positive loadings of Cd and Zn indicating their common source in the estuary. This component could be considered as the anthropogenic component. In the ordination plot (Fig. 5.5), Cr was positioned between the two groups indicating its association to the contaminant group (Zn and Cd). In spite of this, its closeness to the first group indicated the main processes involved are similar to the rest of the metals.

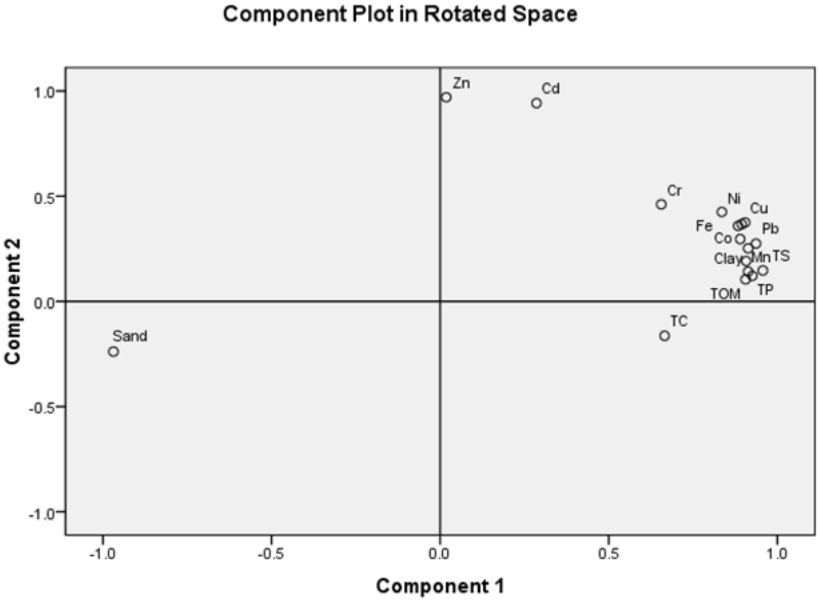


Figure 5.5 Ordination plot of principal components of estuarine sediments during monsoon

During Post-M, PC1 which accounted for 66.30 % of total variance was loaded positively with geochemical parameters and all the metals except Cd, Cr and Zn. PC2 which accounted for 14.66 % of the cumulative variance was positively loaded with Cr and TP attributing this component to the anthropogenic sources. From the ordination plot (Fig. 5.6), we can see that Cr behaved differently from other two groups and the position of TP in between Cr and the PC1 indicated its complex behaviour in the estuarine system during Post-M season. High positive loadings of Cd and Zn in PC3 during this season also indicated their common source of origin in the estuary and this PC explained 13.97 % of the total variance.

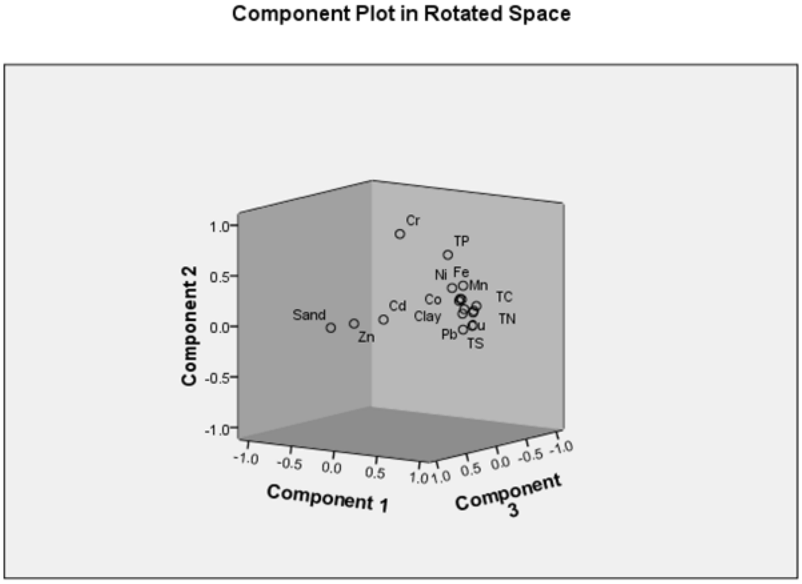


Figure 5.6 Ordination plot of principal components of estuarine sediments during post-monsoon

High loadings of these heavy metals with textural features, other sedimentary parameters and negative loading of sand in all these components indicated the association of these metals with organic components in the sediments of Cochin estuary (Shajan, 2001; Balachandran *et al.,* 2005; Sudhanandh *et al.,* 2011; Deepulal *et al.,* 2012). Organic matter fluxes derived from anthropogenic sources has been reported to be with a higher capacity to bind most of the metals during its transport and export to the bottom sediments (Murray *et al.,* 1999; Reimann and de Caritat, 2005). The association of Fe and

Mn in the PCs with the mud (silt+clay) and organic matter could be interpreted in terms of common detrital and non-detrital association of these elements mainly with fine grained aluminosilicates i.e., clay minerals (Calvert *et al.,* 1993; Oakley *et al.,* 1981; Stumm and Morgan, 1981). Fe–Mn oxyhydroxides were reported to play an important role in scavenging the heavy metals especially in the fine grained sediments (Pruysers *et al.,* 1991; Tessier *et al.,* 1979; Wallace *et al.,* 1988). From the PCA, in the Cochin estuarine sediments also Fe–Mn oxyhydroxides were found to play an important role in scavenging the heavy metals (Jayasree and Nair, 1995; Deepulal *et al.,* 2012; Gireesh Kumar, 2013). Thus, a significant fraction of heavy metals are flocculated along with organic matter or gets adsorbed onto Fe-Mn oxide geochemical phases and thereby controlling the heavy metals in the estuarine sediments.

In the coastal area, two principal components which explained 89.92 % of the variance were obtained from the PCA during Pre-M season. PC1 which accounted for 74.78 % of the cumulative variance was characterised by high positive loadings of silt, clay, TOM, TP, TN, TS, TC and all the metals except Mn. Ni showed moderate positive loading in this component. Sand was negatively loaded in this component. This PC represented the physical control of fine grained materials and organic matter in the abundance and distribution of metals in the sediments (Rubio *et al.,* 2000; Aloupi and Angelidis, 2001; Liaghati *et al.,* 2003; Gomes *et al.,* 2009). PC2 which explained 15.14 % of the cumulative variance was characterised by high positive loading of Mn and moderate positive loadings of Ni, Co and silt. This component revealed the formation of stable hydrous Mn oxides and co- precipitation or adsorption of other heavy metals like Ni and Co onto hydrous Mn oxides and subsequent sinking to the surface sediments. From the ordination plot (Fig. 5.7), we can see that Ni, silt and Co were lying in between Mn and the bigger group associated with clay and TOM contents indicating their complex behaviour. Heavier loading of Ni in PC2 compared to PC1, suggested Ni is involved more in the process associated with PC2.

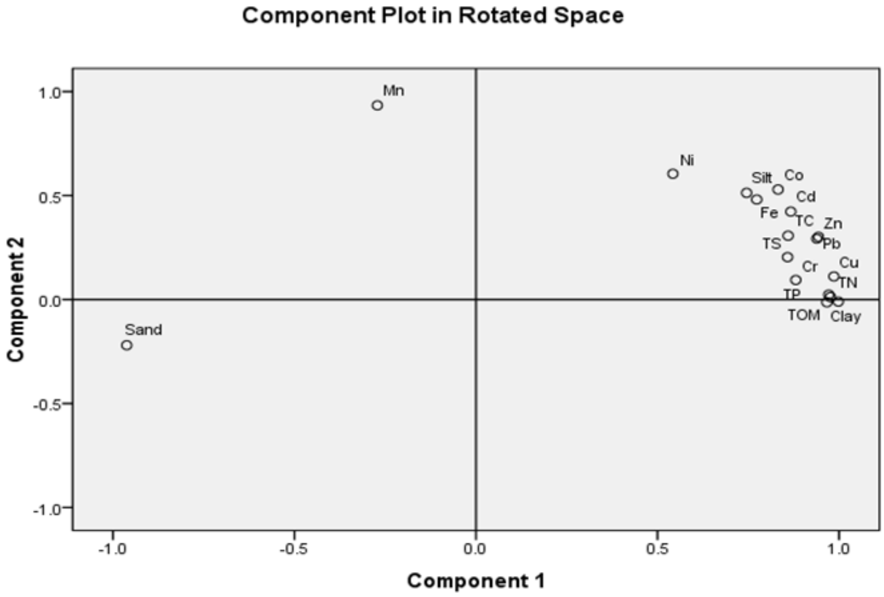


Figure 5.7 Ordination plot of principal components of coastal sediments during Pre-Monsoon

During Mon, three PCs were obtained from the PCA, which explained 92.13 % of variance. PC1 which accounted for 59.62 % of the cumulative variance was characterised by positive loadings of clay, TOM, TP, TN, TS, TC and all the metals except Cr and Mn. Sand was loaded negatively in this component. PC2 was characterised by high positive loading of Cr, moderate positive loadings of Cu, TP and high negative loading of Mn. This component explained 20.92 % of the cumulative variance. From this component it was assumed that the source/behaviour of Cr was entirely different from that of other metals during Mon (Fig. 5.8). Presence of Cu and TP in the two components indicated their complex behaviour during this season. PC3 which accounted for 11.59 % of the cumulative variance was characterised by high positive loading of silt and moderate positive loading of TS. This PC gave an indication about the heavy siltation process during the Mon season and the consequent sulphide formation due to the restricted oxygen levels in the sediments. Although not heavier, negative loading of sand in PC3 indicated the sulphide formation because it occurs in the less sandy-organic rich sediments.

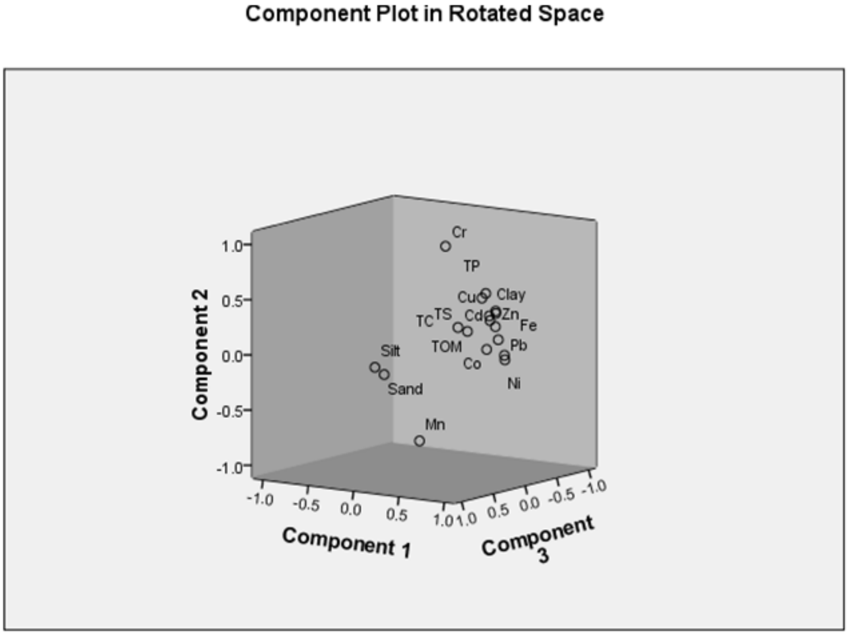
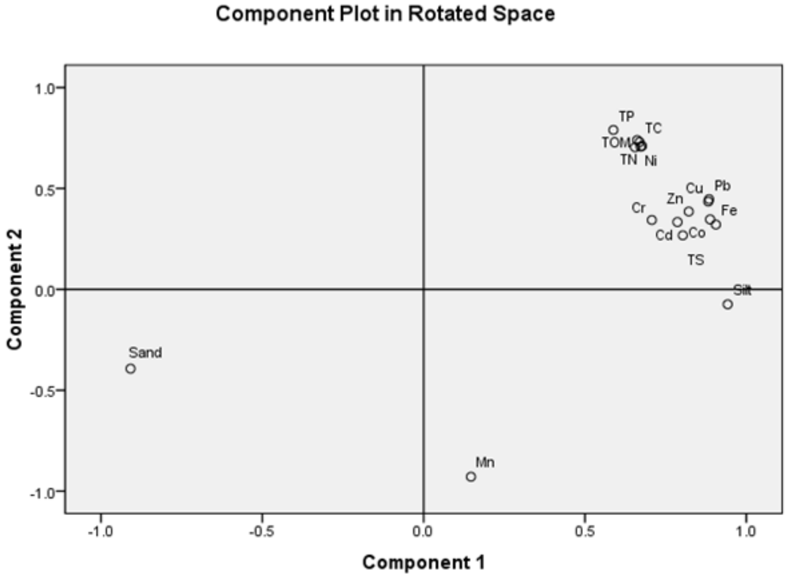

Component Plot in Rotated Space

Figure 5.8 Ordination plot of principal components of coastal sediments during monsoon

Post-M season yielded two principal components with 89.42 % cumulative variance. PC1 which accounted for 58.31 % of the cumulative variance was characterised by high positive loadings of silt, Fe, Pb, Co, Cu, Zn, TS and moderate positive loadings of Cr, Ni, TC, TN, TP, TOM and clay. Sand was negatively loaded in this factor. This PC could be considered as the granulometric component and sorption/desorption on the fine-grained minerals and organic matter. After the heavy siltation during Mon, highly reducing atmosphere in the sediments during the Post-M season, lead to the reductive dissolution of Mn and Fe oxides which remobilize the initially-bound heavy metals which further can be re-adsorbed onto (or co-precipitated with) newly-formed Mn and Fe mineral phases like carbonates, sulphides (Gao *et al.,* 2006; Scholz and Neumann, 2007; Gao *et al.,* 2009; Rigaud *et al.,* 2013). Position of TS with all the metals except Ni in the ordination diagram (Fig. 5.9) pointed to the sulphide formation and hence PC1 might have explained this process. Position of Mn far away from this group and its highly negative loading in PC2 also suggested its entirely different behaviour in the coastal sediments. PC2 which accounted for 31.11 % of the cumulative variance was loaded positively with Ni, TC, TN, TP, TOM, clay and negatively with Mn. This component could be attributed to the flocculation and sedimentation processes of the organic matter during Post-M season.

From the PCA, it could be assumed that the origin or behaviour of Mn is different from that of other metals in this coastal system. The poor association of Mn with other heavy metals suggested that the hydrous Mn oxides might be only a minor host phase for the heavy metals in the coastal environment.



Component Plot in Rotated Space

Figure 5.9 Ordination plot of principal components of coastal sediments during post-monsoon

5.2.2.4 Cluster Analysis

Metals and the environmental data were subjected to Hierarchical cluster analysis (distance cluster combine) and the dendrogram plots using average linkage between groups are shown in Fig. 5.10 to Fig. 5.15.

Two major clusters of stations were obtained in the estuary during Pre-Mon (Fig. 5.10) and the first major cluster was formed by two sub clusters. First sub cluster, which was characterised by higher levels of sand and lower levels of all the metals and other environmental variables, was again subdivided in to two clusters. First one constituted by stations E7, E8, E11 and E13 was characterised by lowest concentrations of Zn, Cd and TP. Second one formed by E2, E3, E9 and E10 were based on similar levels of Cd and TP. Second sub cluster, formed based on the lower distribution of sand and moderately higher distributions of other metals and other geochemical parameters, was again branched in to 3 clusters. First one formed by stations E6 and E12 was characterised by comparable levels of Cd, Pb, Cr, Ni, Co Cu, TP, sand, silt and clay. Second one constituted by stations E15 and E16 were characterised by similar textural distribution and similar distribution of most of the heavy metals. Third one formed by stations E4 and E14 were associated with similar concentration of TP. Second major cluster was constituted by two simplicifolious clusters formed by stations E1 and E5. Highest levels of Cd, Pb, Cu, Zn and clay among the estuarine stations made E1 stood alone in a sub cluster. Highest level of TP; higher levels of Cd and Zn next to E1; moderate levels of other metals and chemical parameters made E5 constitute the second simplicifolious cub cluster.

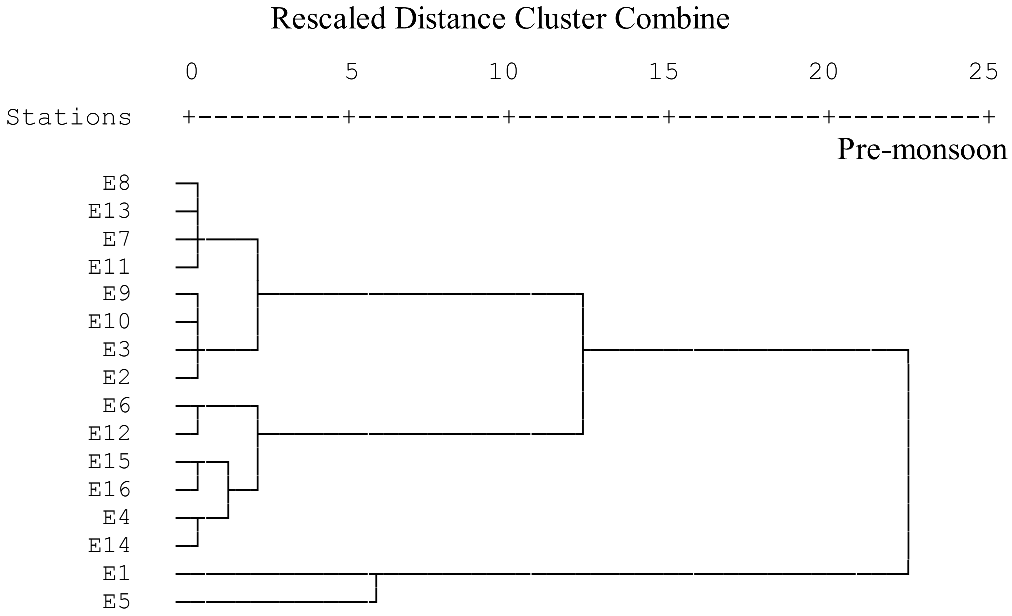


Figure 5.10 Dendrogram showing clusters of sampling locations in the estuary during Pre-Monsoon

During Mon season, estuarine stations were grouped in to three major clusters which were again branched in to many sub clusters (Fig. 5.11). First major cluster was again sub divided in to four sub clusters. First sub cluster formed by the stations E11, E14 & E15 were characterised by lower levels of metals, silt, clay, TC, TN, TP, TOM and higher levels of sand. Stations E10, E12 and E16 which constituted the second sub cluster showed comparable levels of Pb, Co, Cu, Fe and clay. Moderately higher concentrations of Zn made E2 constitute a simplicifolious sub cluster. Comparable levels of the heavy metals and other geochemical parameters made stations E3 and E4 cluster together. Second major cluster was formed based on higher levels of Cu, TP, TS, clay and lower sand content compared to other estuarine stations. Highest concentrations of all metals except Cd and Zn were found in these stations (Pb, Ni & Cu in E6; Co in E7; Cr and Mn in E8 and Fe in E9). Third major cluster formed by stations E1 and E5 were characterised by non-comparably higher levels of Cd and Zn compared to rest of the stations.

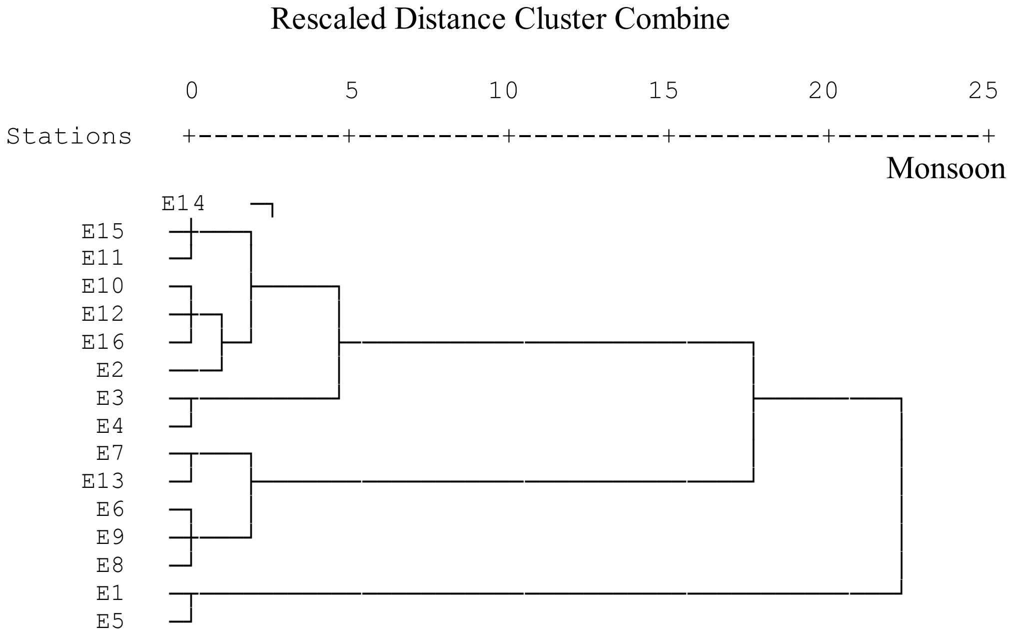


Figure 5.11 Dendrogram showing clusters of sampling locations in the estuary during monsoon

Two major clusters of sampling stations were obtained during Post-M (Fig. 5.12). First major cluster was again sub divided in to four sub clusters. First sub cluster formed by stations E4, E6, E9, E12 and E15 were characterised by similar clay and metal contents. Similar distributions of Cd, Cr, Co, Cu, Fe, TC, TOM and highest clay content brought stations E7 and E13 together in the second sub cluster. Third sub cluster constituted by stations E3, E10, E11, E14 and E16 were characterised by higher sand content, lower clay, silt, metals and other geochemical contents. Stations E1, E2 and E5 formed fourth sub cluster in the first major cluster with higher levels of Cd and Zn. Stations E1 and E5 clustered together during all seasons with higher levels of Cd and Zn compared to other estuarine stations. These are the northern stations having influence of industrial area of Kochi and from the cluster analysis the influence of the industrial effluents was evidenced. E8 stood alone in the second major cluster with highest concentrations of Cr, Ni, Co, Mn, Fe, TN and TP in comparison with other stations.

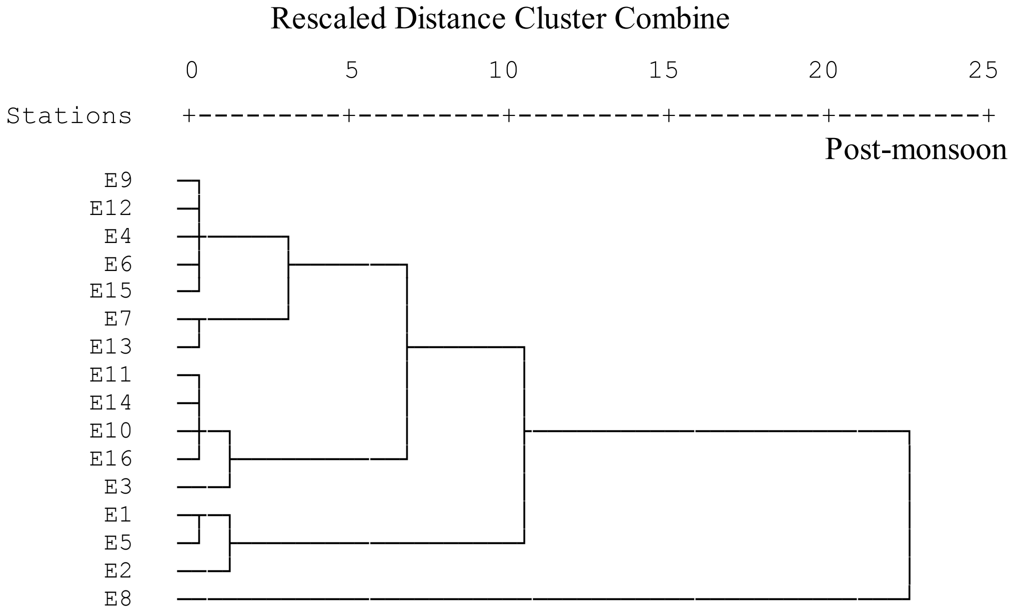


Figure 5.12 Dendrogram showing clusters of sampling locations in the estuary during post-monsoon

Two major clusters of stations were obtained in the coastal area. During Pre-M, the first major cluster was sub divided in to two sub clusters; first sub cluster was again grouped in to two, first one was constituted by stations C8 and C10 (Fig. 5.13). This cluster was characterised by comparable levels of sand and silt, lower clay content and moderately higher metals contents. The second one was a simplicifolious cluster formed by C1 and characterised by highest TS content and moderate heavy metal contents. Second sub cluster in the first major cluster was again branched in to two; first one formed by stations C3, C9 and C11 was characterised by higher sand content and lower metal levels. Station C4 alone constituted the second cluster and showed highest sand content, lowest silt, clay, other environmental variables and heavy metals except Fe among the other coastal stations. Second major cluster formed by C5 & C6 were characterised by lowest sand content and highest levels of clay, silt, other environmental variables and heavy metals except Mn.

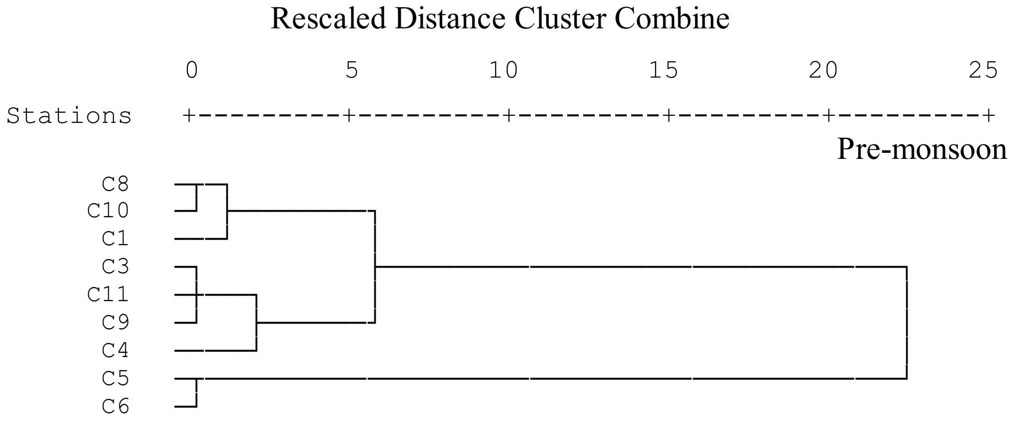


Figure 5.13 Dendrogram showing clusters of sampling locations in the coast during Pre-Monsoon

During Mon, two major clusters of sampling stations were obtained in the coastal area, both of them were again sub clustered in to two (Fig. 5.14). Stations in the first major cluster was characterised with lower sand content and higher metal contents (except Mn) than the stations in the second major cluster. First sub cluster in the first major cluster was again branched in to two clusters; first one of them formed by stations C6, C7 and C8 was characterised by lower sand content, higher metal levels and other geochemical parameters. Second one was a simplicifolious cluster formed by C9 based on the highest concentrations detected for Cd, TC, TS and silt. Station C5 constituted the second sub cluster in the first major cluster. C5 is detected with highest Pb, Cu, Zn, TP and clay contents among the coastal stations and highest Cr and Mn content among the stations in the first major cluster.

First sub cluster in the second major cluster was constituted by stations C3 and C10 characterised by higher sand and lower clay contents. Other chemical parameters and metals except Mn were detected in lower concentrations in C3 and C10 compared to other coastal stations. Cr, Cu, TS, TP, TOM and clay contents were found to be higher in second sub cluster (C1, C2, C4 and C11) compared to the first sub cluster formed by C3 and C10. Second sub cluster was again branched in to three clusters and the first one formed by C2 and C4 were detected with similar distributions for Pb, Co and Fe.

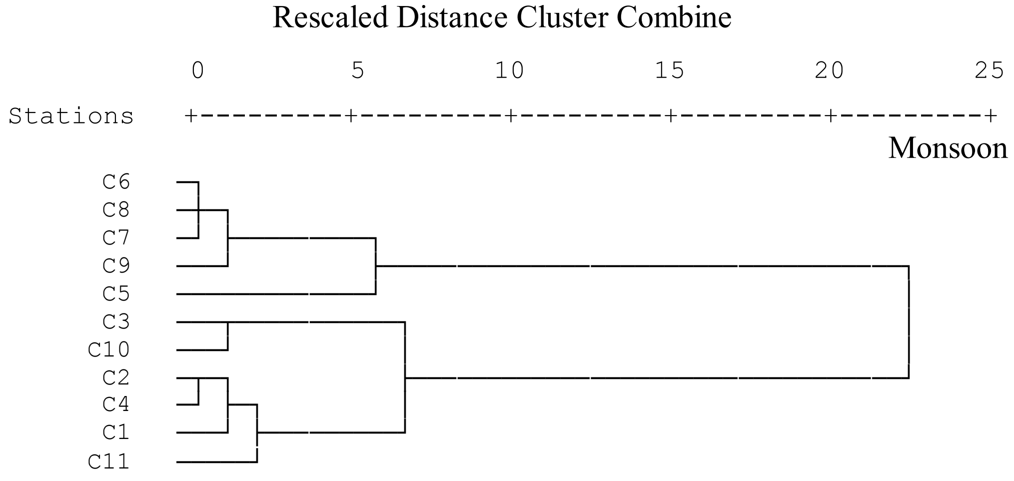


Figure 5.14 Dendrogram showing clusters of sampling locations in the coast during monsoon

Two major clusters of stations were obtained from CA during Post-M season (Fig. 5.15) and this clustering might be based on the difference in organic fraction distributions. First major cluster characterised by high organic contents was sub clustered in to two clusters. First sub cluster also divided in to two clusters; first one formed by C2, C4 was characterised by similar distribution of sand, silt, clay, Pb, Cr, Ni, Co, Cu, TC, TN, TP and TOM. Second cluster formed by C10 and C11 was characterised by similar distribution of silt, Ni, Cu and TP. Second sub cluster formed by Stations C5, C6, C7 & C8 were characterised by higher TOM, TP, TN, TC, clay, metal content (Fe, Cu, Co, Ni, Cr) and lower sand content. Second major cluster based on lower TP and TN values was constituted by three simplicifolious clusters formed by stations C1, C3 and C9. C3 was characterised with lowest concentrations for all the metals except Mn, organic fractions, silt, clay and highest sand content. Station C9 was found to be with higher value of TP compared to C1 and C3.

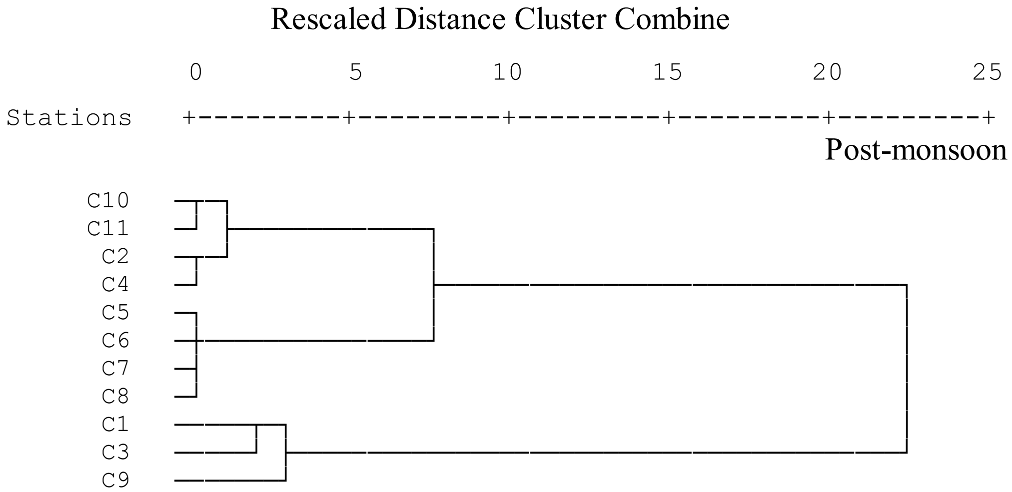


Figure 5.15 Dendrogram showing clusters of sampling locations in the coast during post-monsoon

In the estuary, clustering of stations was mainly based on the anthropogenic inputs of heavy metals especially Zn and Cd, while in the coast clustering was based on the granulometric distributions.

5.3 Conclusions

Cochin estuarine and coastal systems were found to be heavily contaminated with Cd followed by Zinc. Estuarine area was associated with higher concentrations of all the metals under study except Mn. Cr and Fe were also contaminating the system in lesser degree compared to other metals. Mn, Cr and Fe showed low contamination in the coastal system throughout the study period. Heavy metal status of the estuary is controlled mainly by anthropogenic factors. Although the exchange of contaminants occurs from estuary to the coast, rapid dispersal of these pollutants by the coastal currents and rapid removal by the biogenic association are strong enough to prevent the long term accumulation in the coastal system. In the coastal environment also, Cd was observed to be the main polluting metal, all other metals showed low to moderate levels of pollution in the coastal area.

In the estuary, strong association of the heavy metals under study (except Zn) with finer fractions of sediment and TOM suggested enrichment of heavy metals occurred mostly via direct physical adsorption by the clay minerals or by the organic matter which is mounted on the clay surface. The significant correlations for all the metals (except Zn during the entire study period and Cd during Pre-M and Mon in the estuary; Mn during the entire study period, Ni during Pre-M and Cr during Mon in the coast) with organic matter indicated organic associations during their transport in the study area.

The strong relationship of Fe and Mn with TOM and mud fraction during all seasons suggested their presence as a constituent of clay minerals and on coatings on the surface of clay particles. This indicated the significant role of hydrous Fe-Mn oxides and mud (silt & clay) might be playing in controlling the distribution of heavy metals in the estuary. However, significant positive and negative correlations obtained for Mn with sand and clay respectively and lack of significant correlations with other metals indicated that the origin, transport or reaction pathway of Mn is different from that of other metals in the coastal system. Thus, it could be inferred from the correlation analysis that Mn oxides may not have played any significant role in transport of metals in the coastal system while Fe oxides might have been the major carriers of these heavy metals. Negative relationship observed between Fe & Mn also implied that they had entirely different origin or transport pathway in the coastal area.

The distribution of elements in the estuary indicated anthropogenic source of metal contamination. All other metals under study except Zn and Cd (the established contaminants in the Cochin estuary) were associated in a single component in PCA indicating a common transport for these metals in the estuary. Association of anthropogenic metals like Cd and Zn in the same component throughout the study period pointed to the point source of these metals in the estuary. While in the coastal environment, Mn was the metal which behaved differently from other metals under study. Textural features and other sedimentary variables did not show any significant correlations with Zn in the estuary and Mn in the coast suggesting they did not have an important role in the transport of other metals in the estuary and coast respectively.

Cluster analysis indicated that the clustering of estuarine stations was mainly based on the anthropogenic origin of metals which was supported by the results of PCA also. While in the coast, clustering was based mainly on the granulometric distributions. Heavy metal status of the estuary is controlled mainly by anthropogenic factors and the dispersion from the dumping sites might be contributing to the higher metal levels in the coastal sediments. Thus it can be said that the Cochin estuarine system is more polluted than its adjacent coast.

All these results indicated higher heavy metal levels in the study area and it can be said easily that the Cochin estuarine and coastal system is prone to impacts from human activities which may result in the degradation of the resource in the coming days. Accumulation of heavy metals and other persistent environmental contaminants in the sediments are toxic to organisms especially at elevated concentrations. Hence assessment of heavy metal pollution by the application of various indexing methods and effect based sediment quality guidelines are dealt with in the next chapter.

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Chapter 6

HEAVY METAL ENRICHMENT IN SEDIMENTS AND ITS ECOLOGICAL IMPACTS

Contents

6.1 Introduction

Heavy metals are released into the environment in gaseous, particulate, aqueous or solid form through both the natural sources dominated by parent rocks/metallic minerals and the anthropogenic sources. Main anthropogenic activities include unscientific agricultural practices using fertilizers, animal manures, and pesticides containing these metals; metallurgical activities including mining, smelting, metal finishing, and other activities like, energy production, transportation, microelectronic products, and urban waste disposal. Heavy metals contribute to various biogeochemical processes and many of them are essential to the organisms, but in elevated concentrations, they affect the ecosystems through bio-accumulation and biomagnification processes. Hence they are potentially toxic for both the environment and mankind (Manahan, 2000; Gaur and Dhankhar, 2009; Ahmed and Al-Hajri, 2009; Hasan *et al.,* 2010; Resmi *et al.,* 2010; Abdul Aziz *et al.,* 2010; Ahmad *et al.,* 2010; Cui *et al.,* 2011). The toxicity of metals varies significantly among organisms, but generally they are accumulated in tissues as a function of temperature, salinity, diet, spawning, and the ability of organisms to control metal concentrations (Bianchi, 2007). The occurrence of the detoxifying mechanisms in aquatic invertebrates (Deeds and Klerks, 1999) can result in a developed resistance to these contaminants, which can then allow for these compounds to move trophically through food webs (Klerks and Lentz, 1998).

Pollution by toxic heavy metals is one of the major threats facing by the Cochin estuarine system. Despite the numerous industries and the subsequent discharges of effluents containing heavy metals into Cochin estuary, limited studies have been carried out so far on assessing their impacts and the extent to which estuarine sediments have been contaminated by these metal rich effluent discharges (Martin *et al.,* 2012; Robin *et al.,* 2012). Higher concentrations of Fe, Mn, Cu and Zn in the suspended particulates due to the domestic and industrial pollution were reported in the Cochin Estuary (Sankaranarayanan and Stephen, 1978). Large removal of metals from the dissolved phase to the particulate phase with increasing salinity during the non-monsoon periods, due to processes of precipitation, adsorption and flocculation was reported by Shibu (1992). Hence this estuary behaves as a sink to the metals received from the industrial belt of Greater Cochin. The aquatic systems near the industrialized areas contain huge quantity of heavy metals, which have significant ecological significance due to their toxicity, persistence and bio-accumulation. Toxic effects of pollutants, especially of heavy metals on native fauna of the Cochin Estuary and adjoining marine environments were reported by many authors (Sankaranarayanan *et al.,* 1978; Lakshmanan and Nambisan, 1983; Sathyanathan *et al.,* 1988; Nair *et al.,* 1993; Maheswari *et al.,* 1997; Kaladharan *et al.,* 2005; Maheswari Nair *et al.,* 2006;

Ranjitha and Sujatha, 2011; George *et al.,* 2011; Manju and Sujatha, 2013; Rejomon George *et al.,* 2013).

Wetlands act as a sink for heavy metals via adsorption and sedimentation processes (Williams *et al.,* 1994; Larsen and Gaudette, 1995; Cortesao and Vale, 1995; Bruces Williamson *et al.,* 1996; Dassenakis *et al.,* 1997; Balls *et al.,* 1997) and due to this wetland sediments have the main role in transportation of metals in aquatic systems (Larsen and Jensen, 1989). Release/sorption of metals from/to the sediments has a significant influence on the quality of the overlying waters also (Forstner and Muller, 1973; Forstner and Wittman, 1979; Xianghua and Herbert, 1999). Adsorption is considered as the major process affecting the mobility of heavy metals in the soils (Bradl, 2004) and this potentially reduce the concentrations of toxic metals in natural aquatic environments (Jannasch *et al.,* 1988; Comber *et al.,* 1996). The metal fractions associated with the bed sediments are expected to be with no direct adverse effects, unless and until the metal ions which are tightly bound and subsequently got buried at the bottom in course of time are remobilized by any of the physical/chemical/biological processes.

The main limitation of sediment chemistry data is that, it alone cannot provide a basis for assessing the potential biological effects of contaminated sediments without defensible sediment quality guidelines (Jones-Lee and Lee, 2005). The need for chemical guidelines that could be used to predict adverse biological effects in contaminated sediments lead to the development of sediment quality guidelines (USEPA, 1992; Long *et al.,* 1995; Long and Mc Donald, 1998; Mc Donald *et al.,* 2000). Sediment quality guidelines (SQGs) are used to make an initial assessment of sediment toxicity in the absence of direct biological effects data (Batley *et al.,* 2005; Kwok *et al.,* 2013); to evaluate spatial pattern of sediment contamination (Birch and Taylor, 2002); to interpret historical trends, identify deleterious chemicals or reaches in a waterway, interpret or design ambient monitoring programme (Crane and MacDonald, 2003); support or maintain designated uses of freshwater, estuarine, and marine environments; to assist sediment assessors and managers charged with the interpretation of sediment quality (Caeiro *et al.,* 2005); to rank and prioritize the contaminated areas or the chemicals for the further investigation (Farkas *et al.,* 2007) and to classify hot spots and to establish baseline conditions in non-urbanized systems, rank contaminated waterways, help chose sites for more detailed studies (Long and MacDonald, 1998).

Assessment of the overall status of heavy metal pollution and the associated ecological risk are helpful for the management of aquatic environment in a city like Kochi which is undergoing fast industrial transformation. The total concentration and mobility of heavy metals in sediments of Cochin estuary and its adjacent coast has been widely studied in the last decades (Shajan, 2001; Balachandran *et al.,* 2006; Sudhanandh *et al.,* 2011, Bindu *et al.,* 2015). Few studies were reported on assessing the degree of pollution by heavy metals in the Cochin estuary and its adjacent coast. Study of sediments and their sorptive characteristics provide valuable information concerning the tolerance of an aquatic system to increased heavy metal load and the fate and transport of these pollutant metals in the aquatic environment. There are many studies on adsorption of heavy metals by various types of sorbents. However, few studies were reported on sorption of metals by the natural sediments. Adsorption process of metals onto the bed sediments of Cochin estuarine and coastal system is rarely studied. From the previous chapter it could be understood that the study area is having higher metal contents compared to the average shale values. In this context, heavy metal levels in the study area were compared with other coastal systems in order to find out the enrichment of these metals on a global scale and with the previous data in the study area to find out chronological enrichment of these metals. This chapter is aimed at assessing the heavy metal pollution using various indices and toxicity assessment using effect based sediment quality guidelines. This chapter is also aimed to study the adsorption of metals using both the Freundlich and Langmuir adsorption isotherms and to find out the adsorption capacity and intensity of the sediments.

6.2 Results & Discussions

6.2.1 Chronological Enrichment and Comparison with Other Coastal Systems

Although biological and chemical processes are common in all the estuaries, the distributions of heavy metals and their reactivity rates vary greatly among the estuaries, depending on the environmental factors like mixing patterns, hydrodynamic residence times and transport processes (Hatje *et al.,* 2003). Hence, heavy metal behaviour in estuaries lacks a universal pattern (van den Berg, 1999; Camusso *et al.,* 1997). Still, comparison of metal concentrations in the sediments of the study area with the earlier reported values and that of other coastal systems can be generally taken as a quick and practical method for evaluating heavy metal enrichment and associated pollution. The range of concentrations of heavy metals in the sediments of Cochin estuary, adjacent coast and that of other contaminated coastal systems in and abroad India are summarised in the Table 6.1.

Comparison of metal concentrations in the sediments of the study area with the values reported by earlier researchers indicated Cd concentration in the study area was found to be almost doubled over the years (Kaladharan *et al.,* 2005; Balachandran *et al.,* 2006). Zn content was found to be in higher ranges in the sediments of Cochin estuary compared to the reported values (Venugopal *et al.,* 1982; Nair, 1992; Balachandran *et al.,* 2006; Martin *et al.,* 2012). The above results indicated higher degree of contamination of the estuary by Cd and Zn from the industries in its catchment area. Pb was detected in higher concentrations compared to the previous studies in the estuary (Nair, 1992; Balachandran *et al.,* 2006; Deepulal *et al.,* 2012) and the adjacent coast (Kaladharan *et al.,* 2005; Balachandran *et al.,* 2006). Cr content in the estuary was found to be enriched over the years (Nair, 1992; Balachandran *et al.,* 2006; Deepulal *et al.,* 2012). Ni was also found to be enriched in the sediments of the study area (Venugopal *et al.,* 1982; Balachandran *et al.,* 2006; Martin *et al.,* 2012). Co also found to be accumulated over time in the sediments (Venugopal *et al.,* 1982; Balachandran *et al.,* 2006; Deepulal *et al.,* 2012). Cu content in the sediments of the estuary was detected in higher side in comparison to the earlier reports (Venugopal *et al.,* 1982; Nair, 1982; Balachandran *et al.,* 2006). Mn in the coastal sediments showed accumulation when compared to the values reported by Balachandran *et al.* (2006) and in the estuarine sediments also it showed enrichment (Venugopal *et al.,* 1982; Nair, 1992) over the time. Fe showed accumulation over time in the estuarine (Nair, 1992; Balachandran *et al.,* 2006; Martin *et al.,* 2012) and coastal sediments (Balachandran *et al.,* 2006).

Table 6.1 Comparison of heavy metal concentrations in the Cochin Estuary and its adjacent Coast with the average shale value and that of other Indian and globally impacted coastal systems

Location	Cd µg/g	Pb µg/g	Cr µg/g	Ni µg/g	Co µg/g	Cu µg/g	Zn µg/g	Mn µg/g	Fe %	References
Average shale	0.1	14.8	126	56	24	25	65	716	4.32	Wedephol, 1995
Manakudy Estuary, India	2.69 – 3.17	152.25 – 176.88	256.9 – 482.14	20.15 – 28.9	-	37.35 – 45.87	54.58 – 72.62	-	0.46 - 0.49	Kumar & Edward, 2009
Tambaraparni River Estuary, India	0.42 – 0.92	0.3 – 170	58.90 – 110.3	-	-	62.8 – 115	47.3 – 112	-	-	Jayaraju *et al.,* 2011
Tapti Estuary, India	0.74 – 1.25	43.28 – 77.74	48.26 – 72.40	71.13 – 107.82	14.73 – 21.69	123.17 – 170.52	117.47 – 178.8	-	5.66 - 9.0	Bhavna *et al.,* 2013
Elbe, Germany	1.5	81	83	41	-	44	392	-	-	Wetzel *et al.,* 2013
Guadiana Estuary, Spain	0.05 – 1.40	1.30 – 62.5	1.60 – 24.0	0.70 – 41.6	0.46 – 24.8	1.2 – 73.0	4 – 483	-	-	Delgado *et al.,* 2010
Minho River Estuary, Spain	-	11.12 – 18.08	8.7 – 64.6	-	-	1.69 – 26.77	19.4 – 131	160 - 540	0.54 - 4.92	Mil-Homens *et al.,* 2013
Sao Francisco Estuary, Brazil	-	May-16	15 – 69	3 – 27	-	2 – 26	1 – 48	27 – 239	0.59 - 3.58	Santos *et al.,* 2009
Pearl River Estuary, China	-	40.9 – 92.4	74.1 – 123	21.9 – 46.5	-	18.9 – 87.2	100 – 289	0.06 – 0.14	3.24 – 4.13	Yu *et al.,* 2010
CUA ONG Harbour, Vietnam	0.02 – 0.2	4.41	10 – 49	3 – 20	1 – 13	13 – 30	12 – 93	18 – 318	0.48 – 3.72	Hieu Ho *et al.,* 2010
Yangtze River Intertidal Sediments, China	-	27.3	78.9	31.8	-	30.7	94.3	766	3.34	Zang *et al.,* 2009
Hamilton harbour, Canada	-	18 – 1250	5 – 140	8 – 61	-	8 – 135	338 - 5930	42 – 1158	1.22 – 20.4	Poulton *et al.,* 1996
Bergen harbour, Norway	-	24 – 1920	-	-	-	25 – 1090	46 - 2900	-	-	Paetzel *et al.,* 2003
Bay of Bengal, off Ennore, India	6.58	32.36	194.83	38.61	8.1	506.21	126.83	373	2.72	Muthu Raj & Jayapraksh, 2008
Cochin Shelf, India	3.27	13.1 – 39.6	35 – 195	5.1 – 72.1	3.1 – 23.2	6 – 32.7	7 – 132	40 – 210	0.34 – 3.42	Balachandran *et al.,* 2006
Cochin Estuary, India	0.16 – 5.96	1.88 – 28.75	7.5 – 79	6.8 – 72.5	4.38 – 24.61	4.40 – 46.88	3.13 – 433.13	48.8 – 657.5	1.48 – 8.30	Deepulal *et al.,* 2012
Kakinada Bay, India	0.5 – 6.0	2.5 – 38	0.80 – 1.36	13 – 60	27 – 50	30 – 51	-	225 – 666	0.45 – 0.49	Ray *et al.,* 2006
Cochin Estuary	0.25 - 9.39	4.97 - 48.80	6.86 - 192.36	11.92 – 208.83	6.08 – 36.60	5.10 – 42.88	7.28 – 1229.83	63.46 – 334.49	0.49 – 5.23	Present Study
Cochin Coast	0.29 -3.15	3.75 – 42.29	5.50 – 109.88	24.86 – 145.48	6.07 – 36.07	5.02 – 32.32	9.62 – 114.39	92.20 – 427.04	0.16 – 3.93	Present Study

Cd was found to be in higher ranges in the sediments of Cochin estuary compared to the reported values in other Indian and abroad estuaries. Although the Cd content in the Cochin coastal sediments was found to be lower than that in Kakinada Bay and comparable to the Cd content in the Cochin continental shelf, Cd contamination is found to be in higher side compared to other coastal systems. Zn content in the sediments of Cochin estuary was found to be higher in comparison with the Indian and other world estuaries. Coastal sediments showed Zn concentrations higher than some Indian estuaries and abroad harbours. However, it was lower than the values reported in the heavily polluted harbours (Poulton *et al.,* 1996; Paetzel *et al.,* 2003) and continental shelf sediments of Cochin (Balachandran *et al.,* 2006). Pb content in the study area was lower than that in Indian and abroad estuaries, but it was higher than the value reported by Deepulal *et al.,* (2012) in Cochin estuary and Balachandran *et al.,* (2006) in Cochin coast. So it can be said that the study area is accumulating Pb over the years. Pb content of the coastal sediments was also higher than that in Kakinada bay (Ray *et al.,* 2006). Cr content in the estuarine sediments was found to be higher than the abroad estuaries and Indian estuaries except Manakudy estuary. Cr content in the coastal sediments was found to be higher than Kakinada Bay, CUA ONG Harbour and Yangtze River Intertidal Sediments. Whereas, it was lower than that in the sediments of Hamilton harbour and continental shelf sediments of Cochin. Ni content in the Cochin estuary and its adjacent coastal systems was observed to be higher than that in other Indian and world coastal systems. Co concentrations in the study area were found to be higher than all the coastal systems except Kakinada Bay. Cu content in the estuarine sediments was found to be lower than that in all the estuaries except Minho River estuary and Sao Francisco estuary. Cu content in the coastal sediments was also found to be lower than Kakinada Bay, Hamilton harbour and Bergen harbour. Cu content in this study was comparable to that reported in previous studies in Cochin Estuary (Deepulal *et al.,* 2012) and adjacent shelf (Balachandran *et al.,* 2006). It could be said that the study area was not heavily enriched with Cu in comparison to the heavily polluted coastal systems. Mn content in the sediments was found to be lower than the previous report in Cochin Estuary (Deepulal *et al.,* 2012), whereas in the coastal sediments it was higher than the value reported in the Cochin shelf (Balachandran *et al.,* 2006). Mn in the coastal sediments was well below the values reported in Hamilton harbour, Yangtze River Intertidal Sediments and Kakinada Bay. Fe content in the sediments was found to be lower than the previous report in Cochin Estuary (Deepulal *et al.,* 2012), whereas in the coastal sediments it was higher than the value reported in the Cochin shelf (Balachandran *et al.,* 2006). Fe content in the Cochin Estuary was higher than that in other Indian (except Tapti Estuary) and abroad estuaries. Fe content in the Cochin coastal sediments was higher than that in other coastal systems except Hamilton harbour. Cochin estuarine and coastal sediments were found to be polluted with Cd, Zn, Ni, Co and Fe in comparison with other systems indicating the anthropogenic influence on its heavy metal status. Although all the metals under study showed a chronological enrichment, Cd and Zn showed higher intensity in the study area.

6.2.2 Pollution Assessment

The overall pollution status was assessed using various pollution assessment indices like enrichment factor (EF), contamination factor (CF), degree of contamination (C_d), modified degree of contamination (mC_d), pollution load index (PLI) and geoaccumulation index (Igeo).

6.2.2.1 Enrichment Factor (EF)

Impact of natural or anthropogenic pollution of heavy metals is generally evaluated using the enrichment factor (EF) for the heavy metal concentrations above uncontaminated background/reference level (Huu *et al.,* 2010). Fe is used as a normaliser in the present study because it is a major sorbent phase for the metals in the study area and is not substantially enriched in the study area. Enrichment factors of the metals under study in the estuary and coast in the consecutive seasons (appendix 26-28) are represented graphically in Fig. 6.1 (a, b & c) & 6.2 (a, b & c) respectively.

In the estuary, Cd was enriched "significantly - extremely high" levels during Pre-M and Mon seasons. During Post-M, 33 % of the stations came under the "deficient to minimum" enrichment class and rest of the stations were in "significant - extremely high" class. In the coastal area, Cd showed "very high - extremely high" enrichment during Pre-M and "significantly - very high" enrichment in Mon and Post-M seasons. Zn was found to be with "minimum - significant" enrichment in the estuarine sediments irrespective of the seasons and majority of the coastal stations were found to be in "deficient to minimum" enrichment class throughout the study period. Pb showed "moderate" enrichment in the estuary and coast during the entire study period. During Pre-M season, nickel showed moderate – significant and minimum - significant enrichment in the estuarine and coastal sediments respectively. During Mon and Post-M seasons, both the provinces showed moderate and minimum - moderate levels of enrichment during Mon and Post-M seasons respectively.

Cu exhibited "deficient to minimum" enrichment during Mon in the estuary and during Mon and Post-M seasons in the coast. Moderate levels of enrichment was shown by the stations E2 and C4 during Pre-M, E6 and E16 during Post-M and C4 showed significant enrichment during Pre-M season. In the estuary, Co was found to be enriched in minimum to moderate levels. However, enrichment of Co in the coastal sediments was more pronounced during Pre-M season only. C10 during Post-M and C3 during Pre-M and Post-M seasons were the only stations which showed moderate enrichment of Co. Chromium showed “deficient to minimum” enrichment in the estuary during Pre-M and Mon seasons. During Post-M, north and south end members (E2, E3 & E16) were found to be “moderately” enriched with Cr. In the coastal area, Cr was found to be “moderately” enriched in C3 only (Pre-M); Mn was enriched “significantly” in C3 only. Northern estuarine stations showed very high EF values for the metals especially Zn and Cd pointing to the influence of the industrial belt lying north to the Cochin estuary (Shibu *et al.,* 1995; Shajan, 2001; SCMC, 2004; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Paneer Selvam *et al.,* 2012; Deepulal *et al.,* 2012; Shaiju, 2013). Coastal stations near the bar mouth only showed enrichment attributing this to the disbursement of these pollutants by the prevalent northerly currents (Shetye *et al.,* 1991) or biogenic association (Saraladevi *et al.,* 1992) in the coastal area.

Heavy metals with EF values close to 1 are considered mainly of natural origins (Sutherland, 2000) and EF > 1.5 indicated the significant role of external sources of these metals (Zhang *et al.,* 2007). Cd showed EF > 1.5 in the entire study area, except in stations E3, E11 and E16 during Post-M, attesting the enrichment of Cd reported earlier (Paneer Selvam *et al.,* 2012, Deepulal *et al.,* 2012, Shaiju, 2013). Estuarine area was found to be heavily enriched with Zn. Stations E8 and E11 only showed EF < 1.5 throughout the study period pointing to the enrichment of Zn in the estuary. Pb showed EF > 1.5 in the study area attributing this elevated concentrations to the anthropogenic inputs (Nolting *et al.,* 1999). All the coastal stations and majority of the estuarine stations were associated with EF > 1.5, indicating anthropogenic sources of cobalt in the study area. Enrichment factor of majority of the estuarine stations throughout the study period was found to be less than 1.5 suggesting a natural weathering process or crustal input of copper in the estuary.

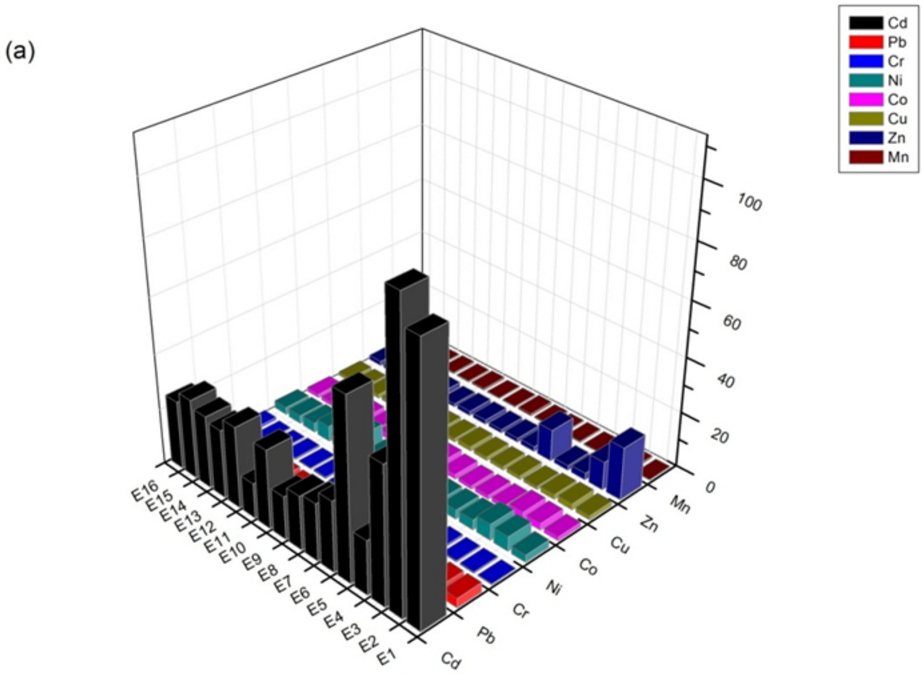

Figure 6.1a Enrichment factors of metals under study in the estuary during pre-monsoon

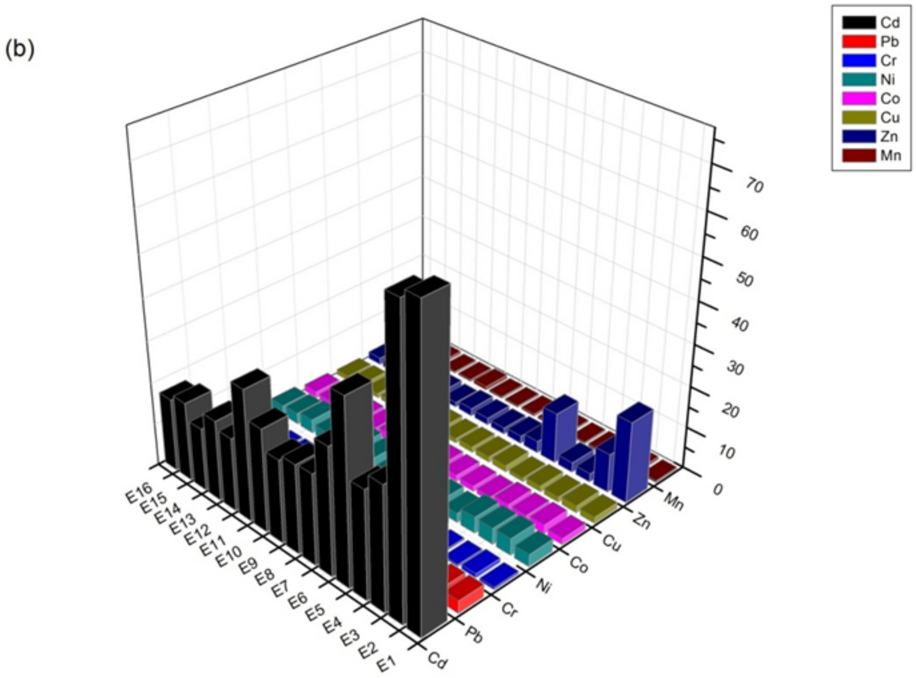

Figure 6.1b Enrichment factors of metals under study in the estuary during monsoon

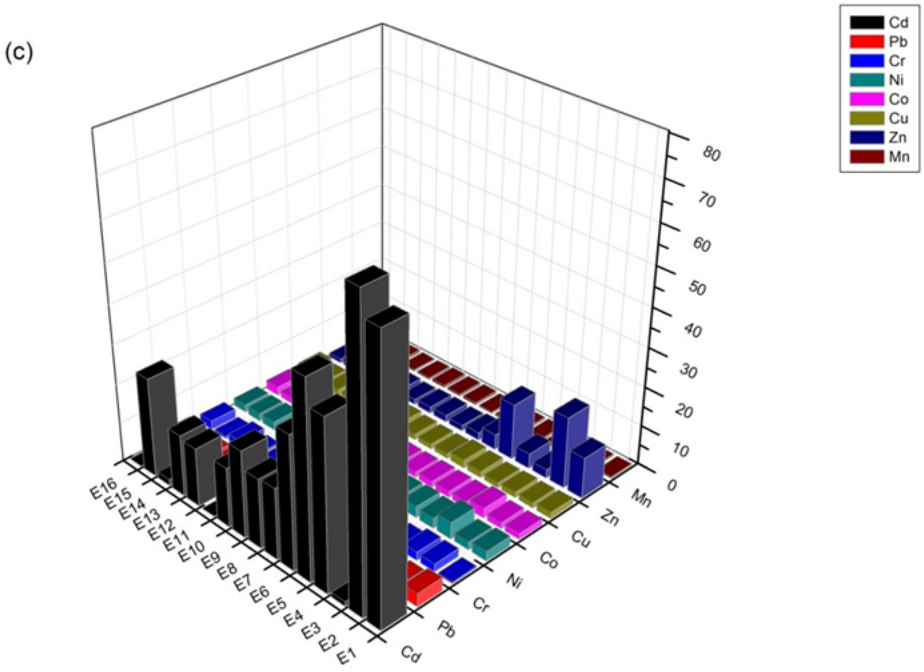

Figure 6.1c Enrichment factors of metals under study in the estuary during post-monsoon

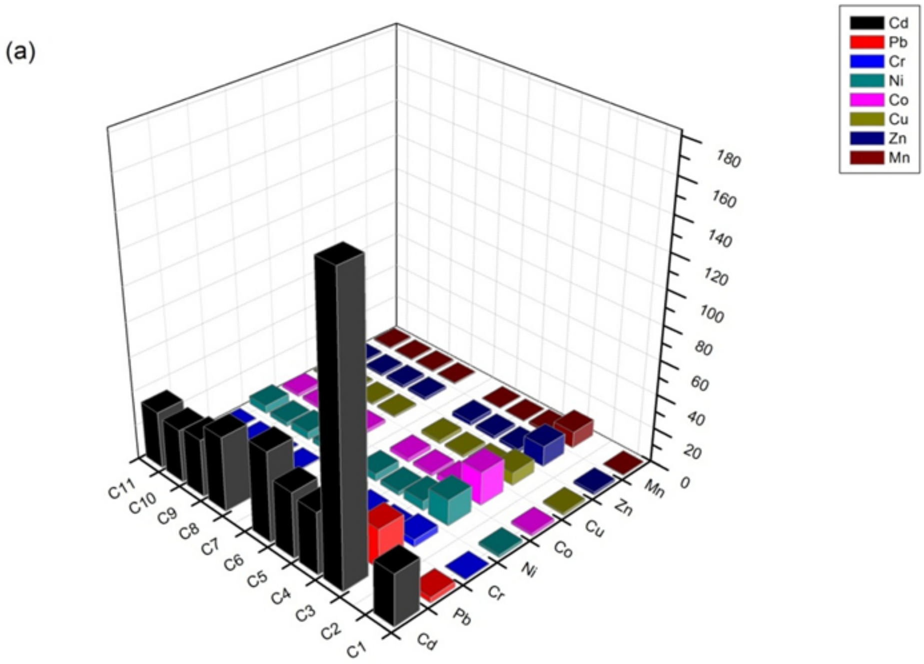

Figure 6.2a Enrichment factors of metals under study in the coast during pre-monsoon

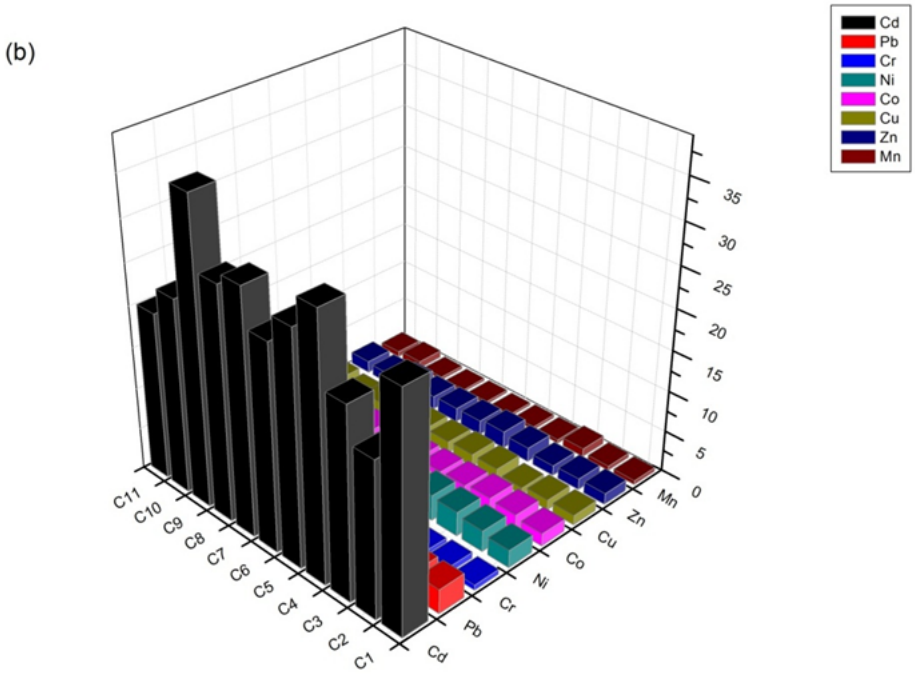

Figure 6.2b Enrichment factors of metals under study in the coast during monsoon

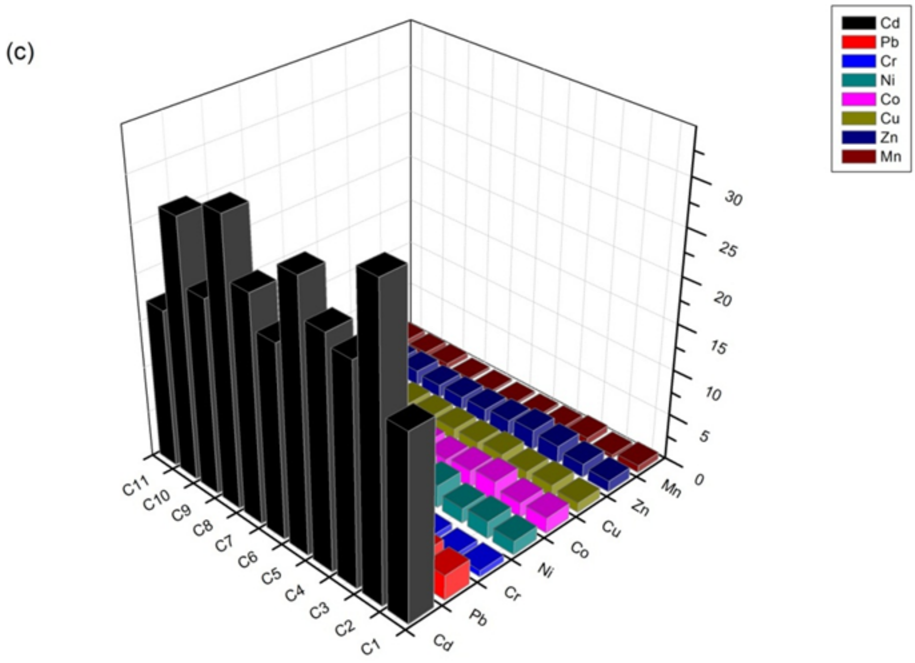

Figure 6.2c Enrichment factors of metals under study in the coast during post-monsoon

Very high EF values observed for the metals suggested high anthropogenic pressure in the study area. EF > 1.5 observed for the metals Cd, Zn, Pb & Ni during the entire study period indicated the significant role of external sources of these metals (Zhang *et al.,* 2007). From the low EF values, it could be suggested that Cr and Mn in the estuarine and coastal sediments were mainly originating from the natural weathering processes and anthropogenic sources were of minor role in their distribution in the estuary.

In case of each metal, EFs were almost similar for all the coastal stations during Mon and Post-M, whereas it was erratic during Pre-M for all the metals. Station C3 near the bar mouth was enriched in exceptionally higher degree with all the metals under study and all other stations except C3 showed similar enrichment factors during Pre-M. From this it could be said that the estuarine input has a significant role in enrichment of these metals in the coast during this season (Balachandran *et al.,* 2006). Thus the exchange of heavy metals from estuary to its adjacent coast was evidenced from EF, but the coastal currents were reported to be capable of dispersing their deposition (Shetye *et al.,* 1991). Unlike the coast, estuarine area had pockets of varying EF values and compared to the middle stations, northern and southern end stations were enriched with the metals under study. Mn was the only metal which did not show any spatial variation in EF both in the coast and estuary.

6.2.2.2 Contamination Factor (CF), Degree of Contamination (C_d) and Modified Degree of Contamination (mC_d)

Contamination factor which is a measure of the degree of overall contamination of surface sediments was used in the present study. Degree of contamination was derived based on integrating data for seven specific heavy metals and polychlorinated biphenyl and all the eight species must be analysed in order to determine the correct degree of contamination. But, modified degree of contamination allows the incorporation of many metals with no upper limit. Contamination factors obtained for the metals under study in the estuary and coast during the consecutive seasons (appendix 29-31) are represented graphically in the Fig. 6.3 (a, b & c) & 6.4 (a, b & c) respectively.

Cadmium showed moderate to very high, considerable to very high and low to very high contamination factors during Pre-M, Mon and Post-M seasons respectively. Majority of the stations were associated with very high CF during the study period and some southern stations only showed low CF suggesting that the northern part of the estuary was greatly influenced by industries on its heavy metal status. Cd showed very high CF in the coastal area, except in C3 (moderate). Stations in the navigational channel (C3 during Pre-M and Post-M; C4 during Pre-M) were associated with low CFs for all other metals except Cd. This could be attributed to the tidal flushing and continuous dredging occurring in the shipping channel which prevent the accumulation of the metals (Mathew and Chandramohan, 1993; Rasheed, 1997; Menon *et al.,* 2000; Gupta *et al.,* 2009). In spite of this, Cd showed high CF pointing to the huge rate of addition of Cd to the coastal environment through the estuary. Zn showed low to very high contamination level in the estuary and low to moderate level of contamination in the coast. In the estuary, Pb was characterised by low to considerable level of contamination. Majority of the sampling stations fell in moderate level of contamination in the estuary with respect to Pb. Ni showed low to considerable level of contamination during Pre-M and Post-M seasons. Mon season was characterised by moderate contamination in the estuarine stations except in E11, which was found to be low in contamination during Post-M season also. Whereas in the coast, Ni showed moderate contamination during the study period, exceptions being the stations C3 &C4 during Pre-M and C3 during Post-M season.

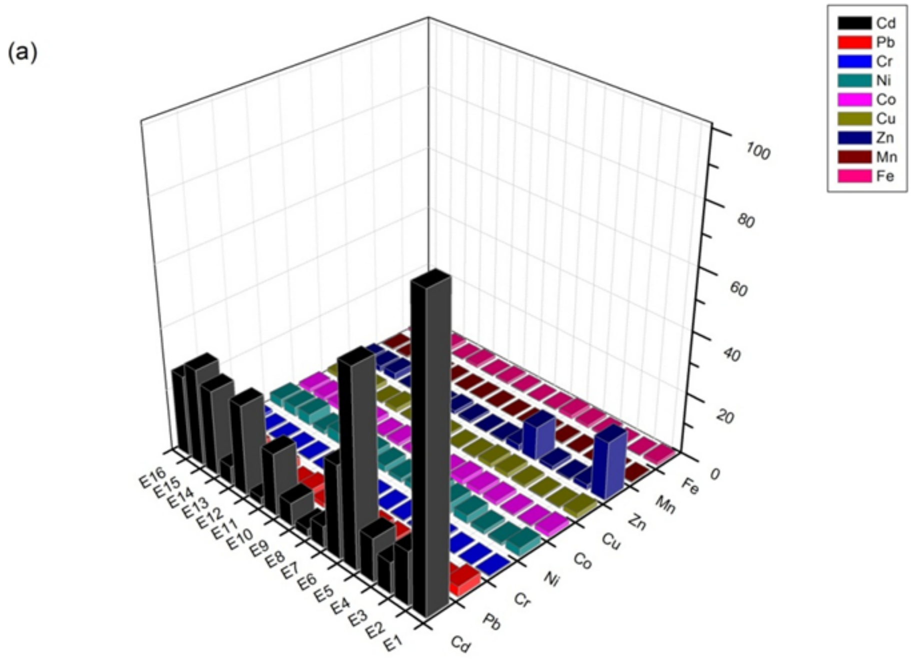

Figure 6.3a Contamination factors of metals under study in the estuary during pre-monsoon

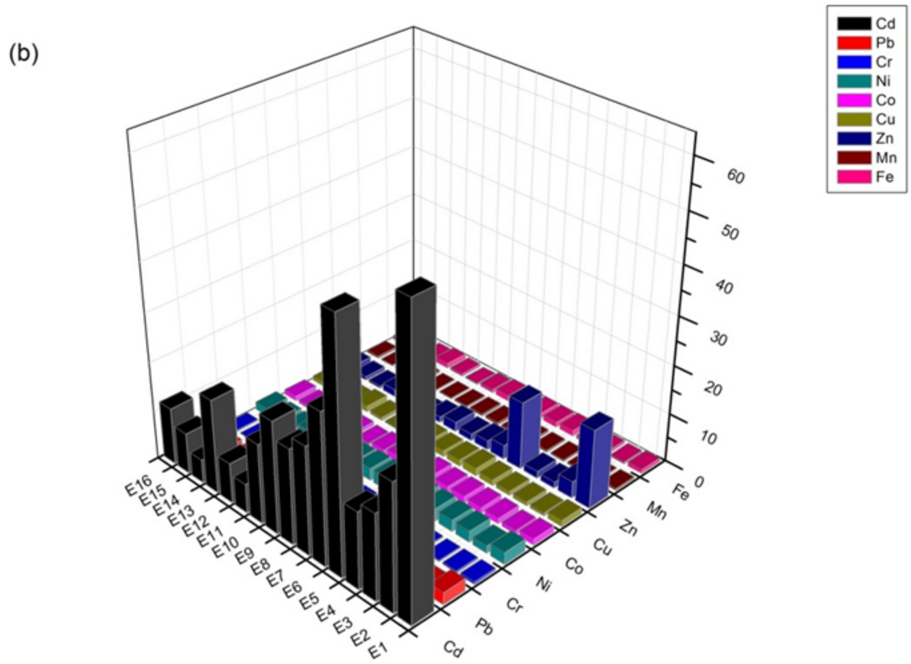

Figure 6.3b Contamination factors of metals under study in the estuary during monsoon

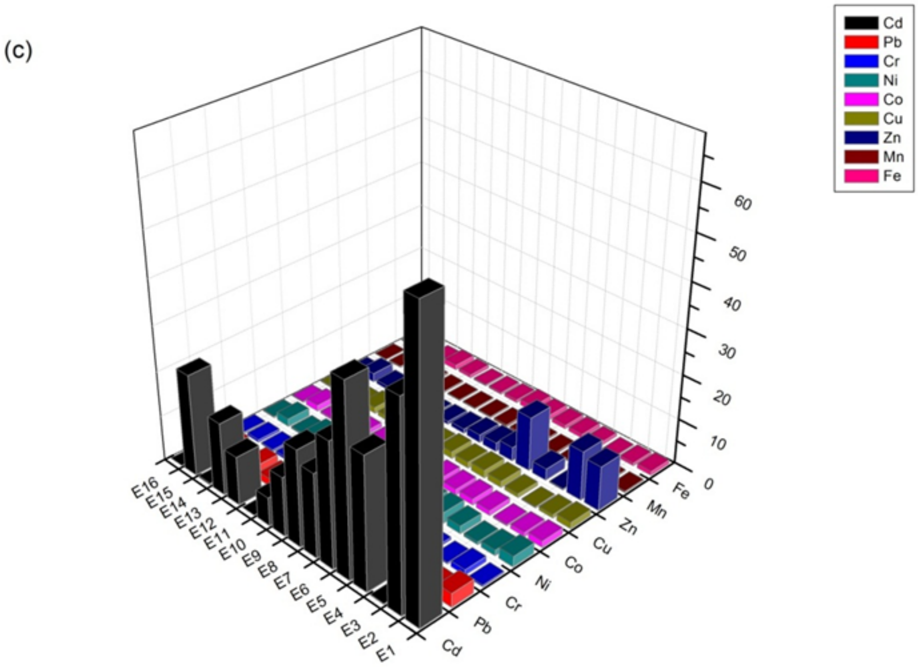

Figure 6.3c Contamination factors of metals under study in the estuary during post-monsoon

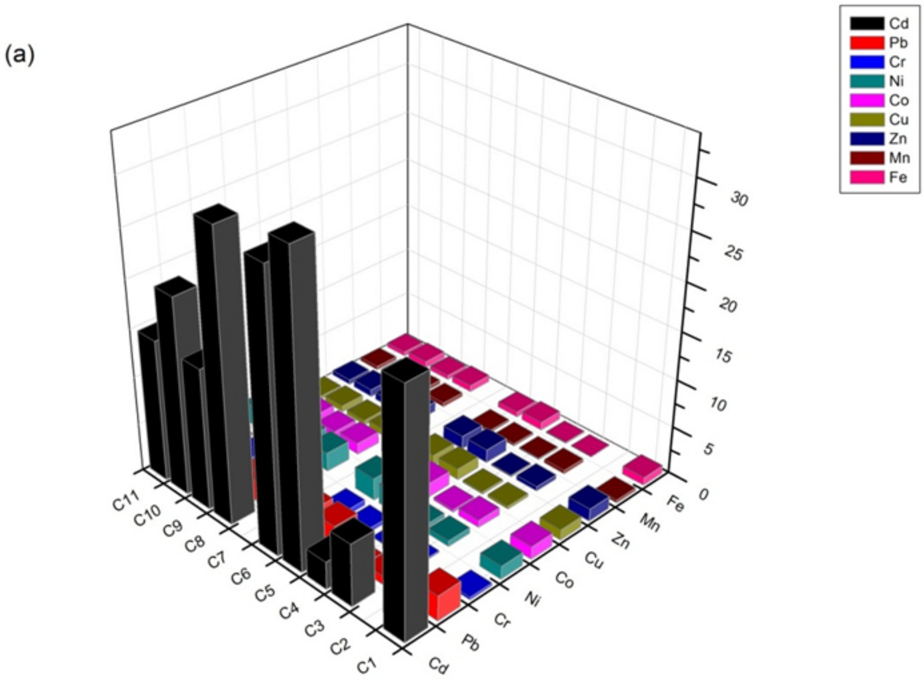

Figure 6.4a Contamination factors of metals under study in the coast during pre-monsoon

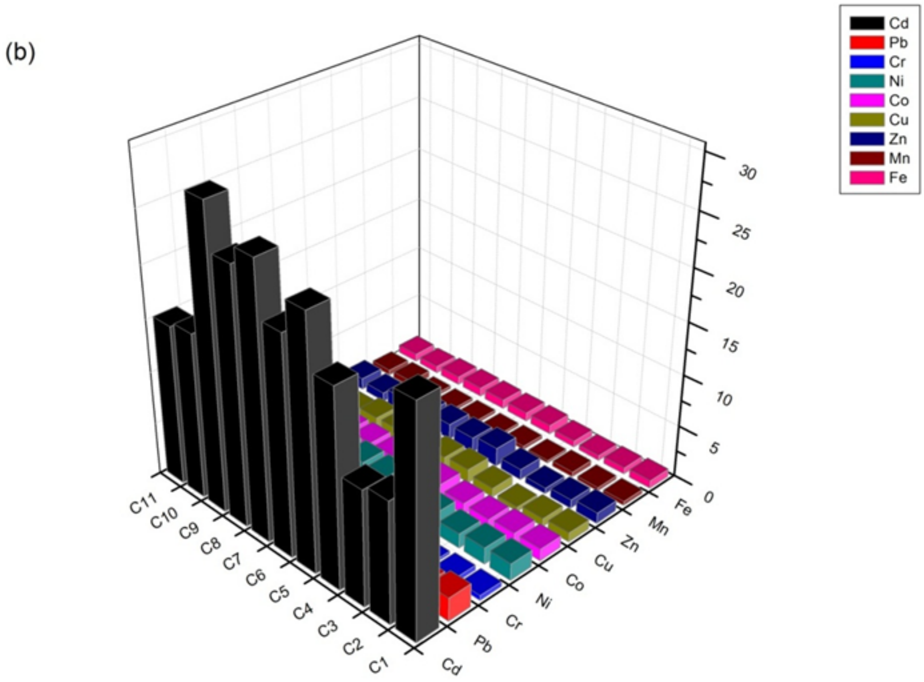

Figure 6.4b Contamination factors of metals under study in the coast during monsoon

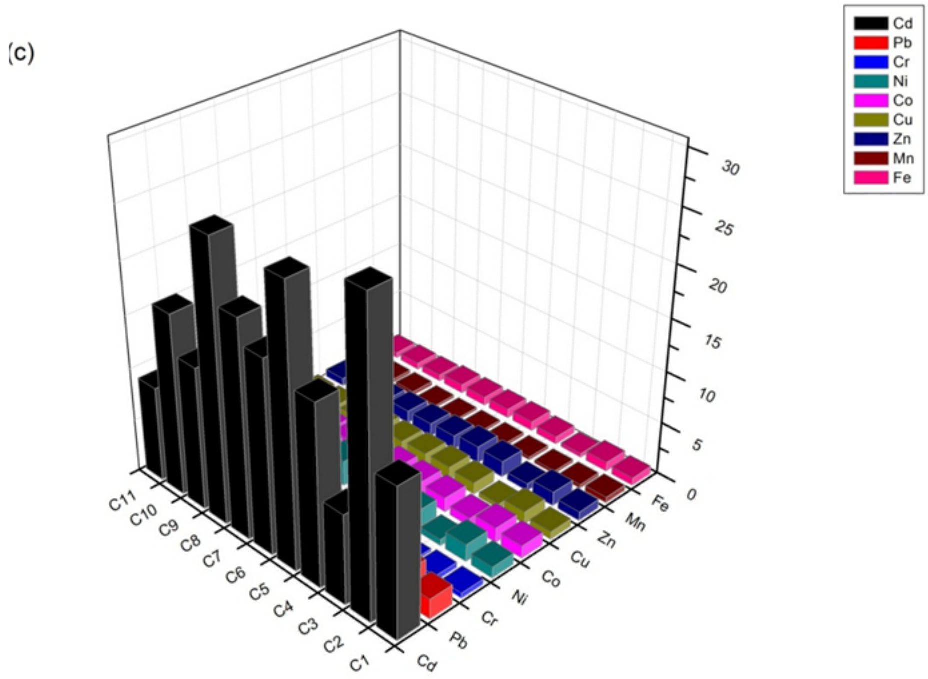

Figure 6.4c Contamination factors of metals under study in the coast during post-monsoon

Cobalt showed low to moderate levels of contamination in the estuary during the study period and in the coast during Pre-M & Post-M and moderate during Mon season. Cu showed low to moderate levels of contamination in the study area. Cr showed low CF in the study area except in stations E2 and E8 during Post-M which showed moderate CF. E8 which is near the Cochin shipyard might be receiving the metal from the ship building activities (Shibu *et al.,* 1995; Shajan, 2001; SCMC, 2004; Balachandran *et al.,* 2005; Balachandran *et al.,* 2006; Deepulal et. al. 2012) and E2 might have received metal from the industrial area. Although Fe showed low to moderate CF in the estuary, majority of the stations showed low contamination. Moderate level of contamination was observed in some southern stations and in Mattanchery channel which can be attributed to the shipping activities. In the coastal environment also, Fe was observed to be causing low levels of contamination. Mn showed low level of contamination in the study area (Deepulal *et al.,* 2012).

Based on contamination factor, the order of heavy metal contamination in the estuary was Cd > Zn > Pb > Ni. Estuary is contaminated moderately and above with all the metals under study except Mn and the exceptions in the coast were Cr, Fe and Mn. Cr and Fe were also found to be contaminating the estuarine system though in lesser degree compared to other metals. From these, it could be said that the coastal sediments were less contaminated compared to the estuary. Rapid dispersal of the pollutants by the coastal currents (Shetye *et al.,* 1991) and their rapid removal by the biogenic association (Saraladevi *et al.,* 1992) have been reported to diminish the effect of pollutants in the coastal environment.

The assessment of sediment contamination was carried out using the contamination factor and the degree of contamination, based on four classification categories proposed by Hakanson (1980) and is represented in

Table 6.2. During Pre-M, season, sediments of the study area fell under low – very high C_d class during Pre-M season. Stations E8, E11, C3 and C4 exhibited low C_d values compared to the rest of the stations. During Mon, estuarine stations fell under moderate – very high C_d class and coastal sediments fell under considerable – very high degree of contamination. Estuarine stations up to E10 were found to be with considerable – very high C_d suggesting very high anthropogenic load to this area along with the increased riverine runoff during Mon season. Whereas southern stations shown moderate – considerable degree of contamination. Estuarine sediments fell under low – very high C_d class during Post-M season. Northern (except E3) and central stations were exhibiting very high Cd values. Coastal stations fell under moderate – very high C_d class during this season. Stations C3 and C11 only exhibited moderate C_d compared to rest of the coastal stations which were associated with high C_d values.

The modified degree of contamination, mC_d classification and description was done according to Abrahim (2005) and is represented in Table 6.2. Estuarine sediments fell under Nil to very low - very high modified degree of contamination (mC_d) during the study period. Stations E1 and E5 (except during Post-M) fell under very high mC_d classification and high mC_d values observed for the stations up to E6 (except E3 during Post-M) suggested a notable degree of contamination in the northern part of the estuary compared to the central and southern estuarine stations. During Pre-M, coastal stations fell under Nil to very low – high mC_d class. C3 and C4 were associated with Nil to very low mC_d values. Stations, C5-C8 were found to be with high mC_d values compared to other stations. During Mon, stations E1 – E6 were classified into moderate - very high mC_d class. During Mon season, coastal sediments were found to be with moderate – high modified degree of contamination. During Post-M, stations E1 – E6 (except E3) were classified into high - very high mC_d class. Coastal stations fell under Nil to low – high mC_d class during this season.

Table 6.2 Pollution load index, contamination degree and modified contamination degree of the sediments of Cochin estuarine and coastal systems

Stations		Pollution Load Index			Contamination Degree			Modified Contamination Degree		
		Pre-M	Mon	Post-M	Pre-M	Mon	Post-M	Pre-M	Mon	Post-M
Estuary	E1	2.45	2.21	2.16	123.44	84.41	83.78	13.72	9.38	9.31
	E2	0.53	1.09	1.69	21.51	34.00	62.01	2.39	3.78	6.89
	E3	0.53	1.11	0.26	14.03	25.48	2.77	1.56	2.83	0.31
	E4	1.20	1.20	1.45	22.88	24.57	38.69	2.54	2.73	4.30
	E5	2.23	2.03	2.18	83.64	72.79	63.34	9.29	8.09	7.04
	E6	1.80	1.79	1.84	43.15	43.88	40.79	4.79	4.88	4.53
	E7	0.62	1.61	1.66	11.68	33.78	30.32	1.30	3.75	3.37
	E8	0.33	1.59	2.01	5.53	30.36	34.94	0.61	3.37	3.88
	E9	0.77	1.64	1.09	13.82	34.64	20.31	1.54	3.85	2.26
	E10	1.12	1.10	0.72	28.58	24.02	11.19	3.18	2.67	1.24
	E11	0.39	0.35	0.39	6.13	8.54	3.50	0.68	0.95	0.39
	E12	1.68	0.70	1.03	41.64	13.22	17.76	4.63	1.47	1.97
	E13	0.46	1.57	1.55	9.60	30.33	26.97	1.07	3.37	3.00
	E14	1.79	0.49	0.37	41.11	8.52	3.71	4.57	0.95	0.41
	E15	1.79	0.67	1.55	43.91	13.39	32.97	4.88	1.49	3.66
	E16	1.86	1.05	0.19	38.65	19.03	1.68	4.29	2.11	0.19
Coast	C1	1.29	1.31	1.16	33.76	29.93	21.43	3.75	3.33	2.38
	C2	-	1.09	1.49	-	18.98	40.33	-	2.11	4.26
	C3	0.44	0.85	0.68	9.93	16.69	12.82	1.10	1.85	1.42
	C4	0.22	1.19	1.36	4.43	26.63	26.54	0.49	2.96	2.95
	C5	1.47	1.62	1.69	41.74	35.05	37.45	4.64	3.89	4.16
	C6	1.42	1.48	1.46	38.69	31.53	28.95	4.30	3.50	3.22
	C7	-	1.58	1.46	-	37.04	30.99	-	4.12	3.44
	C8	1.26	1.49	1.45	38.10	34.88	36.31	4.23	3.88	4.03
	C9	0.93	1.49	1.19	21.36	39.00	21.58	2.37	4.33	2.40
	C10	1.10	1.18	1.13	27.91	24.38	24.79	3.10	2.71	2.75
	C11	0.76	1.33	0.95	20.30	24.75	15.65	2.26	2.75	1.74

Stations E3 and C3 lying in the navigational channel showed low mCd values which can be attributed to the dredging periodic process. Stations E3 and C3 lying in the navigational channel might be exempted because of the presence of low level of pollutants due to the tidal flushing and periodic dredging of the surface sediments (Mathew and Chandramohan, 1993; Rasheed, 1997; Menon *et al.,* 2000; Gupta *et al.,* 2009). Stations E7 – E16 fell under Nil to very low – moderate mC_d class during Mon and Post-M seasons.

6.2.2.3 Pollution Load Index (PLI)

Pollution load index give an estimate of the metal contamination status based on the contamination factors of metals. The PLI represents the number of times by which the metal content in the sediment exceeds the background concentration, and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. Pollution load index of the sediments of the study area is represented in Table 6.2.

During Pre-M, only 56 % of the estuarine stations were found to be with PLI values ≥ 1. Unlike the Mon and Post-M seasons, there was a shift in PLI in the estuary during Pre-M and the central stations were with PLI values < 1. During Mon, 75 % of the estuarine stations were found to be with PLI values ≥ 1 and this monsoonal load can be explained by the increased run off during this season. Southern estuarine stations, E11, E12, E14 and E15 were found to be with PLI values < 1 indicating lesser contamination compared to the northern and central station. During Post-M, all the stations (69 %) except E3, E10, E11, E14 and E16 were associated with PLI values ≥ 1.

Stations E1, E4, E5 and E6 were associated with high PLI irrespective of the seasons, indicating the higher pollution load in the northern estuarine stations. *PLI* value ≥ 1 observed for the northern and central estuarine stations indicate an alarming rate of contamination of the estuary by heavy elements and an immediate intervention to ameliorate pollution by the northern industrial belt should be taken. E3 showed PLI < 1 during Pre-M and Post-M and this may be attributed to the periodic dredging activities occurring in the shipping channel and also to the highly dynamic condition prevailing there which prevent the sedimentation of the fine particles together with the heavy elements.

Coastal stations C1, C5, C6, C8 and C10 were found to be with PLI values > 1 during Pre-M indicating pollution by the metals under study. All the stations except C3 during Mon; C3 and C11 during Post-M were found to be with PLI values > 1 indicating higher pollution during Mon and Post-M seasons compared to the Pre-M season. Station C3 near the bar mouth were with PLI values < 1 during the entire study period. Low level of accumulation of the metals in C3 (bar mouth) can be attributed to the highly dynamic conditions in the bar mouth region which prevent the settling of finer particles containing heavy elements or to the periodic dredging activities occurring in the shipping channel.

6.2.2.4 Geoaccumulation Index (Igeo)

The index of geoaccumulation (Igeo) is used to assess heavy metal contamination by comparing the current levels of metal concentrations and the original pre-industrial concentrations in the sediments. Geoaccumulation index of the metals in the study area during the consecutive season (appendix 32-34) are represented in Fig. 6.5 (a, b & c) & 6.6 (a, b & c) respectively.

The Igeo class varied from metal to metal and place to place. Cd showed higher pollution during Mon followed by Pre-M and Post-M seasons in the estuary. Northern estuarine stations E1 & E5 showed very strong geoaccumulation index (Deepulal *et al.,* 2012). Igeo values varied from 0.73 - 5.97, 1.68 - 5.30 and 0 - 5.42 allocating Cd in the Igeo classes 1-6, 2-6 & 0-6 during Pre-M, Mon and Post-M seasons respectively. In the coast, Cd showed Igeo values 0.94 - 4.39 during Pre-M; 2.87 - 4.25during Mon and 2.49 – 4.25 during Post-M suggesting a polluted coastal environment. During Pre-M, Igeo class was 1-5 and during Mon and Post-M, class was 2-5.

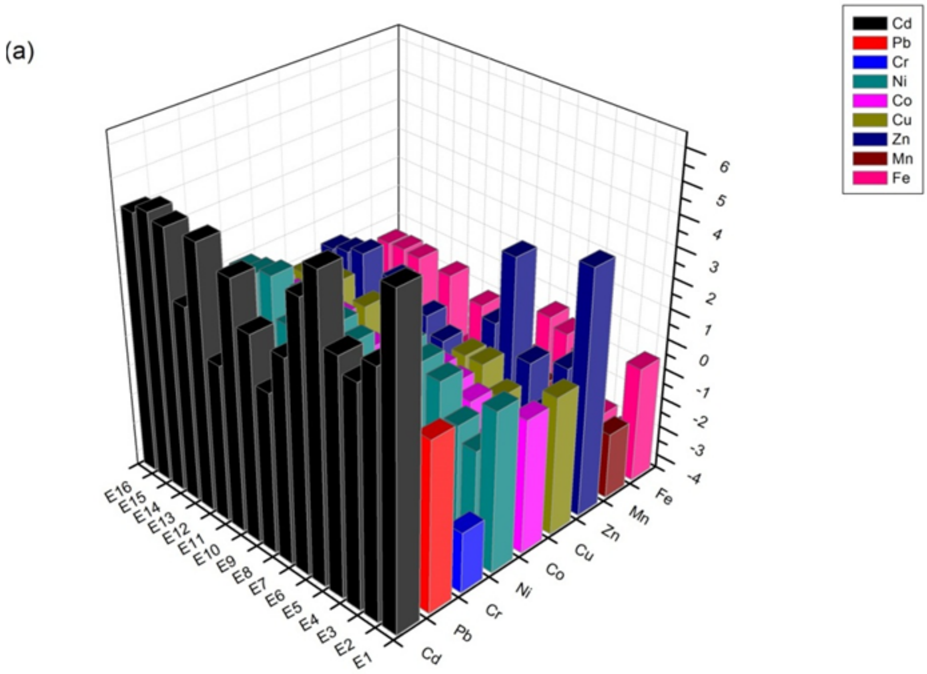

Figure 6.5a Geoaccumulation Index of metals under study in the estuary during pre-monsoon

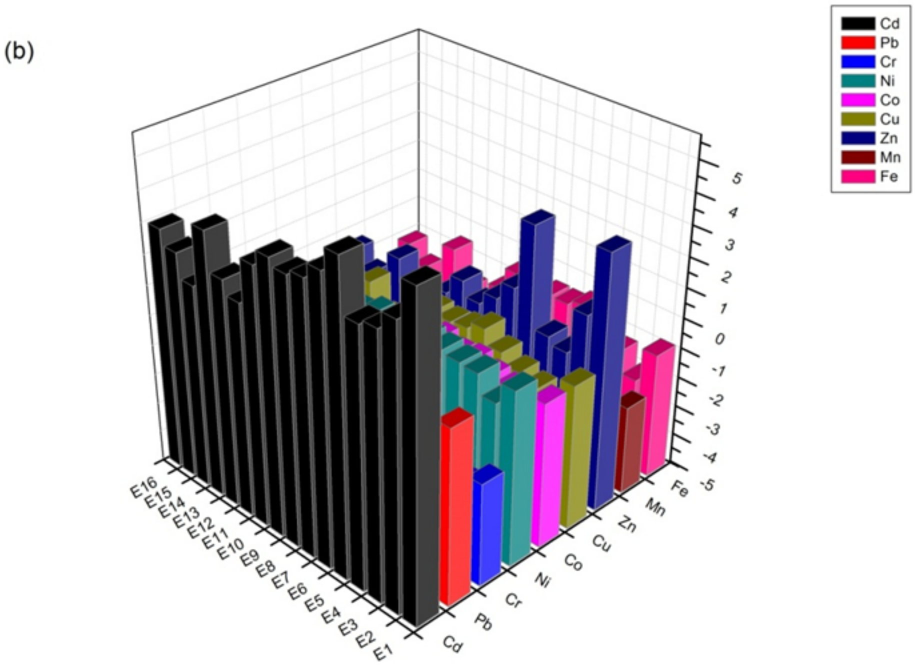

Figure 6.5b Geoaccumulation Index of metals under study in the estuary during monsoon

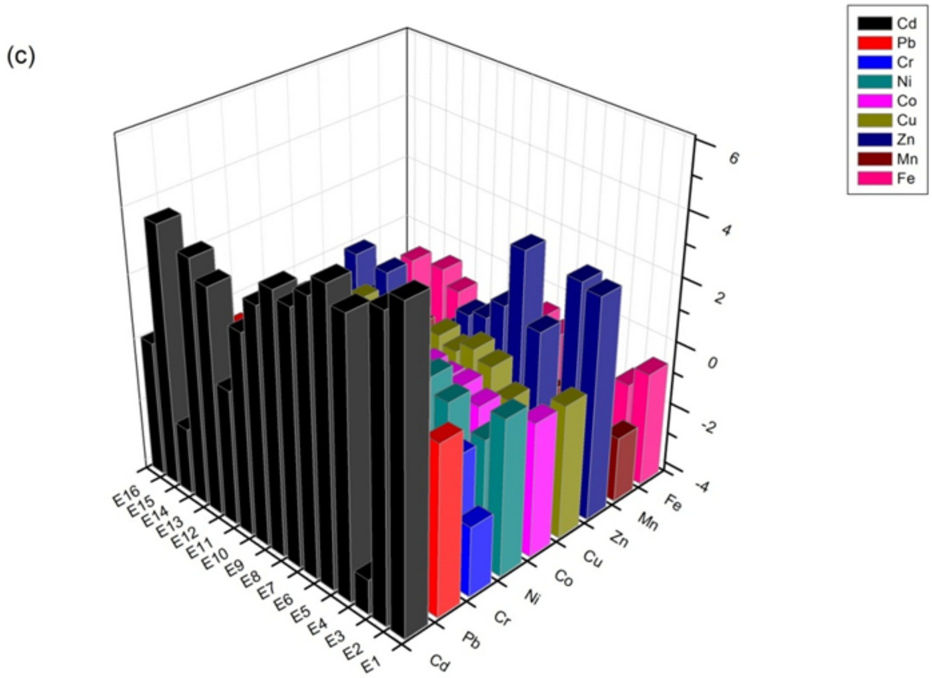

Figure 6.5c Geoaccumulation Index of metals under study in the estuary during post-monsoon

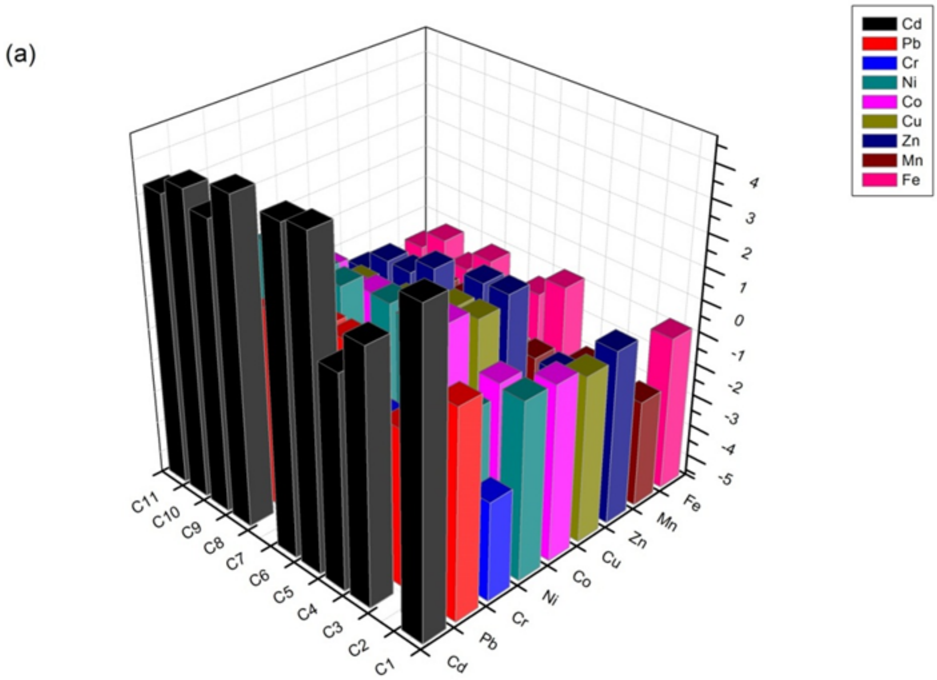

Figure 6.6a Geoaccumulation Index of metals under study in the coast during pre-monsoon

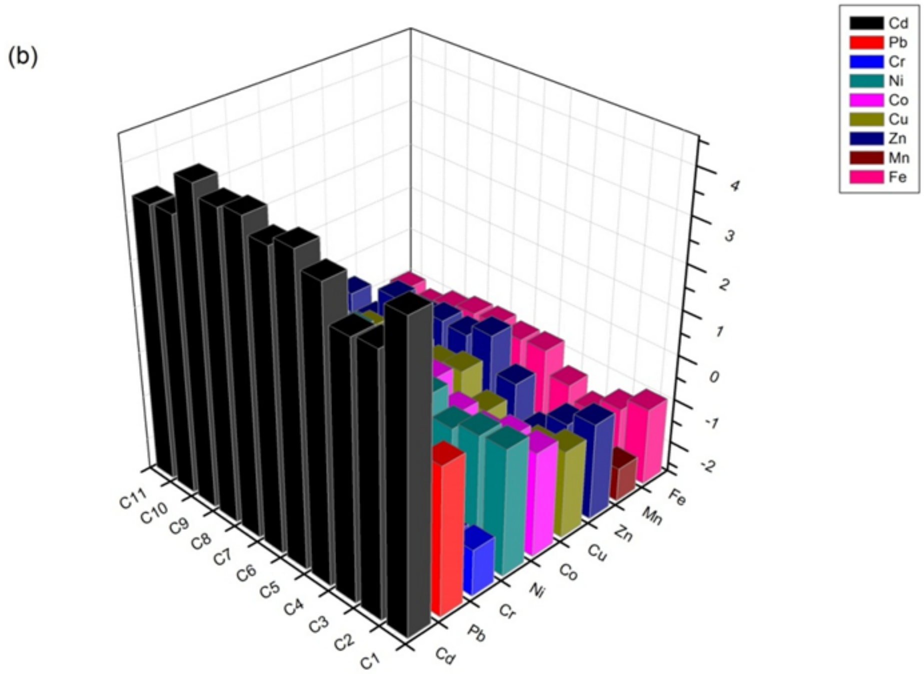

Figure 6.6b Geoaccumulation Index of metals under study in the coast during monsoon

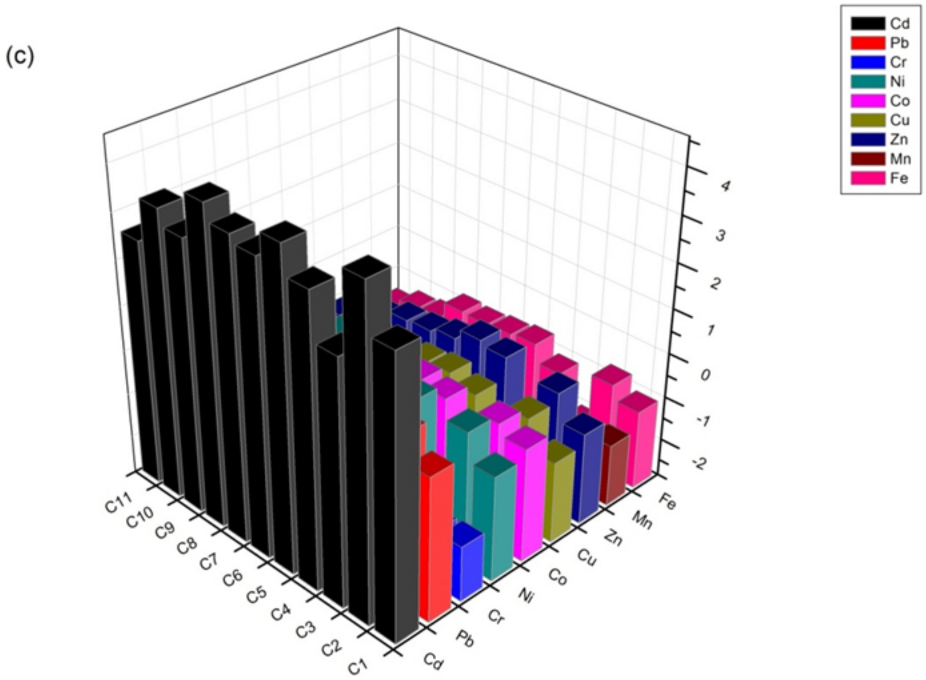

Figure 6.6c Geoaccumulation Index of metals under study in the coast during post-monsoon

In the estuary, Pb was associated with "free" to "moderate" levels of Igeo values throughout the study period, allocating it in the 0-2 class. Igeo values of Pb in the coastal sediments were below one throughout the study period and fell into "free to moderately" polluted class. Mon and Post-M seasons showed Igeo values between zero and one in all the stations except in C3 which lies near the bar mouth and had negative geoaccumulation index during all the seasons.

In the estuary, Co showed negative Igeo values in majority of the estuarine stations. Exceptions were E6, E7 and E8 and they were found to be free to moderately polluted during Pre-M, Mon and Post-M seasons respectively and fell in class 1 during the study period. Negative Igeo values found for Cu except in the stations E1 & E14 (Pre-M); E6 (Mon) and E6 & E8 (Post-M) indicated that the estuary is free from its pollution. Igeo values of these stations designated them into "free to moderate" contaminated sites.

Nickel in the estuarine sediments was associated with "free" to "moderate" levels of geoaccumulation during Pre-M & Post-M and "free" to "free- moderately" during Mon season. Nickel was found to be in 0-1 class ("free" - "free to moderately") throughout the study period in the coast. Mon season was associated with more polluted sites, exception was station C3.

Geoaccumulation index of Zn in the estuary ranged from "free" to "strongly" contaminated during the study period. Stations E1 & E5 showed higher Igeo values. Northern and southern stations showed higher Igeo compared to the central stations. Zn pollution due to the industrial activities in the northern area of Cochin estuary has been reported earlier (CPCB, 1996; Balachandran *et al.,* 2006; Deepulal *et al.,* 2012). During the study period, Zn fell in 0-4 Igeo class. From the geoaccumulation index, it was found that Zn was not a polluting metal in the coastal sediments during Pre-M. While during Mon and Post-M, coastal sediments fell into "free" - "free to moderately" polluted classification. Some of the central stations (C5 & C7 during Mon; C4 & C5 during Post-M) fell into class 1. Disposal of dredge spoil may be the reason for enrichment in the central stations. However, majority of the coastal stations were free from Zn pollution. According to Shetye *et al.* (1991) coastal currents are strong enough to disburse the pollutants received from the Cochin estuary (Shetye *et al.,* 1991). Low Igeo values observed for metals like Cr, Mn and Fe suggested both the estuary and its adjacent coast were free from the pollution by these metals (Balachandran *et al.,* 2006; Deepulal *et al.,* 2012). Cu & Co was also found to be not enriched in the coastal sediments pointing to a natural origin of these metals. Cr showed negative Igeo values in the study area except in station E8 during Post-M which fell into class1, i.e., free to moderately contaminated designation.

6.2.3 Ecological Impact Assessment Using Sediment Quality Guidelines

Contaminants associated with sediments can adversely affect resident sediment-dwelling organisms through direct toxicity or the alteration in the benthic invertebrate community structure (Chapman, 1989). A variety of approaches are used to evaluate the hazard posed by contaminated sediments to ecological receptors (Ingersoll *et al.,* 1997). Numerical sediment quality guidelines have generally been used to identify contaminants in aquatic ecosystem (MacDonald *et al.,* 2000) and these guidelines empirically link biological effects with sediment chemistry by combining the results of toxicity tests using field-collected samples with the concentrations of chemicals in those same samples (Long *et al.,* 1995; MacDonald *et al.,* 1996; MacDonald *et al.,* 2000).

The National Oceanic and Atmospheric Administration (NOAA) developed a set of empirical SQGs (Long *et al.,* 1995) that provides two values which delineate three concentration ranges for each chemical component for the estimation of the potential biological effect. These guidelines were derived from the collection of concurrent sedimentary chemical and biological data collected from the three seaboards of North America, incorporating field and laboratory data from many different methodologies, species and biological endpoints. Chemical concentrations corresponding to the 10th and 50th percentiles of adverse biological effects were the effects range-low (ERL) and effects range-median (ERM) guidelines respectively (Long *et al.,* 1995). The concentrations < ERL represents a minimal-effects range, which is intended to estimate conditions where biological effects are rarely observed. Concentrations ≥ ERL and < ERM represents a range with in which biological effects occur occasionally and concentrations ≥ ERM represents a probable effect range with in which adverse biological effects frequently occur. The guidelines were derived for 25 chemicals, 9 heavy metals, 13 PAHs, 2 OCs and total PCBs have been shown to have some predictive ability although do not account for chemical bioavailability and was not based upon experiments in which causality was determined.

For sediments, multiple screening values are available. Threshold Effects Levels (TEL) and Probable Effects Levels (PEL) based on field data that develop associations between chemical concentrations and biological effects, as well as laboratory toxicity test results (Smith *et al.,* 1996; MacDonald *et al.,* 1996) are also used in this study. The TEL is a conservative screening value, below which concentrations of contaminants have not been shown to cause an effect on aquatic organisms. The PEL is a screening value above which toxic effects are likely to occur, and compounds that exceed it are more probably elevated to toxic levels. The potential acute toxicity of contaminants in sediment sample can be estimated as the sum of the toxic units (ΣTU) defined as the ratio of the determined concentration to PEL value (Pederson *et al.,* 1998). Toxic units (TUs) are used to normalise the toxicities of various heavy metals to allow for the comparison of the relative effects. Based on SQG of USEPA, sediments can be classified into non-polluted, moderately polluted and heavily polluted status (Perin *et al.,* 1997). Effects-range SQGs which are empirically derived do not take into account of the factors affecting the bioavailability of these contaminants and geochemical phases that bind contaminants.

Screening Quick Reference Table, SQuiRT, (Table 6.3) set by NOAA (Buchman, 2008) and the sum of toxic units (∑TU) has been used to assess the sediment toxicity in this study. The guideline values are divided into increasing categories of observable effects (Table 6.4) derived through the use of several approaches (Buchman, 2008). Adverse effects occurred in less than 10% of studies in which concentration was below the respective ERL values, and adverse effects are observed in more than 75% of studies in which concentrations exceeded ERM values (Long *et al.,* 1995; Long *et al.,* 1998).

Sediment toxicity has been assessed by comparing the metal concentrations with the sediment quality guidelines set by National Oceanographic and Atmospheric Administration, NOAA (ERL/ERM and TEL/PEL) and sum of toxic units (∑TU).

Table 6.3 Screening Quick Reference Table (SQuiRT)

Element, (mg/ kg)	Cd	Pb	Ni	Cr	Cu	Zn
ERL	1.20	46.70	20.90	81.00	34.00	150.00
ERM	9.60	218.00	51.60	370.00	270.00	410.00
TEL	0.68	30.20	15.90	52.30	18.70	124.00
PEL	4.20	112.00	42.80	160.00	108.00	271.00

Table 6.4 Sediment guidelines and definitions used in SQuiRT (Buchman, 2008).

Sediment guidelines	Definition
Effects range low (ERL)	10th percentile values in effects
Effects range median (ERM)	50th percentile value in effects
Threshold effects level (TEL)	Maximum concentration at which no effects are observed
Probable effects level (PEL)	Lower limit of the range of concentrations at which adverse effects are always observed

Cadmium

Cd has been reported to cause numerous lethal diseases and various deleterious effects in fish and wildlife (Hammons *et al.,* 1978; NRCC, 1979; Jenkins, 1980; Eisler, 1981; Moulis, 2010) and its effects include skeletal deformities and impaired functioning of kidneys in fish (Eisler, 1993; Levit, 2010). As Cd impairs aquatic plant growth, restrictions in food availability for the aquatic animals have been reported (Wright and Welbourn, 2002; Landis and Yu, 2003; Bradl, 2005). Long-term changes in population structure has been reported in isopods exposed to Cd (Landis and Yu, 2003; Bradl, 2005).

Although Cd detected in the study area was over the background levels (Turekian and Wedepohl, 1961), it was below the limits of concentration (ERM) at which adverse effects become persistent. Majority of the estuarine stations (63, 69 and 63 % during Pre-M, Mon and Post-M seasons respectively) were between ERL & ERM levels (Fig. 6.7). Rest of the stations were below the established limits (ERL) for biological effects (37, 31 and 37 % during Pre-M, Mon and Post-

M seasons). The incidence of effects was usually higher when concentrations exceeded the ERLs than when concentrations were below the ERLs. Majority of the stations were between these values indicating possible detrimental effects to benthic organisms. Northern and central stations were associated with higher Cd content in the sediments and this may be attributed to the industries located downstream of the Periyar River. Several studies have revealed the threatening level of Cd in the sediments of Cochin estuary (Ratheesh Kumar *et al.,* 2010; Sudhanandh *et al.,* 2011; Martin *et al.,* 2012; Deepulal *et al.,* 2012; Shaiju, 2013). Mon season was found to be with more number of stations affected by Cd and it can be due partly to the increased riverine run off during Mon season and partly to the reduced seawater intrusion during this season. Retrieval of saline front to the seaward side due to the increased fresh water inflow increases the area where precipitation of Cd occurs.

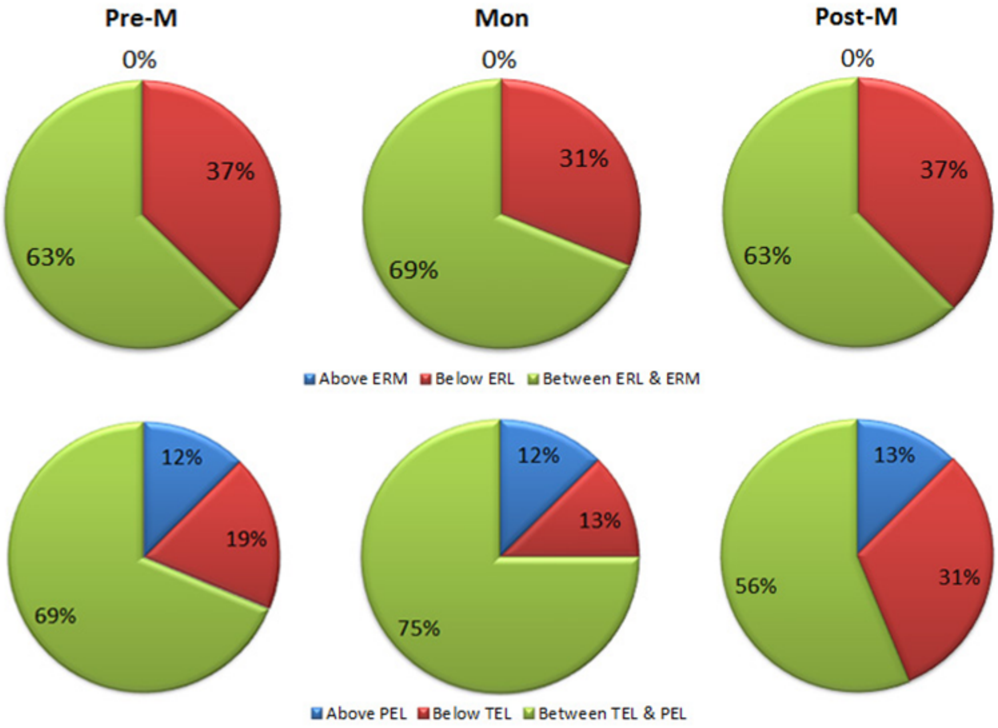

Figure 6.7 Percentage of stations affected by cadmium in the estuary

During Pre-M, 78 % of the coastal stations were between the ERL and ERM values and 22 % of stations were below the ERL value (Fig. 6.8). 82 % of the stations were between the ERL and ERM values and the rest 18 % were below the ERL value during Mon and Post-M seasons indicating the toxicity associated with Cd pollution to biota was more during these seasons. Cd in the coastal sediments was below the ERM values during the study period.

In the estuary, 12 % of the stations exceeded the PEL values during Pre-M and Post-M and 13 % of them were above PEL during Post-M (Fig. 6.7). These were the northern stations indicating the greater input of Cd from the industrial area lying north to these stations. Cd content of the 69, 75 and 56 % of the stations, during Pre-M, Mon and Post-M respectively, fell within the range between TEL and PEL values. 19, 13 and 31 % of the stations were below the TEL values during Pre-M, Mon and Post-M seasons respectively and thus suggesting Post-M season was with more stations rarely to be associated with biological effects followed by Pre-M and Mon seasons. The incidence of effects was usually higher when concentrations exceeded the TEL value than when concentrations were below the TEL value and the PEL values are better indicators of concentrations associated with effects than the TEL values. So, Post-M season was with more stations above PEL value indicating possible detrimental effects to benthic organisms.

78 % of the coastal stations were within the range between TEL and PEL values and 22 % were below the TEL value during Pre-M season (Fig. 6.8). But all the stations were between the TEL and PEL values during Mon and Post-M seasons, suggesting a better quality of the sediments during Pre-M season compared to other seasons. However, none of the coastal stations in the study period were above the PEL value indicating the higher sediment quality with respect to Cd, in comparison with the estuarine sediments.

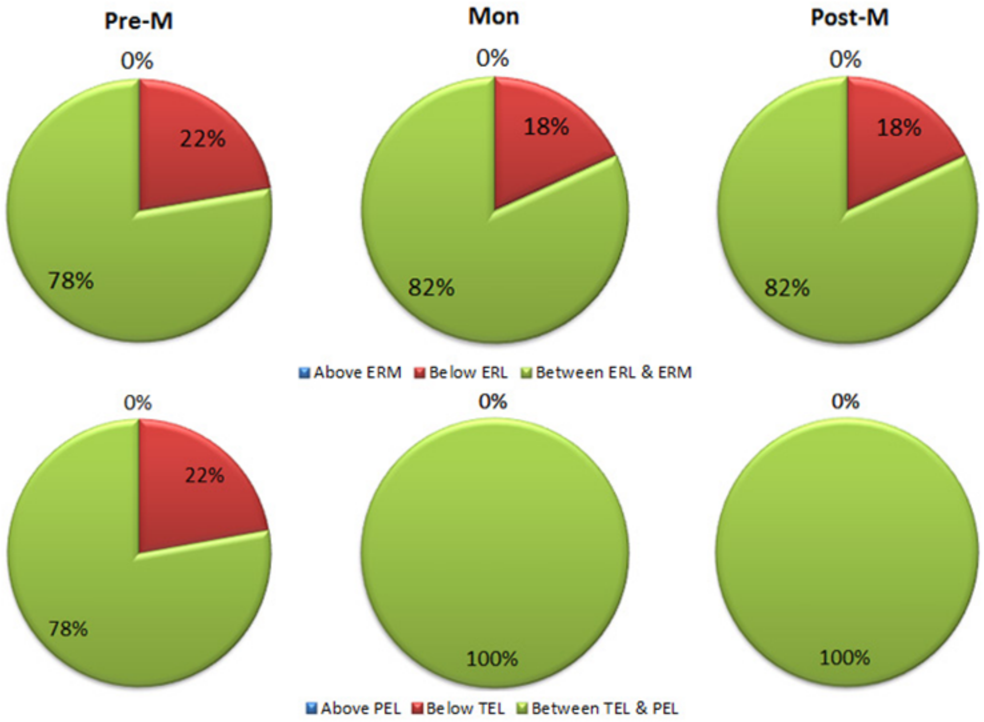

Figure 6.8 Percentage of stations affected by cadmium in the coast

Lead

Lead is a cumulative metabolic poison and its contamination was identified as one of the most significant environmental problems in the world (WHO, 1989; Oje *et al.,* 2010). Pb concentrations higher than 0.5 ppm caused enzyme inhibition (Taub, 2004), decreased algal growth results in reduced food for the grazers which will affect the entire ecosystem. Pb is toxic to all phyla of aquatic biota, though effects are modified significantly by various biotic and abiotic variables (Wong *et al.,* 1978). Fishes especially the embryos and fry are more sensitive to lead and the gill functions would be grossly affected when the lead concentrations exceeded 0.1 ppm.

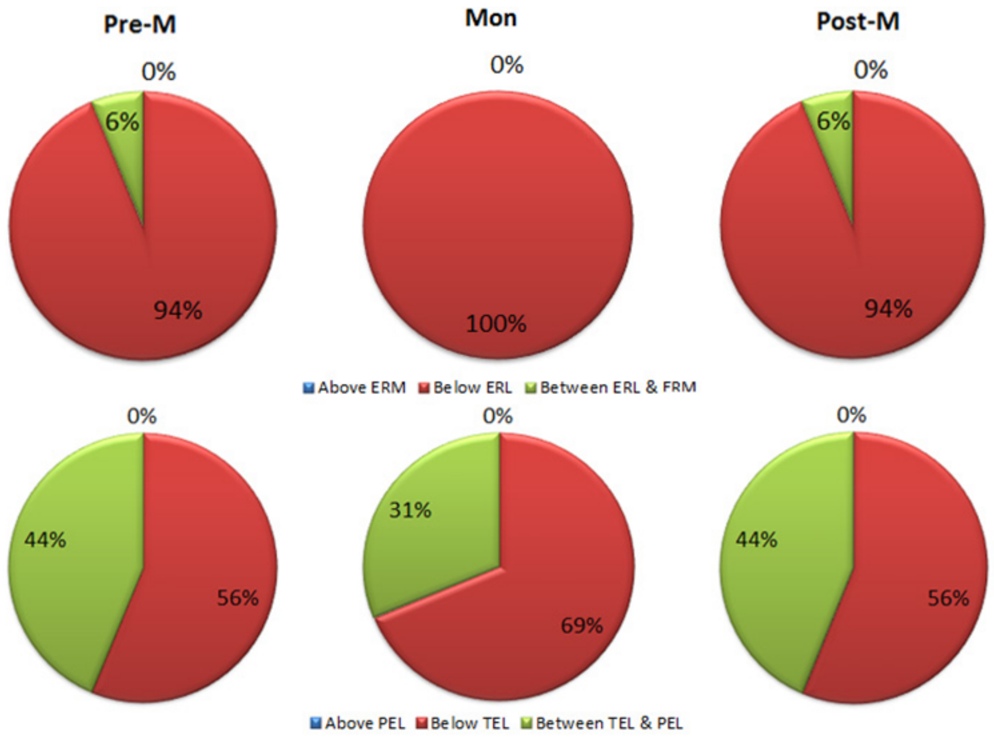

Figure 6.9 Percentage of stations affected by lead in the estuary

Majority of the estuarine stations (94 %) were below the ERL value for Pb and 6 % of the stations fell within the range between ERL and ERM values during Pre-M and Post-M seasons (Fig. 6.9). Station E1 during Pre-M and E6 during Post-M seasons were the only stations which shown Pb concentrations between the ERL-ERM values. All the stations fell under the ERL values during Mon season and hence the toxicity associated with Pb is least likely to be expected. Pb in all the coastal sediments was below the established levels (ERL) for adverse biological effects to occur, suggesting the concentration range of Pb in coastal sediments would rarely be associated with biological effects (Fig. 6.10). During the entire study period, the concentrations of Pb in all the estuarine and coastal stations were lower than ERM value (218 ppm).

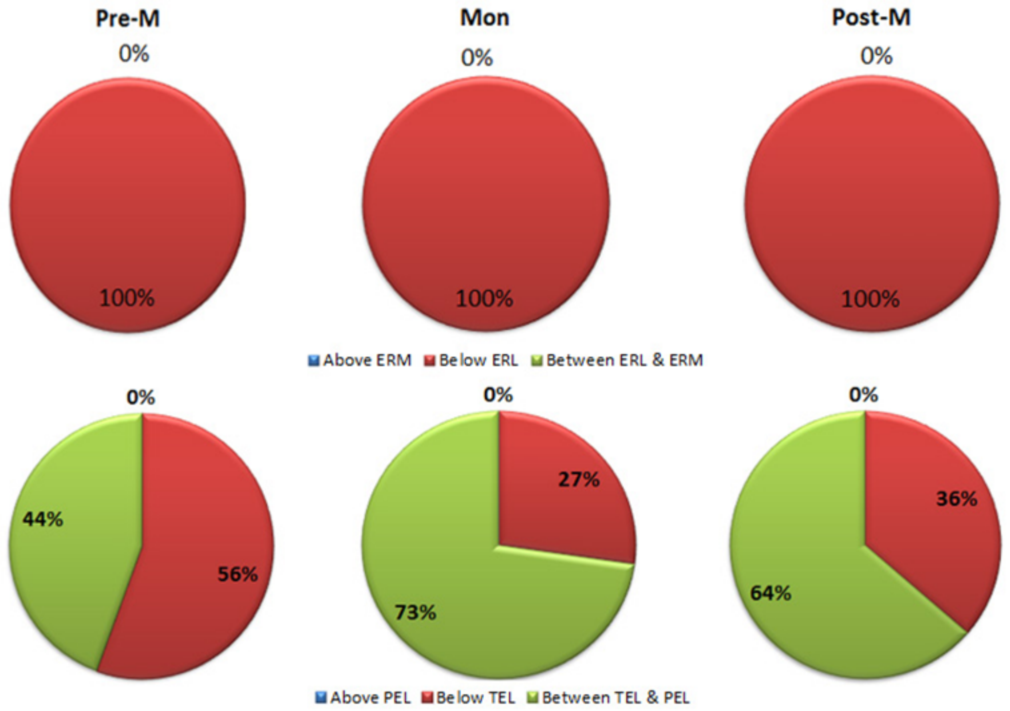

Figure 6.10 Percentage of stations affected by lead in the coast

As per TEL-PEL values, Pb concentration is higher in the study area and more stations fell between the TEL and PEL values. 56 % of the estuarine stations were below the threshold effects level (TEL) during Pre-M and Post-M seasons and 44 % of them fell within the range between TEL and PEL values (Fig. 6.9). Toxicity associated with Pb was lower during Mon compared to Pre-M and Post-M as 69 % of the stations fell below the TEL values and 31 % of them were between TEL and PEL values during Mon season. Coastal stations in which Pb concentration was below the TEL value were 56 %, 27 % and 36 % during Pre-M, Mon and Post-M seasons respectively (Fig. 6.10). 44 %, 73 % and 64 % of the stations fell within the range between TEL and PEL values during Pre-M, Mon and Post-M seasons respectively. Toxicity associated with Pb will be more during Mon followed by Post-M and Pre-M seasons.

As per these guidelines, adverse biological effects associated with Pb is rarely to occur because sediment concentration of Pb in the estuary and coast were below the ERM and PEL values during the entire study period.

Nickel

Although Ni is essential for the normal growth of many species of microorganisms, plants and several species of vertebrates (NAS, 1975; USEPA, 1980; WHO, 1991; USPHS, 1993; Prasad and Gowda, 2005) it is a reproductive toxicant in animals at a higher level (Smialowicz *et al.,* 1984; USEPA, 1986; USPHS, 1993). Nickel toxicity reduces photosynthesis, growth and nitrogenase activity of algae; fermentative activity of a mixed rumen microbiota; metabolism of soil bacteria; mycelial growth, spore germination, sporulation of fungi and growth rate of marine bacteria; (Babich and Stotzky, 1982). Presence of excess Ni have also been observed to cause adverse effects in yeasts, protozoans, molluscs, crustaceans, insects, annelids, echinoderms, fishes, amphibians, higher plants, birds, and mammals (USEPA, 1975). Although aquatic organisms can bioaccumulate Ni, there is little evidence of significant biomagnification along the food chains (NRCC, 1981; Sigel and Sigel, 1988; WHO, 1991).

The ERM and ERL values set up by NOAA to assess the possible toxicity of Ni are 20.9 ppm and 51.6 ppm respectively. ERM values are better indicators of concentrations associated with effects and majority of the estuarine stations were above the ERM value posing threat to the aquatic biota. 94 % of the stations during Pre-M and Mon; 63 % of the stations during Post-M were above the ERM value (Fig. 6.11). The incidence of effects was usually higher when concentrations exceeded the ERL and all the stations were above the ERL value during Pre-M, Mon and Post-M seasons (station E16, being the exception during Post-M). 31 % of the stations were found to be in the range between ERL and ERM values during Post-M and 6 % during Pre-M and Mon seasons. Estuarine sediments during Pre-M and Mon seasons were associated with higher toxicity with respect to Ni.

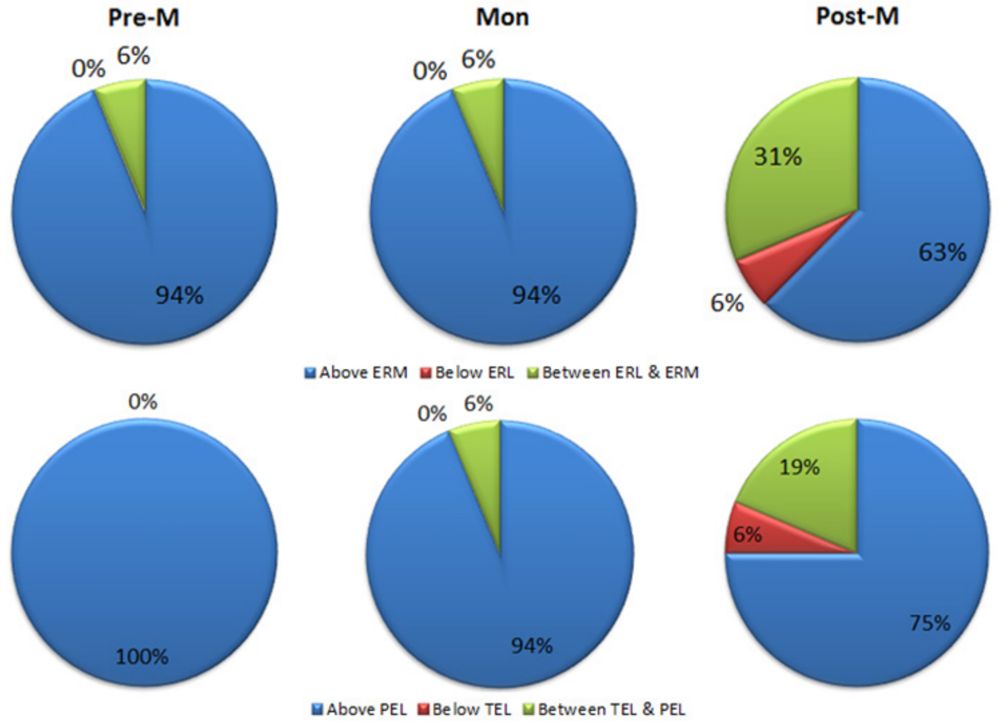

Figure 6.11 Percentage of stations affected by nickel in the estuary

Ni content in all the estuarine sediments was above the PEL value during Pre-M season. Whereas during Mon and Post-M, 94 % and 75 % of the stations respectively were above the PEL value (Fig. 6.11). E11 was the only station which lied between TEL and PEL values during Mon. 19 % of the stations (E3, E11 and E14) fell in the range between TEL and PEL during Post-M and E16 (during Post-M) was the only station which had Ni content less than TEL value in the estuary. As per the TEL-PEL guidelines Ni toxicity was higher during Pre-M followed by Mon and Post-M seasons.

78 %, 100 % and 91 % of the coastal stations were associated with Ni contents higher than ERM value (Fig. 6.12). 22 % (C3 and C4) and 9 % of the stations (C3) during Pre-M and Post-M seasons fell in the range between the ERL and ERM values. Tidal flushing might be the reason for the lower content of Ni in stations C3 and C4, which are near the bar mouth.

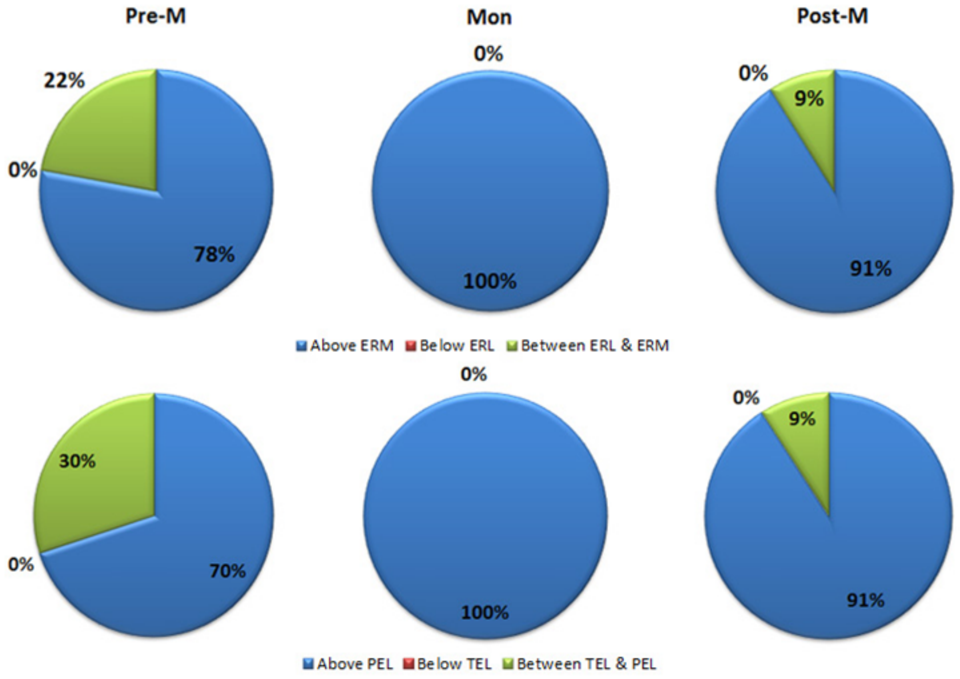

Figure 6.12 Percentage of stations affected by nickel in the coast

During Pre-M, Ni content in 70 % of the coastal stations was above the PEL value and 30 % of them fell between TEL and PEL values (Fig. 6.12). Ni content in the coastal sediments was above the PEL value during Mon indicating alarming condition causing threat to the aquatic life during Mon. 91

% of the stations lied above the PEL value during Post-M and station C3 only fell in the range between the ERL and ERM values during this season.

From the SQGs, it could be understood that the study area is facing high threat with respect to Ni. Ni toxicity is higher during Mon followed Post-M and Pre-M in the coastal sediments. But in the estuarine sediments, Pre-M and Mon seasons were associated with higher Ni content than the Post-M season.

Chromium

Chromium is an essential nutrient required for carbohydrate metabolism (Langard and Norseth, 1979; Post and Campbell, 1980; Li *et al.,* 2012). Cr (III) and Cr (VI) are the major species in aquatic environments and Cr (VI) is the dominant dissolved species under oxygenated conditions and is usually the major species in seawater (Towill *et al.,* 1978). Hexavalent Cr (VI) compounds tend to be oxidizers and are associated with cancer risk, kidney damage (Meyers, 1990; Blasiak, 2000, Dhal *et al.,* 2013), abnormal enzyme activities, altered blood chemistry, behavioural modifications, disrupted feeding, lowered resistance to pathogenic organics, histopathology, osmoregulatory upset, alterations in population structure and species diversity indices, and inhibition of photosynthesis (Eisler, 1986). Excess Cr leads to decreased weight gain, increased oxygen consumption, impaired reproduction, and increased haematocrit in polychaete worms, clams, crabs, oysters, and fish (Moore *et al.,* 1990). Cr and Cd interact synergistically i.e., the combined toxicities of these two metals are greater than the sum of their individual toxicities (Lasheen *et al.,* 1989). Cr has been listed as one of 129 priority pollutants by EPA (Keith and Telliard, 1979) and is one of the top 20 contaminants on the superfund priority list of hazardous substances for the past 15 years (Chrysochoou and Johnston, 2012).

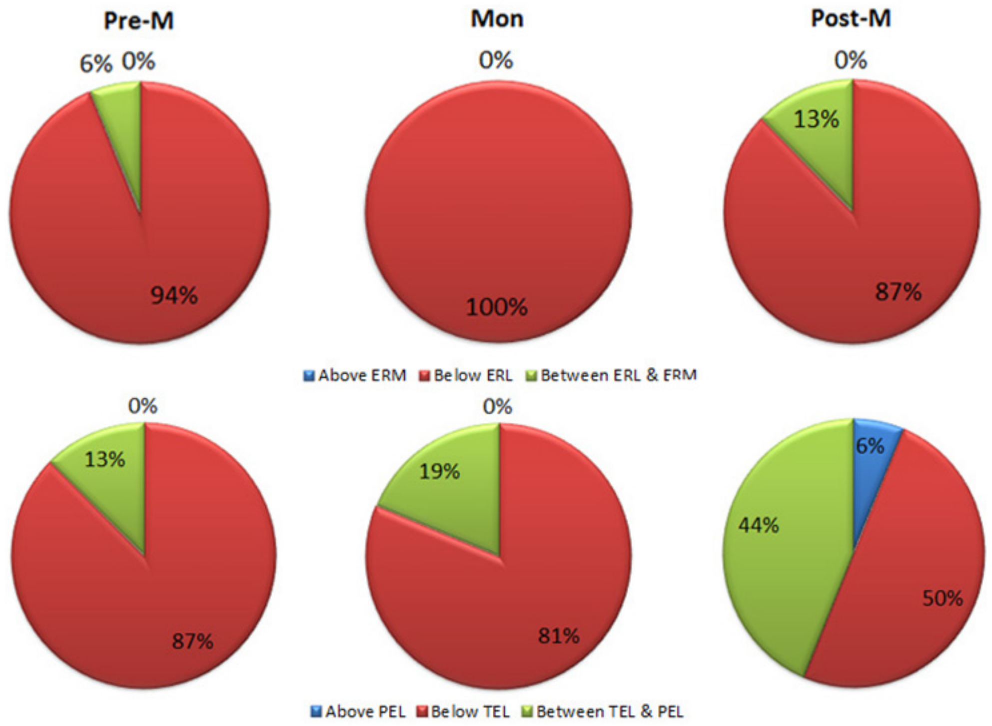

Figure 6.13 Percentage of stations affected by chromium in the estuary

Cr concentration in the study area was below the ERM value during the study period suggesting no deleterious threat to the biota with respect to Cr (Fig. 6.13). Cr content of 94 %, 100 % and 87 % estuarine stations were below the ERL value values during Pre-M, Mon and Post-M seasons respectively. Stations, E16 during Pre-M; E2 and E8 during Post-M only had Cr concentrations between ERL and ERM values. Also, none of the stations were above the ERM value suggesting low risk with respect to Cr in the estuarine sediments. All the coastal stations were below the ERL values during Pre-M and Mon seasons (Fig. 6.14). However, 82 % of them were below the ERL value during Post-M and stations C5 and C7 showed Cr concentrations between the ERL and ERM values.

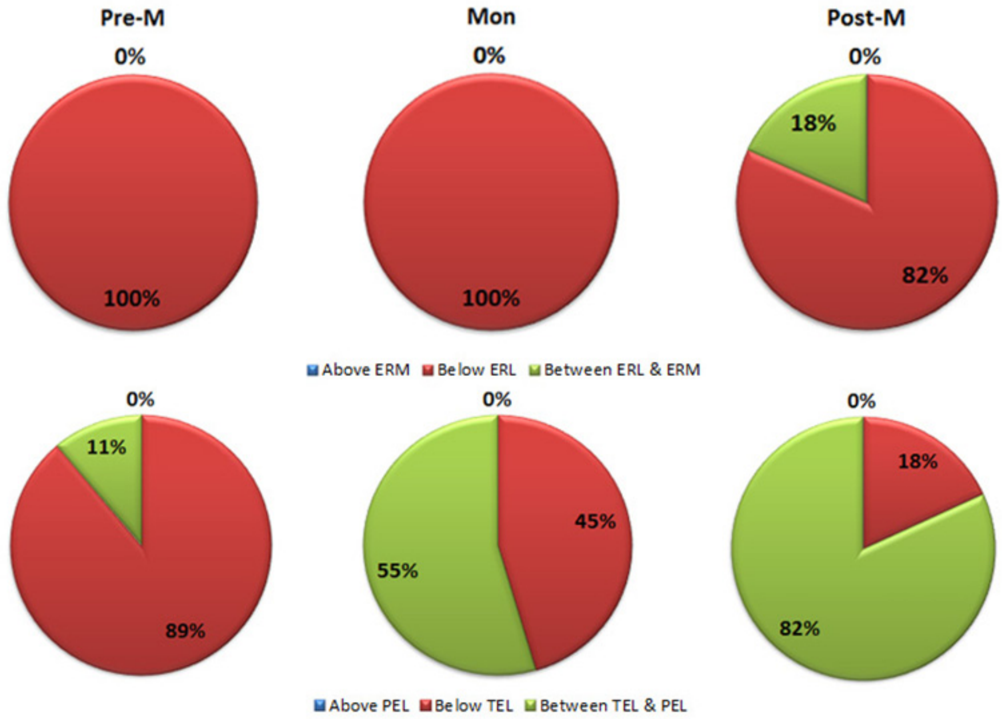

Figure 6.14 Percentage of stations affected by chromium in the coast

Cr content in station E8 during Post-M was above the PEL value suggesting risk to the biota and this higher value can be attributed to the ship building activities in the nearby shipyard. 13 %, 19 % and 44 % of the estuarine stations fell in the range between TEL and PEL values; 87 %, 81 % and 50 % of them were below the TEL value during Pre-M, Mon and Post-M seasons respectively (Fig. 6.13). All of the coastal stations were below the PEL value. 11 %, 55 % and 82 % of the stations fell in the range between Tel and PEL values; 89 %, 45 % and 18 % of them were below the TEL value during Pre-M, Mon and Post-M seasons respectively (Fig. 6.14). As per the TEL-PEL guideline it could be understood that Cr toxicity in the study area was higher during Post-M, followed by Mon and Pre-M seasons.

From the ERL-ERM and TEL-PEL guidelines it could be understood that in the estuary Post-M season was associated with higher toxicity with respect to Cr.

Copper

Although Cu is an essential micronutrient required by all life forms and is involved in a variety of biological processes, it is toxic to aquatic life at concentrations approximately 10 to 50 times higher than normal and acute poisoning of copper may lead to death (Klaassen, 1986). Aquatic toxicity of Cu is often due to the disruption of internal ion balance (Rand *et al.,* 1985; Lee *et al.,* 2010). Free Cu^{2+} ion is considered to be the most toxic form of Cu rather than the complex forms in aquatic systems (Allen and Hansen*,* 1996; Ma *et al.,* 1999; Lee *et al.,* 2010). Cu is very toxic especially in early developmental stages of many organisms due to its radical character (Spear and Pierce, 1979; Maharajan *et al.,* 2011) and at natural environmental concentrations, it adversely affects resistance of fishes to bacterial diseases, disrupts migration, alters locomotion through hyperactivity, impairs respiration, disrupts osmotic regulation through inhibition of gill Na+-K+-activated ATPase, impairs functions of olfactory organs and brain, changes the blood chemistry, enzyme activities and corticosteroid metabolism (Gardner and La Roche, 1973; Hodson *et al.,* 1979; Iger *et al.,* 1994). Cu is listed by the Environmental Protection Agency (EPA) as one of 129 priority pollutants (Keith and Telliard*,* 1979).

Cu did not exceed the ERM value during the study period in the estuary and coast, thus posing no deleterious threats to the aquatic biota (Fig. 6.15 & 6.16). Majority of the stations were below the ERL value (34 ppm) in the estuary and 25 % (E1, E5, E6 and E14), 6 % (E6) and 31 % (E1, E5, E6, E8 and E15) of the stations fell in the range between the ERL and ERM values during Pre-M, Mon and Post-M seasons respectively. Thus, toxicity of Cu to the aquatic biota could be higher during Post-M followed by Pre-M and Mon seasons. Northern, central and few of the southern stations were associated with high Cu content and this could be attributed to the northern industries, shipyard and port. All of the coastal stations were below the limits of concentration (ERL) at which adverse effects become persistent. Although ERL values were not intended as concentrations that are always predictive of toxicity, it should be used primarily as estimates of the concentrations below which toxicity is least likely. Hence the coastal sediments were assessed to be free from the toxicity with respect to Cu. Pollution indices like EF, CF and Igeo also suggested low level of contamination caused by this metal in the study area.

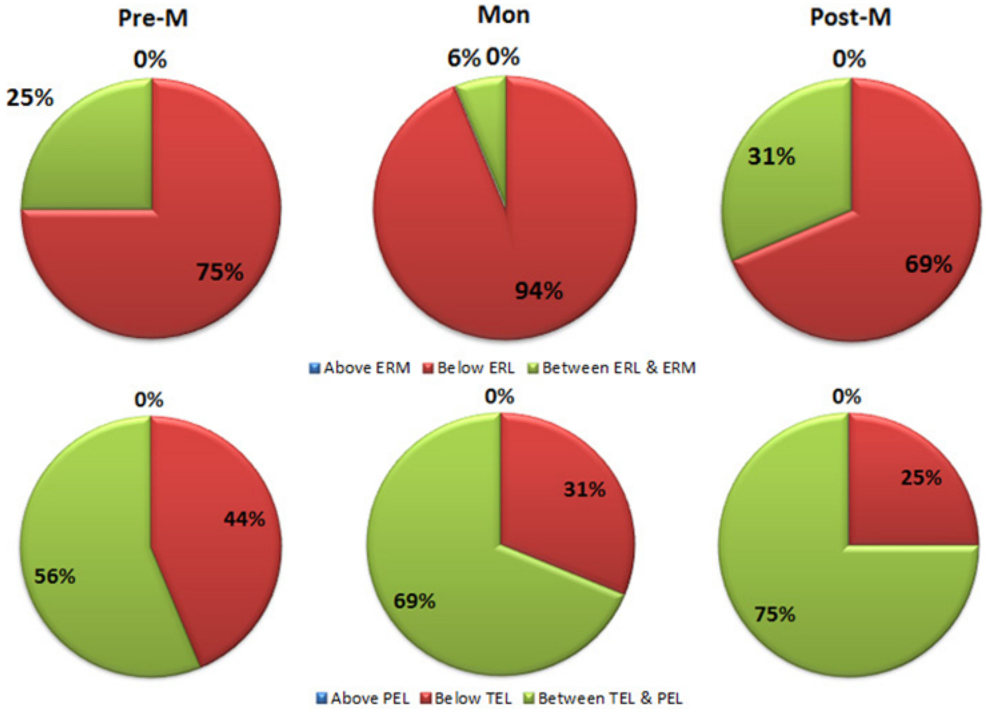

Figure 6.15 Percentage of stations affected by Cu in the estuary

As per the TEL-PEL guidelines also, Cu did not exceed the PEL value during the study period in the estuary and coast, thus posing no threats to the aquatic biota (Fig. 6.15 & 6.16). 56 %, 69 % and 75 % of the estuarine stations fell in the range between Tel and PEL values during Pre-M, Mon and Post-M seasons respectively. In contrast to the effect range guidelines, majority of the estuarine stations were above the TEL value (18.70 ppm) indicating possible detrimental effects to benthic organisms as per TEL-PEL guidelines. 44 %, 31 % and 25 % of the estuarine stations were below the TEL value during Pre-M, Mon and Post-M seasons respectively. 67 %, 18 % and 36 % of the coastal stations were below the TEL value during Pre-M, Mon and Post-M seasons respectively. 33 %, 82 % and 64 % of the stations fell in the range between TEL and PEL values, during Pre-M, Mon and Post-M seasons respectively, indicating sediment contamination higher during Mon followed by Post-M and Pre-M seasons.

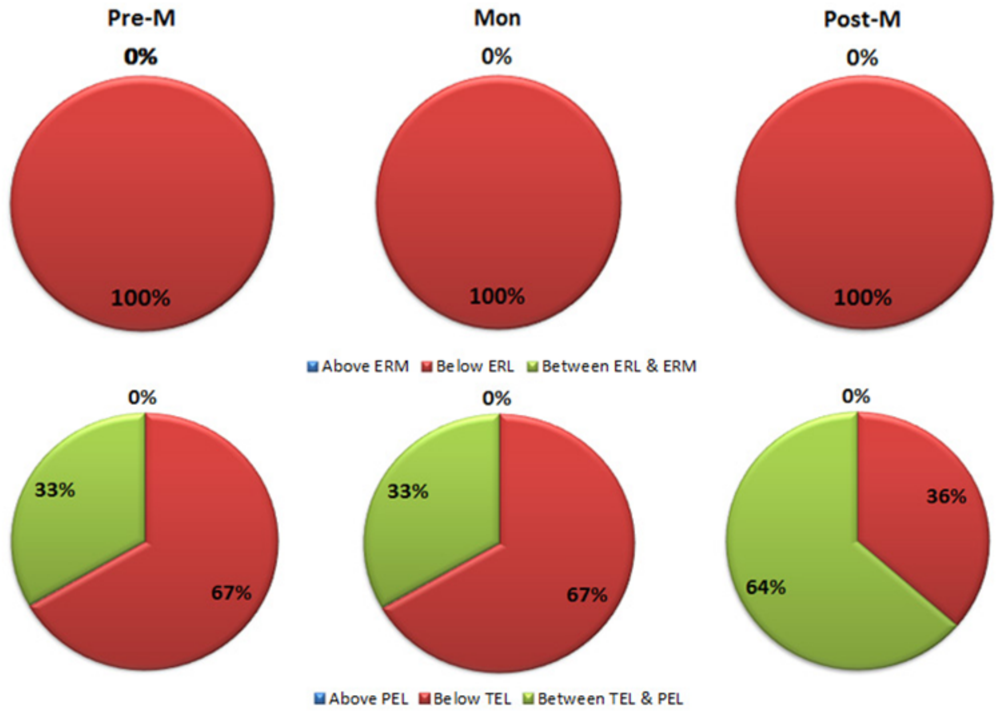

Figure 6.16 Percentage of stations affected by Cu in the coast

Zinc

Zinc, which is a constituent of more than 200 metallo-enzymes and other metabolic compounds is essential for all living organisms. Yet at higher concentrations it turns to be detrimental. In natural waters, dissolved Zn speciates into the toxic aquo ion $[Zn(H_2O)_6]^{2+}$, other dissolved chemical species (Spear, 1981; Black *et al.,* 2011) and various inorganic and organic zinc complexes. Aqua ions and other toxic species are most harmful to aquatic life under conditions of low pH, low dissolved oxygen, and elevated temperatures (Weatherley *et al.,* 1980). Most of the Zn released into aquatic environments is eventually partitioned into the sediments.

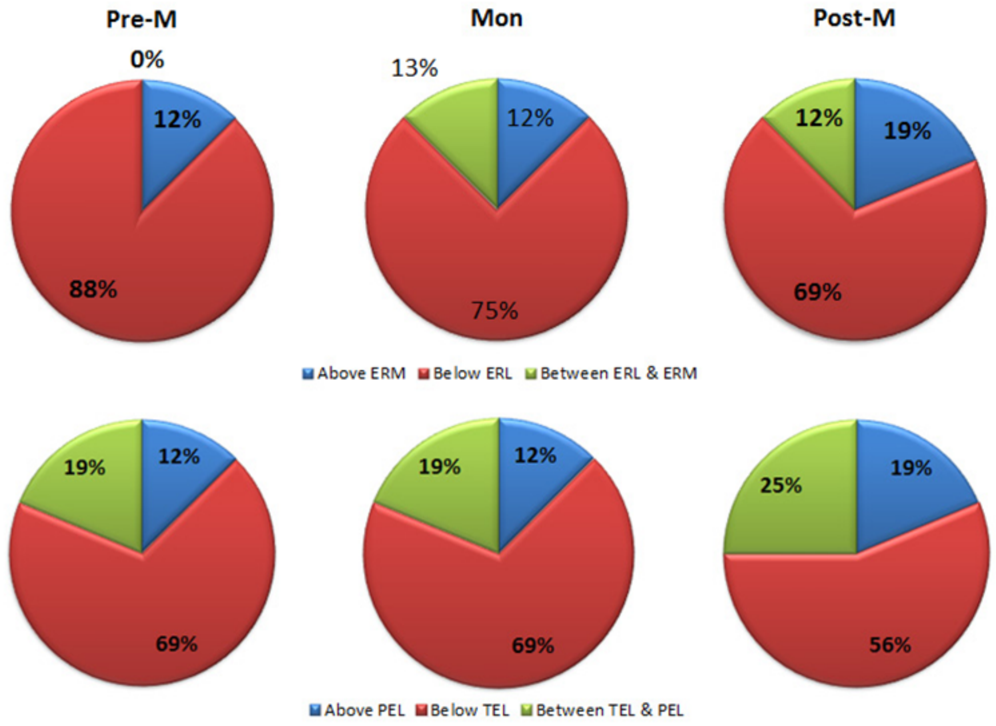

Figure 6.17 Percentage of stations affected by zinc in the estuary

Zn bioavailability from sediments is enhanced under conditions of high dissolved oxygen, low salinity, low pH, and high levels of inorganic oxides and humic substances (Spear, 1981). Aquatic populations are frequently demolished in Zn polluted waters (Solbe and Flook, 1975; Everall *et al.,* 1989; Zhong *et al.,* 2011). Excess Zn is teratogenic to frog and fish embryos (Dawson *et al.,* 1988; Fort *et al.,* 1989; Guy *et al.,* 2006; Hallare *et al.,* 2011), it exerts a critical influence on mammalian and piscine immune systems (Ghanmi *et al.,* 1989) and cause physical damage to the fish gills (Palaniappan *et al.,* 2010).

In the estuary, 12 % (during Pre-M and Mon) and 19 % (during Post-M) of the stations were associated with Zn content greater than the ERM and PEL values suggesting the alarming pace of contamination of the estuarine habitats with Zn (Fig. 6.17). Northern estuarine stations E1, E2 and E5 were associated with higher Zn content pointing to the addition of Zn from the northern industrial area. 88 %, 75 % and 69 % of the stations were below the ERL value. As per the ERL- ERM guidelines Zn contamination was higher during Post-M, followed by Mon and Pre-M seasons.

69 % (during Pre-M and Mon) and 56 % (during Post-M) of the estuarine stations were below the TEL value. 19 % of them fell in the range between TEL and PEL during Pre-M and Mon seasons, whereas, 25 % of them fell in the range between TEL and PEL during Post-M. As per TEL-PEL values Post-M season was associated with greater toxicity with respect to Zn. All the coastal stations were below the established limits (ERL and TEL) for biological effects during the study period indicating no threat to the living organisms i.e., Zn would rarely be associated with biological effects in the coastal sediments (Fig. 6.18).

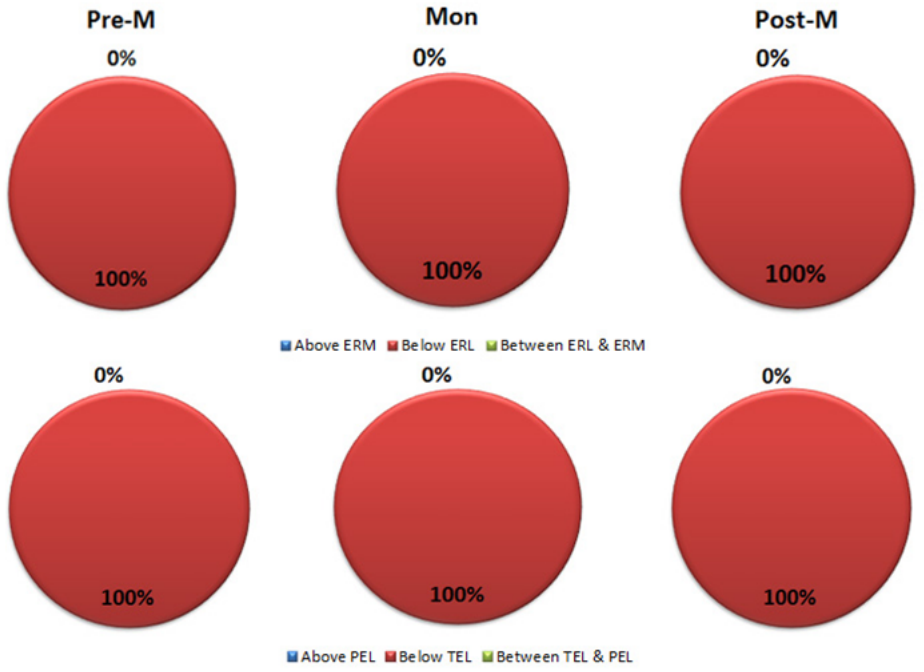

Figure 6.18 Percentage of stations affected by zinc in the coast

Sediments were classified into non-polluted, moderately polluted and heavily polluted based on effect based sediment quality guideline (SQG) of USEPA (Perin *et al.,* 1997). Average concentration of heavy metals in the sediments was compared with the SQGs (Table 6.5). Average Zn concentration of northern estuarine stations (E1-E5) was greater than 400 mg/kg and that of rest of the stations (E6-E16) was below 90 mg/kg suggesting this area have less pressure compared to the northern estuary. But the average Zn concentration in the estuary exceeded 200 mg/kg during Mon and Post-M and it was around the SQG during Pre-M. Hence, based on the Zn content, the estuarine sediments could be categorised into heavily polluted sediments, while the coast was non-polluted with respect to Zn. The sediments in the Cochin estuary and its adjacent coast is heavily polluted with Ni and moderately polluted with Cr. The study area was classified into non-polluted sediments with respect to Pb and Cu contents.

Table 6.5 Classification of the sediments based on Sediment Quality Guidelines

Element, mg/kg	Sediment Quality Guideline			Estuary			Classification	Coast			Classification
	Non-polluted	Moderately polluted	Heavily polluted	Pre-M	Mon	Post-M		Pre-M	Mon	Post-M	
Zn	<90	90-200	>200	187.76	202.74	204.35	Heavily polluted	55.74	76.65	73.20	Non polluted
Ni	<20	20-50	>50	134.70	111.34	83.39	Heavily polluted	90.00	116.84	93.68	Heavily polluted
Cr	<25	25-75	>75	35.05	34.15	68.34	Moderately polluted	31.62	51.91	64.57	Moderately polluted
Pb	<40	40-60	>60	26.98	27.18	27.48	Non polluted	25.77	34.63	33.59	Non polluted
Cu	<25	25-50	>50	22.66	23.52	24.56	Non polluted	16.51	23.37	22.99	Non polluted

The potential acute toxicity of contaminants in sediment sample was estimated as the sum of the toxic units (ΣTU) defined as the ratio of the determined concentration to PEL value (Pederson *et al.,* 1998). Sum of toxic units of the estuarine sediments ranged from 2.10 to 11.29, 1.34 to 9.46 and 0.62 to 8.12 during Pre-M, Mon and Post-M seasons respectively (Fig. 6.19). ∑TU of the coastal sediments ranged from 0.80 to 5.09, 2.67 to 5.37 and 1.54 to 5.41 during Pre-M, Mon and Post-M seasons respectively (Fig. 6.20).

Toxic unit values suggested estuarine station E1 as the heavily contaminated station, which is associated with huge amount of heavy metals, followed by E5 during Pre-M and Mon. During Post-M, the position switched among these stations which can be due to the heavy sedimentation in E5, which is a null zone. Although some southern estuarine stations exhibited high toxic units during Pre-M season, northern stations were found to be more polluted.

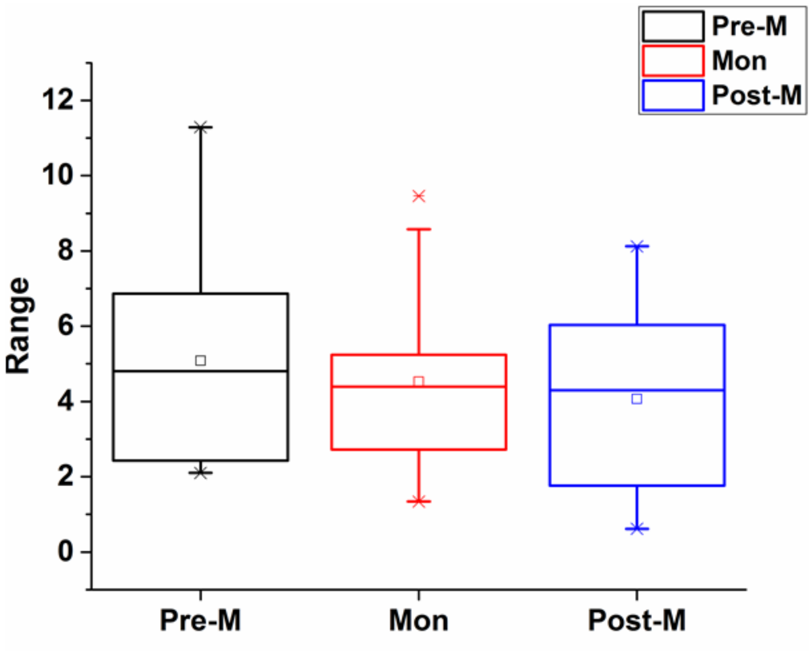

Figure 6.19 Sum of toxic units of the heavy metals in the estuarine sediments

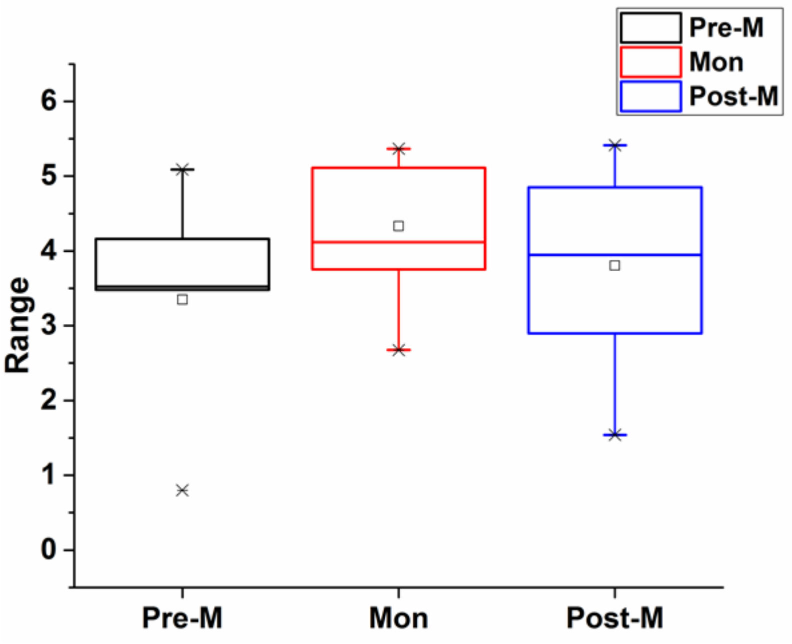

Figure 6.20 Sum of toxic units of the heavy metals in the coastal sediments

Coastal stations just south of the bar mouth region were found to be with highest toxic units compared to others. These stations (C5-C8) might be accumulating pollutant metals due to the dumping of the dredge spoils which is discharged at about 12 m depth each on the south and north of the navigational channel (Balachandran, 2001).

6.2.4 Adsorption of Metals on to the Sediments

In the aquatic systems, suspended and bed load have the important function of buffering higher metal concentrations in the aqueous phase through the processes of adsorption or precipitation. Adsorption of heavy metals on sediments represent an important control on their speciation and hence on their bioavailability and mobility in the aquatic environment. Exobiological factors like temperature, ion number, sediment characteristics, pH and the nature of metals involved and competition for sorption sites (Zhou and Kot, 1995) were found to have influence in the adsorption process. Adsorption of a metal is reported to be lower in the competitive systems compared to its mono-metal behaviour (Harter, 1992). Salinity and pH affect the speciation of metal ions and greatly interfere with their fixation on clay minerals. Sediment composition has significant role in removal of metal pollutants from aqueous phase and hence exerts control on water pollution. Although the mud fraction (clay and silt) adsorb metal ions much better than the coarse fraction (sand) of sediment, in systems with high sand (90-95 %) and low mud (0-10 %) contents, the overall contribution of the sand content in adsorbing the metal ions could be comparable or even higher than that of the mud fraction (Jain and Ram, 1997a & b; Jain and Ali, 2000). Adsorbabilities of heavy metals on sediments increase with increasing OM content and hence organic content in the sediments can be used as a simple index for assessing the degree of pollution of the sediments (Lin and Chen, 1998). In natural systems, each of different origin, many factors vary simultaneously and the effect of individual factors cannot be isolated.

Adsorption analysis give an idea to what extend these sediments will further adsorb heavy metals. Batch tests are generally used for studying adsorption process, although advection and dispersion may occur in highly dynamic coastal systems justifying the need of flow experiments (Miretzky *et al.,* 2006). Information from batch experiment on metal adsorption capacity can be used to estimate the maximum immobilization of metals. Adsorbed concentration of heavy metals against the applied initial metal ion concentration are given in the appendix 35.

For the same equilibration time, the metal ion adsorbed is higher for greater values of initial metal ion concentrations. This is obvious because more efficient utilization of the adsorptive capacities of the adsorbent is expected due to a greater driving force i.e. by a higher concentration gradient pressure (Jain, 2001). The percentage adsorption is more for lower concentration of metals and it decreased with increase in initial metal ion concentration. Considering the difference between the initial and final concentration of the dissolved metals, the order of adsorption of metals by the estuarine sediments was Pb > Cd > Co > Zn > Cu and that in the coastal sediments was Pb > Zn > Cu > Co > Cd. Pb was found to be the most retained metal by the sediments, suggesting the risk associated with dissolved Pb is less as it is easily adsorbed by the particulates and deposited in the bottom sediments. This fraction of Pb will not pose any ecological risk unless and until the sediments are disturbed by any of the physical/chemical/biological disturbances which result in remobilisation of the metal. Cadmium in the coastal environment preferred to be in dissolved phase and thus pose great risk to the biota. But in the coastal environment, Cd form stable Cd-Chloro complexes (Bourg, 1987; Elbaz-Poulichet *et al.,* 1987; Comans and van Dijk, 1988) which are less available from solution, thus decreasing its bioavailability (Wright and Welbourn, 2002; Bradl, 2005).

Distribution Coefficients (Kd)

Distribution coefficient (Kd) is used to compare the sorptive capacities of different adsorbents for any particular ion, when measured under the same experimental conditions (Alloway, 1995). The distribution coefficients (Kd) were calculated using the equation,

$$\text{Kd} = \frac{\text{Equilibrium metal concentration adsorbed}}{\text{Equilibrium metal concentration in solution}}$$

where the equilibrium metal concentration adsorbed is expressed per unit weight of sediment and the equilibrium metal concentration in solution per unit volume of liquid.

The higher the Kd of a metal the stronger is its sorption onto the soil surfaces and thus the lower will be its solubility. Hence distribution coefficients can be used to evaluate heavy metal mobility in adsorption experiments (Cruz-Guzman *et al.,* 2006; Antoniadis *et al.,* 2007). Distribution coefficients (Kd) of metals are furnished in Table 6.6.

Lead was associated with the highest Kd value showing that it was the most retained cation. Highest Kd values obtained for Pb indicated its leaching loss potential. Lower Kd values were shown by Cd and Cu in C9 & E9; Cu and Zn in E12 and E9. In C1 and C5, lower Kd values were shown by Co with the lower initial metal concentrations; Cu and Cd with the higher initial metal concentrations.

Table 6.6 Distribution coefficients of heavy metals between the particulate and dissolved phases

Stations	Adsorbate concentration, mg/L	Distribution Coefficient, L/kg				
		Cd	Pb	Co	Cu	Zn
C1	50	492.21	1822.22	428.54	558.53	436.37
	100	313.18	1843.15	249.08	327.03	296.00
	150	200.75	783.84	225.90	277.76	257.54
	200	130.13	449.82	171.33	170.01	207.62
	250	158.71	376.32	169.80	112.56	196.57
	300	148.56	639.02	171.98	172.55	168.14
C5	50	708.87	334.62	714.87	1510.72	1068.19
	100	511.27	3769.92	383.13	497.71	709.76
	150	1020.12	2198.24	316.15	320.20	486.04
	200	321.89	1218.44	315.63	231.50	398.74
	250	191.91	768.32	251.42	171.14	361.24
	300	189.13	926.25	258.56	617.21	325.97
C9	50	453.56	459.66	558.01	855.29	613.63
	100	292.66	2918.60	342.86	306.13	312.54
	150	232.42	1473.70	276.61	223.27	290.44
	200	187.50	811.44	265.14	208.58	293.55
	250	161.34	789.83	195.86	145.45	208.96
	300	143.28	723.52	198.59	193.97	185.66
E9	50	374.29	-547.37	1116.23	300.36	505.92
	100	329.68	1081.06	339.60	222.01	401.56
	150	383.13	603.03	301.33	143.48	263.50
	200	147.75	430.42	172.89	151.69	229.91
	250	160.42	297.16	158.46	128.78	218.76
	300	164.43	495.15	138.38	147.69	208.86
E12	50	437.86	421.04	342.58	249.37	289.13
	100	306.26	1070.49	254.51	172.96	192.17
	150	629.52	540.13	275.53	168.32	143.37
	200	253.82	386.92	160.83	160.70	122.38
	250	400.16	266.45	135.78	59.40	132.84
	300	217.55	521.90	149.56	173.68	118.52
E13	50	615.44	-299.64	1517.63	495.58	539.88
	100	365.04	1517.02	1110.26	297.79	289.13
	150	330.74	944.70	237.42	178.51	180.70
	200	202.34	518.96	196.81	188.57	195.87
	250	335.96	315.38	182.65	114.68	131.38
	300	186.69	439.96	185.96	142.85	114.15

Application of the Freundlich and Langmuir Models

Freundlich and Langmuir models are generally used to describe the experimental data of adsorption. In the present study, adsorption data of the metal ions has been analysed with the help of both the models to describe the relationship between the amount of heavy metal adsorbed and its equilibrium concentration in solutions and also to evaluate the mechanistic parameters associated with the adsorption process, viz. monolayer capacity and sorption intensity (Table 6.7). Freundlich and Langmuir isotherms for the adsorption of heavy metals by the sediments are represented in Fig. 6.21 to 6.25.

Freundlich Isotherm

The linearised form of the Freundlich isotherm model is given by the following equation,

$$\ln q_e = \ln k + \frac{1}{n} \ln c_e$$

where Ce (mg/L) is the concentration of metal in solution at equilibrium, q_e (mg/kg) is the mass of metal adsorbed to the sediment, k and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively, of the sorbent. The values of k and 1/n can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of ln qe versus ln Ce.

Table 6.7 Isotherm constants for the adsorption of heavy metals on sediments of Cochin estuary and adjacent coast

Location	Cd µg/g	Pb µg/g	Cr µg/g	Ni µg/g	Co µg/g	Cu µg/g	Zn µg/g	Mn µg/g	Fe %	References
Average shale	0.1	14.8	126	56	24	25	65	716	4.32	Wedephol, 1995
Manakudy Estuary, India	2.69 – 3.17	152.25 – 176.88	256.9 – 482.14	20.15 – 28.9	-	37.35 – 45.87	54.58 – 72.62	-	0.46 - 0.49	Kumar & Edward, 2009
Tambaraparni River Estuary, India	0.42 – 0.92	0.3 – 170	58.90 – 110.3	-	-	62.8 – 115	47.3 – 112	-	-	Jayaraju *et al.*, 2011
Tapti Estuary, India	0.74 – 1.25	43.28 – 77.74	48.26 – 72.40	71.13 – 107.82	14.73 – 21.69	123.17 – 170.52	117.47 – 178.8	-	5.66 - 9.0	Bhavna *et al.*, 2013
Elbe, Germany	1.5	81	83	41	-	44	392	-	-	Wetzel *et al.*, 2013
Guadiana Estuary, Spain	0.05 – 1.40	1.30 – 62.5	1.60 – 24.0	0.70 – 41.6	0.46 – 24.8	1.2 – 73.0	4 – 483	-	-	Delgado *et al.*, 2010
Minho River Estuary, Spain	-	11.12 – 18.08	8.7 – 64.6	-	-	1.69 – 26.77	19.4 – 131	160 - 540	0.54 - 4.92	Mil-Homens *et al.*, 2013
Sao Francisco Estuary, Brazil	-	May-16	15 – 69	3 – 27	-	2 – 26	1 – 48	27 – 239	0.59 - 3.58	Santos *et al.*, 2009
Pearl River Estuary, China	-	40.9 – 92.4	74.1 – 123	21.9 – 46.5	-	18.9 – 87.2	100 – 289	0.06 – 0.14	3.24 – 4.13	Yu *et al.*, 2010
CUA ONG Harbour, Vietnam	0.02 – 0.2	4.41	10 – 49	3 – 20	1 – 13	13 – 30	12 – 93	18 – 318	0.48 – 3.72	Hieu Ho *et al.*, 2010
Yangtze River Intertidal Sediments, China	-	27.3	78.9	31.8	-	30.7	94.3	766	3.34	Zang *et al.*, 2009
Hamilton harbour, Canada	-	18 – 1250	5 – 140	8 – 61	-	8 – 135	338 - 5930	42 – 1158	1.22 – 20.4	Poulton *et al.*, 1996
Bergen harbour, Norway	-	24 – 1920	-	-	-	25 – 1090	46 - 2900	-	-	Paetzel *et al.*, 2003
Bay of Bengal, off Ennore, India	6.58	32.36	194.83	38.61	8.1	506.21	126.83	373	2.72	Muthu Raj & Jayapraksh, 2008
Cochin Shelf, India	3.27	13.1 – 39.6	35 – 195	5.1 – 72.1	3.1 – 23.2	6 – 32.7	7 – 132	40 – 210	0.34 – 3.42	Balachandran *et al.*, 2006
Cochin Estuary, India	0.16 – 5.96	1.88 – 28.75	7.5 – 79	6.8 – 72.5	4.38 – 24.61	4.40 – 46.88	3.13 – 433.13	48.8 – 657.5	1.48 – 8.30	Deepulal *et al.*, 2012
Kakinada Bay, India	0.5 – 6.0	2.5 – 38	0.80 – 1.36	13 – 60	27 – 50	30 – 51	-	225 – 666	0.45 – 0.49	Ray *et al.*, 2006
Cochin Estuary	0.25 - 9.39	4.97 - 48.80	6.86 - 192.36	11.92 – 208.83	6.08 – 36.60	5.10 – 42.88	7.28 – 1229.83	63.46 – 334.49	0.49 – 5.23	Present Study
Cochin Coast	0.29 -3.15	3.75 – 42.29	5.50 – 109.88	24.86 – 145.48	6.07 – 36.07	5.02 – 32.32	9.62 – 114.39	92.20 – 427.04	0.16 – 3.93	Present Study

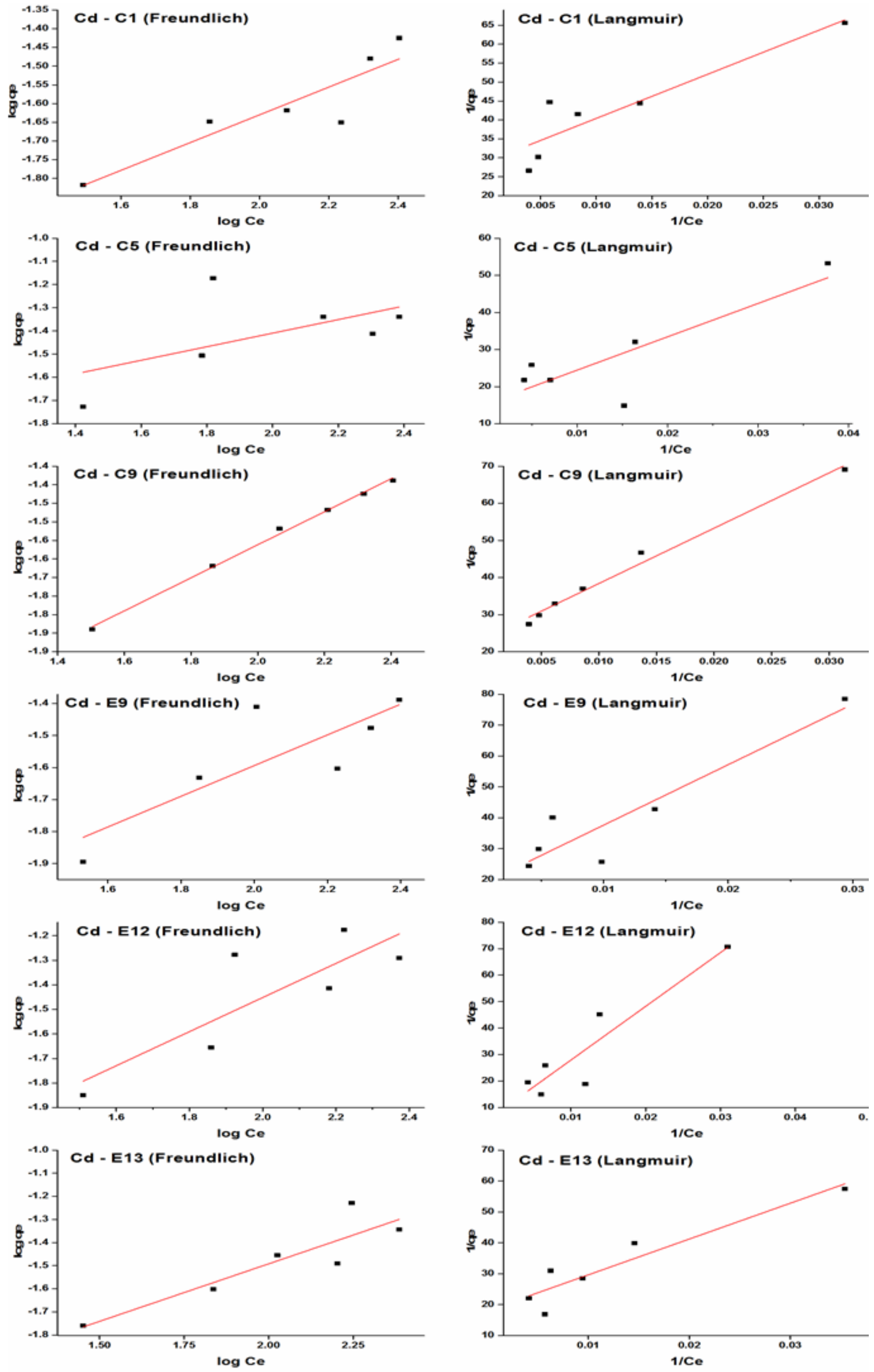

Figure 6.21 Linearised Freundlich and Langmuir isotherms for adsorption of Cadmium by the sediments

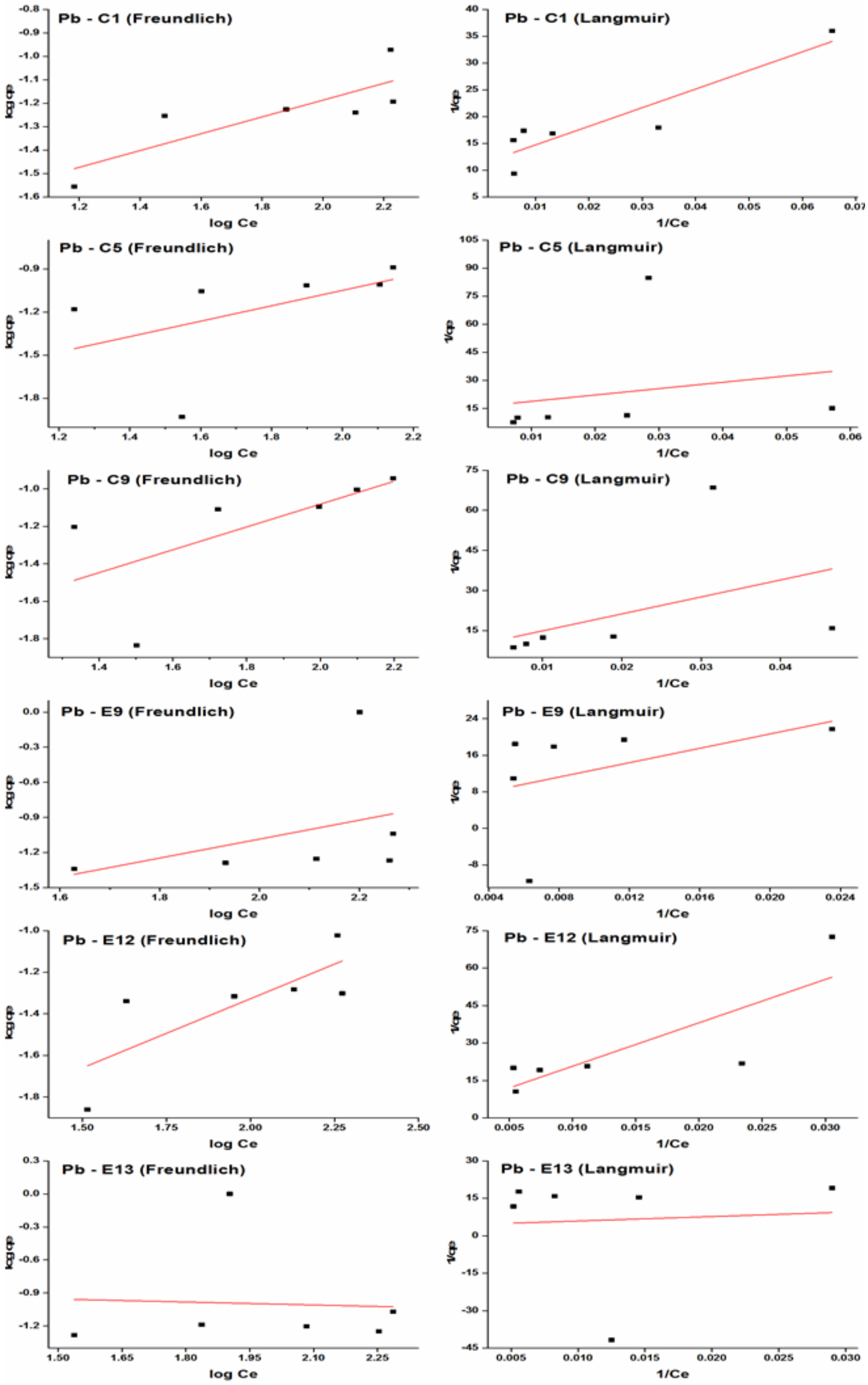

Figure 6.22 Linearised Freundlich and Langmuir isotherms for adsorption of Lead by the sediments

Adsorption capacities (K) of the sediments determined by the Freundlich isotherms were in the order of Pb > Cu > Cd > Zn > Co in C1, Cu > Cd > Pb > Zn > Co in C5, Cu > Pb > Zn > Cd > Co in C9, Co > Cd > Zn > Pb > Cu in E9, Pb > Co > Zn > Cd > Cu in E12 and Pb > Co > Zn > Cu > Cd in E13. The n value obtained from the Freundlich isotherm indicates the degree of nonlinearity between solution concentration and adsorption, i.e., n = 1 means adsorption is linear, n < 1 means adsorption is a chemical process and n > 1 indicate the adsorption is a physical process (Desta, 2013). The value of n greater than one may be due to the distribution of surface sites or any factor that causes a decrease in adsorbent adsorbate interaction with increasing surface density (Reed and Matsumoto, 1993; Desta, 2013). Values of n within the range of 1–10 represent a favourable adsorption (McKay *et al.,* 1980; Goldberg, 2005; Ozer and Pirincci, 2006; Dada *et al.,* 2012). In this study, n value lies between 1 and 10 (except in the case of Pb in E13) indicating the physical adsorption of metals on to the sediments. Negative value of sorption intensity found for Pb in E13 indicated competition caused decrease in the adsorption of the metal.

Values of 1/n below and above one indicate normal and cooperative adsorptions respectively (Mohan and Karthikeyan, 1997). In the present study, value of 1/n was found to be below one in the case of all the metals suggesting a normal adsorption process.

Langmuir Isotherm

The Langmuir isotherm model is based on the assumption that binding sites are distributed homogeneously over the adsorbent surface and have same affinity for adsorption as a single molecular layer and there is no interaction between adsorbed molecules. The linearized form of the Langmuir isotherm model can be represented as follows,

$$\frac{1}{qe} = \frac{1}{a} + \frac{1}{ab} \times \frac{1}{c_e}$$

where q_e is the amount of metal adsorbed at equilibrium (mg/kg), Ce is the concentration of the metal (mg/L) in solution at equilibrium, and a (mg/kg) and b (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the binding strength of the metal respectively. Langmuir constants a and b can be evaluated from the intercept and the slope of the linear plot of equilibrium data of 1/qe versus 1/Ce.

Adsorption capacity a (mg/kg) of the sediments determined by the Langmuir isotherms were in the order of Pb > Zn > Co > Cu > Cd in C1, Zn > Pb > Cd > Co > Cu in C5, Cu > Pb > Co > Zn > Cd in C9, Pb > Zn > Cd > Cu > Co in E9, Pb > Cd > Co > Zn > Cu in E12 and Pb > Cd > Co > Cu >Zn in E13. Sediments C1, E9 and E12 showed highest 'a' values for Pb

Adsorption capacity (a) of the sediments decreased in the order C9 > C5 > E9 > C1 > E13 > E12 for Cu, C5 > C9 > E12 > C1 > E13 > E9 for Co, E12 > E13 > E9 > C9 > C1 > C5 for Pb, E12 > C5 > E9 > E13 > C9 > C1 for Cd and C5 > E9 > C1 > C9 > E12 > E13 for Zn. Coastal sediments showed higher adsorption capacities for metals except Pb and Cd. Sediment C5 with highest mud (silt + clay) and organic matter contents showed highest adsorption capacity for the metals Cu, Co and Zn showing the influence of fine texture on the adsorption processes. E12 showed highest adsorption capacity in the case of Pb and Cd.

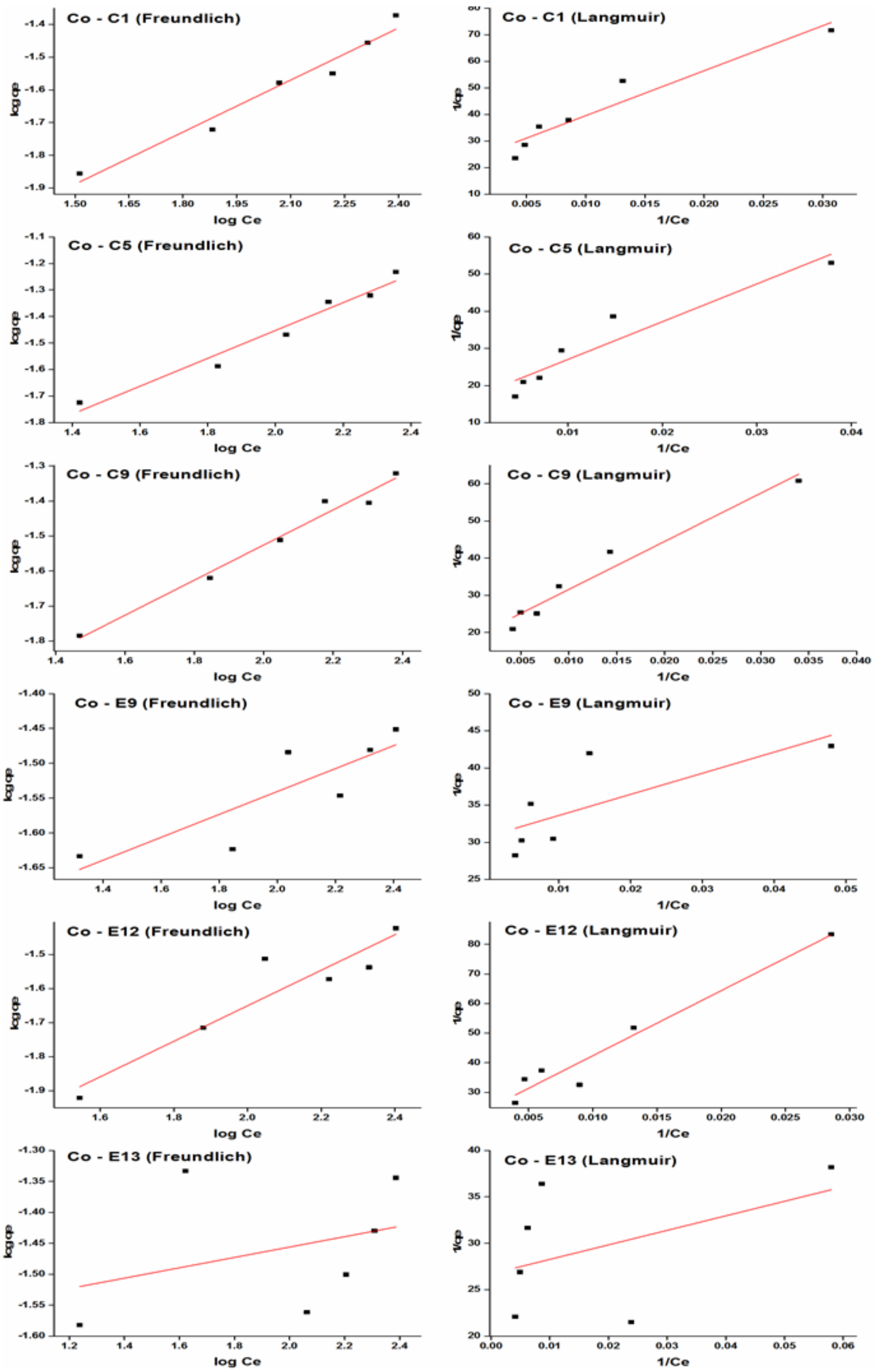

Figure 6.23 Linearised Freundlich and Langmuir isotherms for adsorption of Cobalt by the sediments

Binding strength constant of the metals were in the order Pb > Cu > Cd > Co > Zn in C1, Cu > Pb > Zn > Cd > Co in C5, Cu > Zn > Cd > Co > Pb in C9, Co > Zn > Cu > Pb > Cd in E9, Zn > Cu > Co > Cd > Pb in E12 and Co > Zn > Cu > Pb > Cd in E13. Although the b values determined from the sorption isotherms should only be considered qualitatively (Sparks, 1995), it can be compared to the free energy change of adsorption of different species (Van Riemsdijk *et al.,* 1985) Higher b values usually related to specifically sorbed metals at high energy surfaces with low dissociation constants and vice versa (Ma and Rao, 1997; Adhikari and Singh, 2003). Adsorption is the main mechanism of metal retention in the batch experiments which is conducted in aerobic condition with the air-dried sediments. But the sediments were in anoxic condition in the natural environmental condition (Eh < 100 mV) and in such reducing environments, sulfate could be reduced to H_2S and metals get precipitated as insoluble metal sulfides (Seo *et al.,* 2008). Thus besides the adsorption, surface precipitation also contribute to the sedimentary metal pool. So the sediments accumulate more metal than the capacity found in this experiment. Hence metals discharged into the study area will be retained by the sediments but under favourable conditions these metals will be remobilized /released back to the water column increasing the bioavailability and hence toxicity.

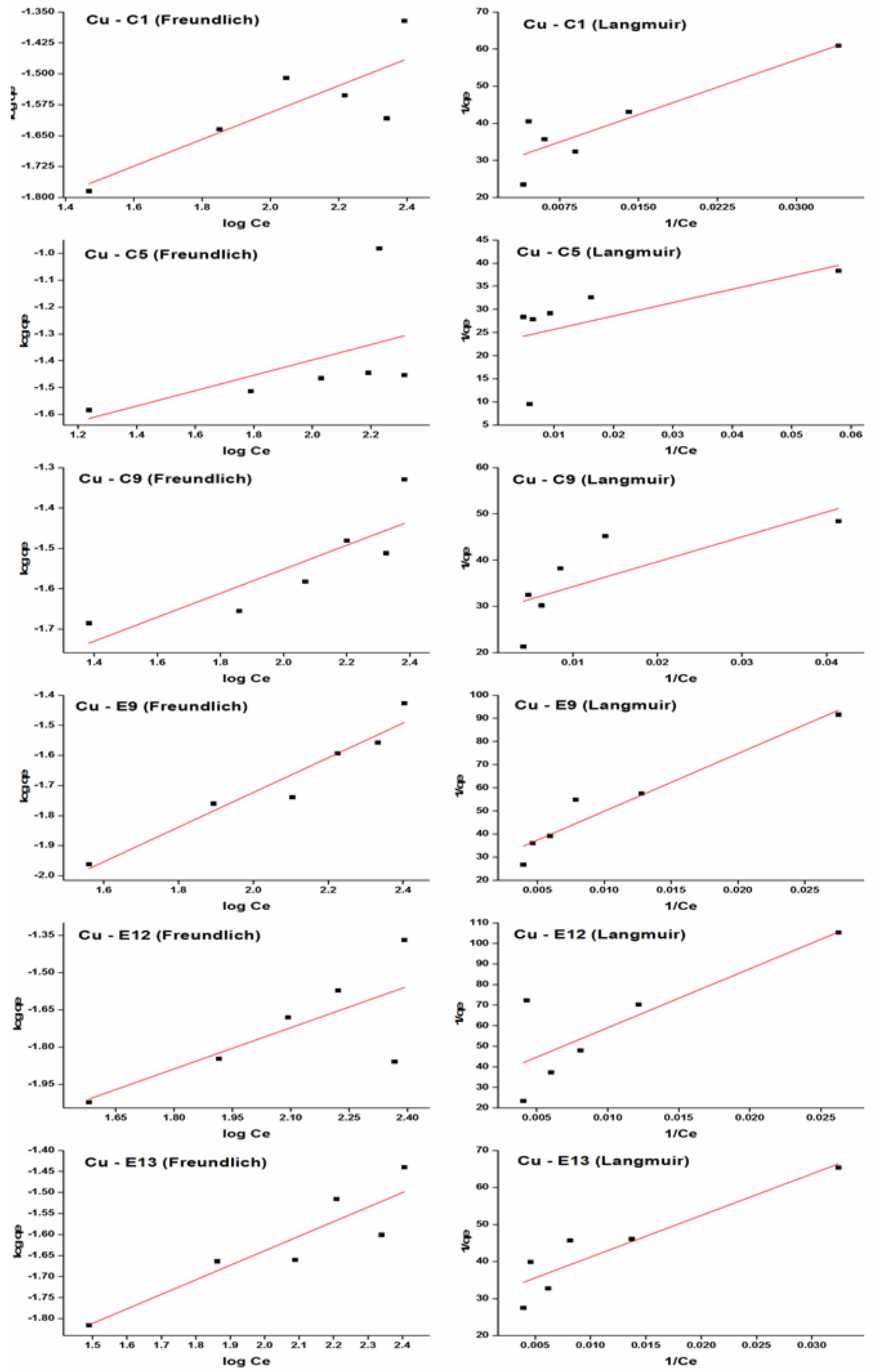

Figure 6.24 Linearised Freundlich and Langmuir isotherms for adsorption of Copper by the sediments

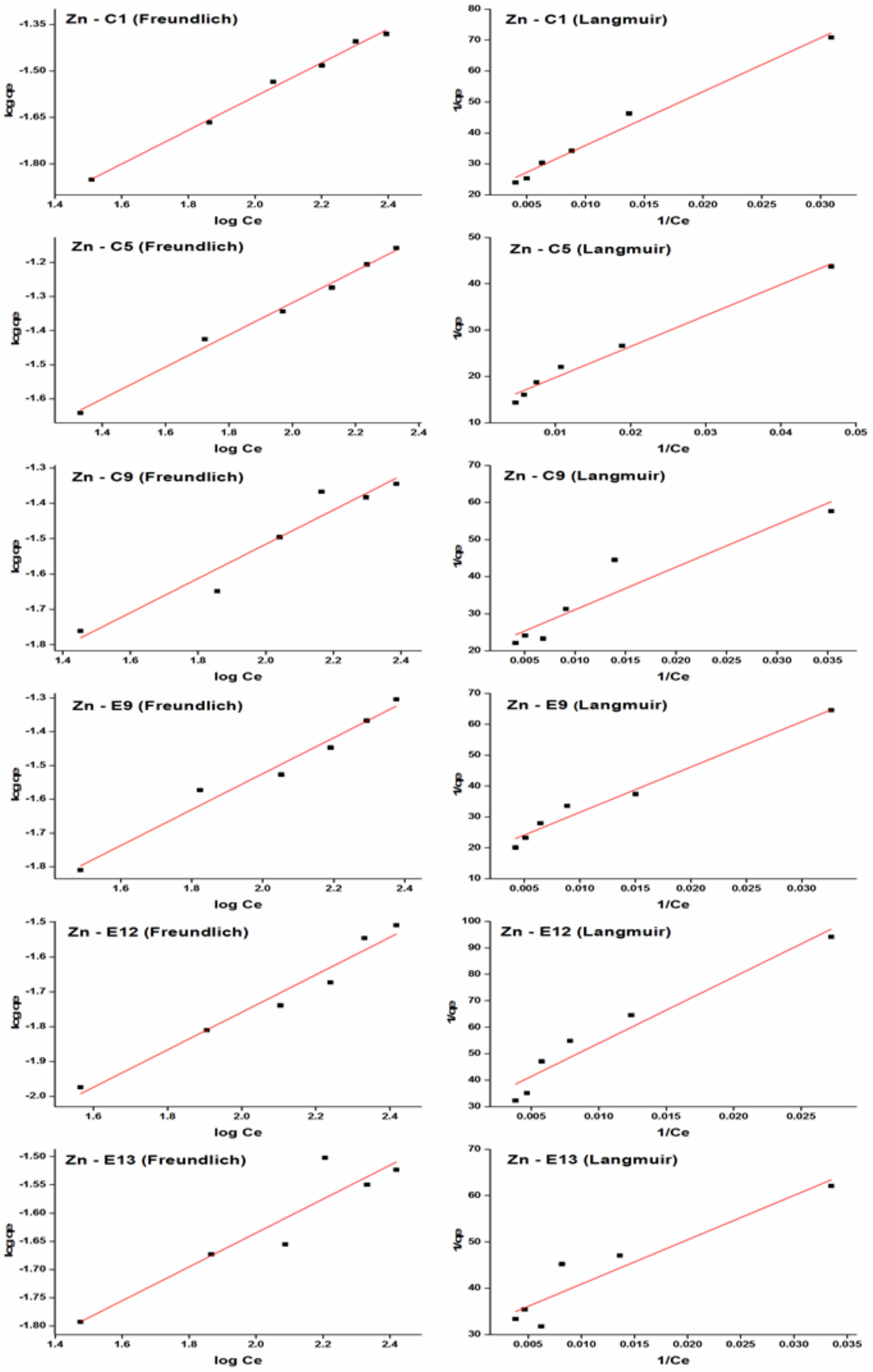

Figure 6.25 Linearised Freundlich and Langmuir isotherms for adsorption of Zinc by the sediments

Fitness of Isotherms

Langmuir model succeeded in explaining the removal of Cd. Although both the models were successful in explaining removal of Cd in C9, Freundlich was associated with high r^2 value than Langmuir model in C9. Both the models were not able to explain the adsorption of Cd by the sediment in E9. In the case of Pb, C1 and E12 were found to be associated with moderately high r^2 values. All other sediments showed low r^2 values indicating poor fitness to both the models.

Freundlich model fit to the adsorption of Co in sediments C1, C5, C9 and E9. E12 showed best fit to the Langmuir model and E13 showed poor fitness to both the models.

C1, E12 and E13 were more fitted to Langmuir model and C9 to Freundlich model. Although removal in E9 fitted to both the models, slightly higher r^2 value was obtained for Freundlich model. Adsorption of Cu by the sediment in C5 showed poor fitness to both the models.

Removal of Zn fitted to Freundlich model in C1, C5, C9 and E12. Adsorption in E9 showed more fitness to Langmuir model and E13showed similar fit to both the models. Adsorption in E9 and E13 showed poor fitness to the models.

Langmuir model (monolayer adsorption) succeeded in explaining the adsorption of Cd (mono and multi), Co in (multi), Zn (multi), Cu (mono) and Pb (only C1 & E12 in mono) and Freundlich model succeeded in explaining the adsorption of Zn in (mono) and Co (mono). Both the models were not fitted to the adsorption process of Cu (multi) and Pb (mono & multi). So the optimum adsorption isotherm for predicting metal removal was found to be the Langmuir model.

6.3 Conclusions

Comparison with other systems indicated that the Cochin estuarine and coastal systems are facing anthropogenic pressure on its heavy metal status. Transport of metals from the estuarine environment to the coast was evidenced from the pollution indices. Pollution indices suggested that both the systems were enriched with the metals especially Cd, Zn, Pb and Ni. Although the estuarine area had pockets of varying EF values, it showed higher enrichment in comparison with the coastal sediments - which was associated with a similar EF in almost all the stations. Majority of the estuarine stations documented very high CF throughout the study period with the exception of some southern stations with low CF, indicating that the industries has a profound influence on the heavy metal status of the northern side of Cochin estuary. High mC_d values in the northern stations suggested a notable degree of contamination in the northern part of the estuary. Coastal sediments were found to be contaminated in lesser degree compared to the estuary. Igeo values of metals like Cr, Cu, Mn, Fe and Co suggested the coastal environment to be free from their pollution. Pollution Indices suggested both the estuary and its coast to be highly enriched with respect to Cd. From the EF, CF and Igeo values it was inferred that all the metals except Cr, Mn & Fe showed low to extremely high levels of pollution in the study area. PLI value > 1 observed for the northern and central estuarine stations indicated an alarming rate of contamination of the estuary by heavy metals and an immediate intervention to ameliorate pollution by the northern industrial belt should be taken. Coastal stations except C3 were also associated with higher PLI values.

Nickel was the only element detected in higher concentrations than the PEL and ERM values and hence to associate with biological effects. The order of toxicity associated with the elements in the estuary was Ni > Zn > Cd > Cu

> Cr > Pb. While in the coastal sediments, the order of effect toxicity was Ni > Cd > Cr > Pb > Cu. Unlike the estuarine sediments, Zn was found to be below the ERL/TEL values to cause any biological effects in the coastal environment. Hence, on an effect based approach, Zn poses no threat to the coastal biota. Classifications based on the SQGs, categorised Cochin estuarine sediments into heavily polluted with respect to Zn and Ni; moderately polluted with respect to Cr and non-polluted with respect to Pb and Cu. Coastal sediments were heavily polluted with Ni and moderately polluted with Cr and the coastal area was non-polluted with respect to Zn, Pb and Cu. Sum of the toxic units suggested heavy anthropogenic pressure in the northern estuarine area and in the coastal area, accumulation of the metals was more in coastal stations just south of the bar mouth. From this study, it could be concluded that the Cochin estuary is heavily polluted with respect to the metals under study compared to the coast.

Heavy metals which enter an aquatic system through the disposal of municipal/industrial effluents or by biological and chemical degradation undergo phase transitions depending on the environmental conditions. Adsorption of heavy metals by the natural sediments plays an important control on their speciation and hence their bioavailability and mobility in the aquatic environment. The present study revealed the potentiality of surface sediments to adsorb heavy metals. The percentage of metal ion removal at equilibrium decreases with increasing metal dose even though the sediments have further capacity to absorb more metals. This suggested that the huge addition of metals will mobilize them even from previously adsorbed sites due to competition among the ions and this will be deleterious to the aquatic biota.

Although batch experiments are used to study the adsorption process generally, they cannot provide an accurate estimation of the longevity of sediments in heavy metal removal. Adsorption on natural sediments will not be ideal like that in the pure systems. Moreover, adsorption in the laboratory conditions, will be different from the adsorption in natural environmental conditions where different types of sorption sites are present. Reaction mechanisms and kinetics will be heterogeneous in the real systems like natural sediments. So the information obtained from the present study might be interpreted bearing the above things in mind.

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SUMMARY

Coastal systems have great role in the development of the human civilizations as we depend on their numerous living and non-living resources. They have high socio-economic importance and increased human interventions in the catchment of these coastal systems disrupt the natural equilibrium and biodiversity. Among the various pollutants which contribute to the pollution of the aquatic environments, heavy metals are of great significance as they are non-biodegradable unlike others. Many of them are considered as essential metals which have beneficial health effects, but are deleterious to the organisms at elevated concentrations and they get transferred along the food web through biomagnification. Heavy metals in an aquatic system are partitioned among the dissolved, colloidal, particulate and sediment phases. Switching over between theses phases is dependent on the hydrographical and sedimentological features of the aquatic environment. Sediments represent the ultimate sink for these contaminants unless and until they are disturbed by any of the physical/chemical/biological disturbances. It is the bioavailable fraction of the metal that determines the toxicity to the aquatic inhabitants.

Cochin estuary is a part of the Ramsar site, Vembanad-Kol Wetland system (No. 1214, November 2002), which has been included in the list of wetlands to be protected considering its socio-economic importance and threats faced by this area. Cochin estuary faces numerous pollution problems, of which, heavy metal pollution is of major concern as there is huge addition of metals through the discharge of untreated or partially treated effluents from the industries in its catchment. Many studies have been reported on the metal levels of dissolved, particulate and sedimentary compartments separately, yet an integrated study which will give a clear picture of the dynamics of the metals in the entire system is rare. Study on the influence of the estuary on the coastal metal levels is also important in the context of heavy anthropogenic influence from the industrial belt of Greater Cochin. Study of the adsorption capacity of the sediments can give an idea to what extent these sediments will further adsorb the metals. Together with strengthening and supplementing existing database, the current study will also help spearhead designing of action plans for effective and sustained management of Cochin estuarine system.

Evaluation of the general hydrographical and sedimentary parameters like pH, redox potential, organic matter content and texture suggested that the study area is favourable for metal precipitation and accretion. Dominance of fine grained sediments also favours the accumulation of heavy metals. As can be seen from the Eh and TOC : TS ratios, surface sediments of the study area was characterised with a noticeable reducing environment. Under these conditions, the metal contaminants will be strongly partitioned to their sulphide/oxide phases in the sediment–water interface and/or in the suboxic zone. Once buried in the anoxic zone, the metal host phases are stable for long periods of time and these phases are recalcitrant at near-neutral pH. However, oxidation of the reduced sediments by the processes like dredging, bioturbation and other marina activities will increase the dissolved metal concentrations. But the hazard to biota will be mitigated by their sorption to or co-precipitation with oxide substrates.

Organic matter plays a significant role in heavy metal dynamics in the aquatic systems as they are good scavengers of heavy metals. Systems which receive heavy organic load bring in huge amount of heavy metals together with the organic matter from the land. The extent of terrigenous organic matter input can be understood from the sedimentary TAN & LIG concentrations as they are the higher vascular plant constituents. Higher tannin and lignin content found in estuarine sediments against their comparatively lower content in the coastal sediments suggested that the estuary act as a depository of the terrigenous organic matter content which it receives and a little organic matter is reaching to the coastal sediments. Contrary to this observation, total organic matter content of both the provinces was comparable. Hence it could be inferred that the origin of coastal organic matter is mainly marine and not terrestrial. Upwelling phenomena in these coastal area is predominant leading to the deposition of marine organic matter thereby limiting the influence of the terrestrial and estuarine inputs. The predominance of carbohydrates over sedimentary proteins pointed to the faster mineralization of proteinaceous organic matter in the surface sediments and the system behaves as a detrital trap for the accumulation of aged organic matter. Faster utilization/ degradation of proteinaceuos organic matter might have led to the higher C : N ratio found in the coastal sediments, against the lower tannin and lignin contents. Deposition of organic matter in the estuarine sediments suggested the deposition of metals associated with organic matter in the estuary itself. PCA suggested deposition and accumulation of organic matter in the estuary while diagenetic process was active in the coastal area.

Northern and central estuarine area was found to be associated with higher dissolved metal content suggesting the influence of industrial inputs in the Cochin estuarine system. In comparison to the coast, the estuary was found to be associated with higher levels of all the dissolved metals except Pb and Ni. Northern estuary was found to be associated with higher content of all the particulate metals except Ni. Huge inputs of heavy metals in to the Cochin estuary by anthropogenic means, both in the dissolved and particulate forms make the partitioning complex between various phases in the aquatic environment. However, very high levels of Zn, Cd and Pb in the suspended particles of Cochin estuary indicated that in the estuarine environment, the suspended particles play a vital role by acting simultaneously as a source and sink for heavy metals. High partition coefficients observed for all the metals indicated the affinity of these elements to be associated, and transported with the particulate phase in the study area. Increased association of heavy metals to particles at high salinities favour the retention of these metals in the estuary itself. Lower dissolved and higher particulate metal concentrations indicated the significant geochemical contribution of SPM to the distribution of metals between the dissolved and particulate phases. Thus the fate of these metals in the study area is the burial with SPM through sinking to the bottom sediments.

Sedimentary analysis of the metals suggested heavy contamination of the Cochin estuarine and coastal system with the metals especially, Cd followed by Zinc. Estuarine area was associated with higher concentrations of all the metals under study except Mn. Cr and Fe were also contaminating the system in lesser degree compared to other metals. Mn, Cr and Fe showed low contamination in the coastal system throughout the study period. In the coastal environment also, Cd was observed to be the main polluting metal, all other metals showed low to moderate levels of pollution in the coastal area. Higher concentrations of Cd in the entire study area, its significant spatial variations and the lack of temporal variations in its distribution suggested the influence of point sources of Cd operating irrespective of the seasons in the estuary. Zn also showed same behaviour in the estuary, while its behaviour in the coast was different, hence, not posing threat in the coastal environment.

Strong association of the metals under study (except Zn in the estuary and Mn in the coast) with finer fractions of sediment and TOM suggested that the enrichment of heavy metals occurred mostly via direct physical adsorption by the clay minerals or by the organic matter which is mounted on the clay surface. Textural features and other sedimentary variables did not show any significant correlations with Zn in the estuary and Mn in the coast suggesting they did not have an important role in the transport of these metals in the estuary and coast respectively. Significant correlations observed for Fe and Mn with TOM and mud fraction during the study period suggested the significant role of hydrous Fe-Mn oxides and mud (silt & clay) might be playing in controlling the distribution of heavy metals in the estuary. However in the coast, significant negative correlations of Mn with Fe and clay; positive correlation with sand and lack of significant correlations with other metals indicated that the origin, transport or reaction pathway of Mn may be different from that of other metals.

Principal component analysis revealed the anthropogenic influence in the estuary. Association of anthropogenic metals like Cd and Zn - the established contaminants in the Cochin estuary - in the same component throughout the study period pointed to the point source of these metals in the estuary. All other metals under study were associated in a single component indicating a common transport for these metals in the estuary. While in the coastal environment, Mn was the metal which behaved differently from other metals under study. Cluster analysis also attested the observation from the PCA. Clustering of estuarine stations was mainly based on the anthropogenic origin, while that in the coast was mainly based on the granulometric distributions.

Comparison with earlier works indicated chronological enrichment of metals in the study area. Comparison with other polluted global coastal systems also suggested huge heavy metal contamination in the study area. Higher pollution degree found in the northern stations suggested heavy contamination in the northern estuary which is influenced by the discharge of effluents from the northern industrial belt of Cochin. Pollution load index of northern and central estuarine stations suggested heavy contamination in this area. Higher PLI values observed for coastal stations other than the barmouth region also suggested contamination of the coastal environment. Transport of metals from the estuarine environment to the coast was evidenced from the pollution indices as the stations near the bar mouth were associated with high values. Pollution indices suggested that both the systems were enriched with the metals especially Cd, Zn, Pb and Ni and the study area is less enriched with respect to the following metals Cr, Mn and Fe.

Accumulation of heavy metals and other persistent environmental contaminants in the sediments are toxic to organisms especially at elevated concentrations. Toxicity assessment of the sediments using effect based sediment quality guidelines set by NOAA suggested nickel was the only element with concentrations above both the PEL and ERM values and hence to associate with biological effects. Zinc the established metal contaminant in the Cochin estuary was found in higher concentrations than the SQGs suggesting the probability to associate with biological effects in the estuary. However, the toxicity associated with zinc was found to be lower in the coastal sediments. Classifications based on the SQGs, categorised Cochin estuarine sediments in to heavily polluted with Zn and Ni; moderately polluted with Cr and non-polluted with Pb and Cu. Coastal sediments were classified in to heavily polluted with Ni; moderately polluted with Cr and non-polluted with Zn, Pb and Cu. Sum of the toxic units suggested heavy anthropogenic pressure in the northern estuarine stations and in the central coastal stations. Accumulation of the metals was more in coastal stations just south of the bar mouth due to the dumping of dredge spoil from the navigational channel.

This study indicated that Cochin estuary is heavily polluted with respect to the metals under study compared to the coast. Heavy metal status of the Cochin estuary is controlled by anthropogenic inputs from the industrial area. Heavy metal status of the coast is also controlled by the anthropogenic activity i.e. the disposal of the dredge spoil just south of the navigational channel which used to spread around region near Kannammali. Dispersion from the dumping sites might be contributing to the higher metal levels in the coastal sediments and the low concentrations of metals found in the southern end coastal stations suggested rapid dispersal by the coastal currents and rapid removal by the biogenic association are acting strong enough to prevent the long term accumulation of these pollutants in the coastal system. Thus, although the exchange of contaminants occurs from estuary to the coast, the above coastal mechanisms are effective in diluting the effects of metal inputs from the estuary. All these results indicated higher metal levels in the study area and it can be said easily that the Cochin estuarine and coastal system are prone to impacts from human activities which may result in the degradation of the resource in the coming days.

Adsorption analysis revealed the potentiality of the surface sediments to adsorb heavy metals. The percentage of metal ion removal at equilibrium decreased with increase in metal dose even though the sediments have further capacity to absorb more metals. This suggested that the huge addition of metals will mobilize the metals even from the previously adsorbed sites due to competition among the ions and this will be deleterious to the aquatic biota.

Anthropogenic inputs of heavy metals pose a big pollution problem in the study area, especially the Cochin estuarine system. Heavy metals finally sunk to the bottom sediments through its transport path: dissolved, suspended particulate and finally the sediment retaining the treat to the biological life of the system. Also the general partitioning trend of all the heavy metals revealed a net accumulation of them in the bottom sediments over time coupled with biological and geological contribution. Thus, the management and sustenance of this ecosystem warrants monitoring and setting of control over the anthropogenic additions of the contaminants which include point sources such as the discharge of industrial effluents and domestic waste disposal and nonpoint sources such as agricultural discharges at the upper reaches.

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APPENDIX

Appendix 1 Distribution of hydrographic parameters in the surface waters of the study area during pre-monsoon

Station	Temperature, ^{0}C	pH	DO, mg/L	Salinity, ppt	Phosphate, μM/L	Ammonia, μM/L	Nitrite, μM/L	Nitrate, μM/L	Silicate, μM/L	SPM, mg/L	Chlorophyll-a , g/L
E1	29	8.82	5.05	24.44	9.49	5.12	0.74	3.16	39.95	28.00	6.05
E2	29	8.08	8.25	16.01	3.03	5.12	0.18	3.94	78.33	6.60	16.01
E3	29	8.18	6.23	33.29	2.10	1.97	0.11	4.73	30.68	35.80	5.97
E4	29	8.10	5.55	32.44	1.03	20.09	0.15	7.63	12.54	48.50	7.91
E5	30	7.96	5.72	26.97	6.41	7.88	0.61	1.84	72.92	7.50	4.27
E6	30	7.80	5.55	26.54	2.35	22.45	1.16	6.05	28.17	36.50	4.93
E7	30	7.40	5.05	26.54	4.21	12.21	0.42	7.36	20.64	24.00	5.78
E8	30	7.70	5.22	29.91	0.83	26.79	0.26	7.36	8.68	40.20	6.96
E9	29	7.74	5.72	21.91	2.59	4.33	0.29	5.52	38.99	17.50	15.24
E10	28	7.90	7.57	20.65	2.64	4.33	0.07	4.47	10.61	14.10	19.62
E11	28	7.60	5.55	23.17	2.20	16.94	0.28	4.73	12.16	29.80	4.49
E12	28	7.88	5.72	24.44	2.94	7.88	0.53	3.16	35.50	10.90	12.55
E13	30	7.80	6.73	21.07	0.83	15.36	0.22	6.05	36.28	22.60	9.14
E14	28	8.10	5.55	30.76	2.53	4.73	0.29	2.10	3.67	24.00	6.75
E15	29	7.92	5.22	29.49	5.15	16.15	0.37	2.89	7.72	24.80	4.92
E16	29	7.87	4.90	23.59	4.28	30.73	0.50	2.37	12.54	22.50	4.52
C1	30.00	8.16	5.55	33.03	2.06	BDL	0.72	2.37	24.89	38.00	3.46
C2	30.00	8.16	6.06	34.55	2.79	1.18	0.31	3.68	20.45	53.50	5.51
C3	30.00	8.15	6.23	32.02	5.53	0.79	0.83	5.52	14.28	58.20	5.53
C4	30.00	8.16	6.23	31.60	2.06	12.61	0.26	1.58	16.40	9.50	6.82
C5	29.00	8.17	6.06	31.18	1.96	BDL	0.18	2.37	10.42	16.20	7.36
C6	29.00	8.18	6.56	32.44	2.06	8.27	0.22	5.00	4.82	27.00	6.88
C7	28.00	8.25	5.39	33.71	0.44	5.91	0.06	2.37	2.32	23.50	5.97
C8	29.00	8.27	6.40	32.44	2.59	2.36	0.06	2.89	2.32	16.00	7.57
C9	29.00	8.25	6.56	32.44	1.13	1.97	0.06	2.10	15.24	6.80	3.32
C10	28.00	8.23	6.56	32.44	1.42	BDL	0.02	1.84	10.03	15.60	4.43
C11	29.00	8.25	6.56	27.81	1.76	BDL	0.39	1.84	19.68	13.80	7.03

BDL Below Detectable Limits

Appendix 2 Distribution of hydrographic parameters in the bottom waters of the study area during pre-monsoon

Station	Temperature, ^{0}C	pH	DO, mg/L	Salinity, ppt	Phosphate, µM/L	Ammonia, µM/L	Nitrite, µM/L	Nitrate, µM/L	Silicate, µM/L	SPM, mg/L	Chlorophyll-a , g/L
E1	29	8.82	5.05	24.44	9.49	5.12	0.74	3.16	39.95	28.00	6.05
E2	29	8.08	8.25	16.01	3.03	5.12	0.18	3.94	78.33	6.60	16.01
E3	29	8.18	6.23	33.29	2.10	1.97	0.11	4.73	30.68	35.80	5.97
E4	29	8.10	5.55	32.44	1.03	20.09	0.15	7.63	12.54	48.50	7.91
E5	30	7.96	5.72	26.97	6.41	7.88	0.61	1.84	72.92	7.50	4.27
E6	30	7.80	5.55	26.54	2.35	22.45	1.16	6.05	28.17	36.50	4.93
E7	30	7.40	5.05	26.54	4.21	12.21	0.42	7.36	20.64	24.00	5.78
E8	30	7.70	5.22	29.91	0.83	26.79	0.26	7.36	8.68	40.20	6.96
E9	29	7.74	5.72	21.91	2.59	4.33	0.29	5.52	38.99	17.50	15.24
E10	28	7.90	7.57	20.65	2.64	4.33	0.07	4.47	10.61	14.10	19.62
E11	28	7.60	5.55	23.17	2.20	16.94	0.28	4.73	12.16	29.80	4.49
E12	28	7.88	5.72	24.44	2.94	7.88	0.53	3.16	35.50	10.90	12.55
E13	30	7.80	6.73	21.07	0.83	15.36	0.22	6.05	36.28	22.60	9.14
E14	28	8.10	5.55	30.76	2.53	4.73	0.29	2.10	3.67	24.00	6.75
E15	29	7.92	5.22	29.49	5.15	16.15	0.37	2.89	7.72	24.80	4.92
E16	29	7.87	4.90	23.59	4.28	30.73	0.50	2.37	12.54	22.50	4.52
C1	30.00	8.16	5.55	33.03	2.06	BDL	0.72	2.37	24.89	38.00	3.46
C2	30.00	8.16	6.06	34.55	2.79	1.18	0.31	3.68	20.45	53.50	5.51
C3	30.00	8.15	6.23	32.02	5.53	0.79	0.83	5.52	14.28	58.20	5.53
C4	30.00	8.16	6.23	31.60	2.06	12.61	0.26	1.58	16.40	9.50	6.82
C5	29.00	8.17	6.06	31.18	1.96	BDL	0.18	2.37	10.42	16.20	7.36
C6	29.00	8.18	6.56	32.44	2.06	8.27	0.22	5.00	4.82	27.00	6.88
C7	28.00	8.25	5.39	33.71	0.44	5.91	0.06	2.37	2.32	23.50	5.97
C8	29.00	8.27	6.40	32.44	2.59	2.36	0.06	2.89	2.32	16.00	7.57
C9	29.00	8.25	6.56	32.44	1.13	1.97	0.06	2.10	15.24	6.80	3.32
C10	28.00	8.23	6.56	32.44	1.42	BDL	0.02	1.84	10.03	15.60	4.43
C11	29.00	8.25	6.56	27.81	1.76	BDL	0.39	1.84	19.68	13.80	7.03

BDL Below Detectable Limits

Appendix 3 Distribution of hydrographic parameters in the surface waters of the study area during monsoon

Station	Temperature, ^0C	pH	DO, mg/L	Salinity, ppt	Phosphate, μM/L	Ammonia, μM/L	Nitrite, μM/L	Nitrate, μM/L	Silicate, μM/L	SPM, mg/L	Chlorophyll-a , g/L
E1	29	8.82	5.05	24.44	9.49	5.12	0.74	3.16	39.95	28.00	6.05
E2	29	8.08	8.25	16.01	3.03	5.12	0.18	3.94	78.33	6.60	16.01
E3	29	8.18	6.23	33.29	2.10	1.97	0.11	4.73	30.68	35.80	5.97
E4	29	8.10	5.55	32.44	1.03	20.09	0.15	7.63	12.54	48.50	7.91
E5	30	7.96	5.72	26.97	6.41	7.88	0.61	1.84	72.92	7.50	4.27
E6	30	7.80	5.55	26.54	2.35	22.45	1.16	6.05	28.17	36.50	4.93
E7	30	7.40	5.05	26.54	4.21	12.21	0.42	7.36	20.64	24.00	5.78
E8	30	7.70	5.22	29.91	0.83	26.79	0.26	7.36	8.68	40.20	6.96
E9	29	7.74	5.72	21.91	2.59	4.33	0.29	5.52	38.99	17.50	15.24
E10	28	7.90	7.57	20.65	2.64	4.33	0.07	4.47	10.61	14.10	19.62
E11	28	7.60	5.55	23.17	2.20	16.94	0.28	4.73	12.16	29.80	4.49
E12	28	7.88	5.72	24.44	2.94	7.88	0.53	3.16	35.50	10.90	12.55
E13	30	7.80	6.73	21.07	0.83	15.36	0.22	6.05	36.28	22.60	9.14
E14	28	8.10	5.55	30.76	2.53	4.73	0.29	2.10	3.67	24.00	6.75
E15	29	7.92	5.22	29.49	5.15	16.15	0.37	2.89	7.72	24.80	4.92
E16	29	7.87	4.90	23.59	4.28	30.73	0.50	2.37	12.54	22.50	4.52
C1	30.00	8.16	5.55	33.03	2.06	BDL	0.72	2.37	24.89	38.00	3.46
C2	30.00	8.16	6.06	34.55	2.79	1.18	0.31	3.68	20.45	53.50	5.51
C3	30.00	8.15	6.23	32.02	5.53	0.79	0.83	5.52	14.28	58.20	5.53
C4	30.00	8.16	6.23	31.60	2.06	12.61	0.26	1.58	16.40	9.50	6.82
C5	29.00	8.17	6.06	31.18	1.96	BDL	0.18	2.37	10.42	16.20	7.36
C6	29.00	8.18	6.56	32.44	2.06	8.27	0.22	5.00	4.82	27.00	6.88
C7	28.00	8.25	5.39	33.71	0.44	5.91	0.06	2.37	2.32	23.50	5.97
C8	29.00	8.27	6.40	32.44	2.59	2.36	0.06	2.89	2.32	16.00	7.57
C9	29.00	8.25	6.56	32.44	1.13	1.97	0.06	2.10	15.24	6.80	3.32
C10	28.00	8.23	6.56	32.44	1.42	BDL	0.02	1.84	10.03	15.60	4.43
C11	29.00	8.25	6.56	27.81	1.76	BDL	0.39	1.84	19.68	13.80	7.03

BDL Below Detectable Limits

Appendix 4 Distribution of hydrographic parameters in the bottom waters of the study area during monsoon

Station	Temperature, ^{0}C	pH	DO, mg/L	Salinity, ppt	Phosphate, µM/L	Ammonia, µM/L	Nitrite, µM/L	Nitrate, µM/L	Silicate, µM/L	SPM, mg/L	Chlorophyll-a , g/L
E1	29	7.29	5.44	3.33	3.72	0.85	0.85	21.55	0.41	16.30	6.59
E2	29	6.97	4.96	4.99	3.23	0.96	0.96	16.35	1.08	19.20	6.28
E3	26	7.68	2.56	28.69	2.01	0.50	0.50	7.24	0.92	15.80	3.49
E4	28	7.70	5.28	17.05	2.15	0.59	0.59	13.61	0.96	24.60	5.77
E5	30	7.80	7.68	1.91	3.18	1.38	1.38	17.83	1.37	33.00	9.92
E6	28	7.00	4.35	9.56	4.31	0.96	0.96	12.84	0.88	16.00	7.47
E7	28	7.08	3.58	22.04	3.13	0.75	0.75	7.79	0.77	11.60	8.65
E8	30	7.37	4.35	6.32	2.64	0.75	0.75	9.21	1.00	11.50	5.60
E9	27	7.36	2.80	22.87	3.18	0.59	0.59	7.72	0.69	52.30	11.63
E10	29	6.96	6.24	0.69	2.89	0.72	0.72	11.30	1.04	35.90	7.64
E11	29	7.16	6.08	0.50	3.23	0.90	0.90	9.71	1.18	22.30	12.42
E12	31	6.75	4.04	0.83	2.94	0.57	0.57	23.17	0.40	51.80	3.63
E13	30	7.01	5.91	1.91	2.45	0.59	0.59	12.97	0.86	16.40	4.52
E14	29	7.21	6.24	0.32	3.43	1.25	1.25	6.33	1.04	35.10	9.89
E15	32	7.00	4.20	1.33	5.14	0.98	0.98	17.31	0.67	21.10	7.45
E16	29	7.12	6.24	0.26	1.76	0.88	0.88	8.39	0.89	44.80	12.08
C1	28	7.40	3.84	32.42	1.66	0.41	0.41	BDL	0.61	47.00	49.21
C2	28	7.65	4.80	34.79	1.52	0.26	0.26	0.53	0.57	32.40	30.61
C3	28	7.55	4.80	31.63	1.13	0.17	0.17	2.76	0.66	33.20	10.29
C4	28	7.70	4.32	35.58	2.69	0.28	0.28	1.52	0.65	81.20	5.95
C5	28	7.53	3.68	33.21	4.01	0.15	0.15	1.77	0.67	48.60	32.20
C6	28	7.49	2.72	35.58	2.69	0.09	0.09	1.95	1.11	88.80	8.25
C7	28	7.60	3.52	34.00	2.45	0.13	0.13	1.67	0.76	104.30	13.75
C8	29	7.60	4.48	34.00	1.47	0.24	0.24	2.37	0.81	31.30	10.76
C9	29	7.55	4.00	33.21	1.42	0.18	0.18	1.82	0.56	33.70	22.78
C10	29	7.47	2.72	34.00	1.96	0.31	0.31	1.89	0.54	31.80	13.84
C11	29	7.32	3.04	35.58	0.93	0.35	0.35	1.53	0.23	21.90	9.67

BDL Below Detectable Limits

Appendix 5 Distribution of hydrographic parameters in the surface waters of the study area during post-monsoon

Station	Temperature, ^0C	pH	DO, mg/L	Salinity, ppt	Phosphate, μM/L	Ammonia, μM/L	Nitrite, μM/L	Nitrate, μM/L	Silicate, μM/L	SPM, mg/L	Chlorophyll-a , g/L
E1	31	7.80	6.86	4.27	2.10	27.18	0.55	18.34	5.28	6.70	7.81
E2	30	7.90	6.53	1.92	1.57	88.24	0.75	21.94	4.91	7.70	5.10
E3	30	7.90	5.71	7.69	2.59	45.30	0.72	11.54	4.35	5.60	9.82
E4	30	7.80	5.88	7.04	2.35	50.03	0.74	12.90	4.56	5.00	5.48
E5	29	8.30	7.38	14.30	3.43	3.94	0.81	7.86	3.51	12.30	13.71
E6	30	7.90	5.22	13.24	2.15	22.06	0.53	8.98	1.20	9.00	2.62
E7	30	7.80	5.55	6.83	2.45	33.48	0.59	11.92	2.49	6.40	2.39
E8	29	7.80	5.71	9.39	2.94	66.18	0.74	11.24	2.09	9.00	13.89
E9	30	7.70	6.53	3.84	2.20	22.45	0.55	11.87	1.46	16.10	5.89
E10	30	7.40	5.06	5.98	3.28	26.79	0.64	9.93	2.34	11.40	5.27
E11	30	7.40	5.55	2.35	3.28	55.94	0.75	12.97	2.68	19.80	8.70
E12	31	7.80	5.55	2.78	4.50	24.03	0.81	6.00	5.78	32.30	28.04
E13	31	7.50	6.37	2.56	2.40	23.24	0.57	14.12	2.40	16.00	8.84
E14	30	7.00	5.39	4.91	3.62	70.12	1.03	6.99	3.13	16.60	5.57
E15	31	7.60	6.37	3.20	2.64	18.91	0.88	13.65	5.06	12.60	19.59
E16	31	7.50	5.39	4.27	1.81	53.58	0.59	8.97	2.63	10.10	8.59
C1	29	8.20	6.12	35.01	0.73	4.73	0.11	0.88	0.25	15.90	5.76
C2	29	8.20	5.65	33.73	0.49	55.25	0.11	1.49	0.56	13.00	6.89
C3	30	8.20	5.65	32.45	1.13	12.21	0.37	1.96	0.90	12.80	0.00
C4	31	8.20	5.34	30.74	1.03	23.64	0.26	2.39	1.37	10.80	11.06
C5	30	8.20	6.12	34.16	0.93	14.18	0.22	0.28	0.82	15.00	17.49
C6	30	8.20	6.91	34.16	0.20	BDL	BDL	0.34	0.62	9.70	1.70
C7	30	8.30	5.18	35.01	0.20	3.15	BDL	1.03	0.33	9.70	0.71
C8	30	8.30	6.59	34.16	0.49	0.39	BDL	0.95	0.41	8.40	1.40
C9	30	8.30	6.59	35.01	0.44	BDL	0.07	0.19	0.53	8.80	0.95
C10	30	8.30	7.06	34.16	0.49	BDL	0.09	BDL	0.35	10.10	3.23
C11	30	8.20	6.12	34.16	0.39	4.73	0.07	0.31	0.53	8.10	7.07

BDL Below Detectable Limits

Appendix 6 Distribution of hydrographic parameters in the bottom waters of the study area during post-monsoon

Station	Temperature, ^{0}C	pH	DO, mg/L	Salinity, ppt	Phosphate, µM/L	Ammonia, µM/L	Nitrite, µM/L	Nitrate, µM/L	Silicate, µM/L	SPM, mg/L	Chlorophyll-a , g/L
E1	29	7.60	4.41	7.86	3.23	56.73	0.90	14.55	4.74	14.80	4.59
E2	29	7.60	5.06	8.75	2.06	76.82	0.92	10.25	2.58	12.60	6.97
E3	30	8.10	4.57	24.55	2.84	48.85	0.81	2.61	1.77	23.90	5.37
E4	29	8.00	4.41	23.70	2.30	65.39	0.53	3.37	1.79	6.70	3.44
E5	30	8.30	6.59	17.72	12.67	33.88	2.92	3.88	3.79	23.10	11.34
E6	30	7.90	4.90	14.73	3.62	21.27	0.68	8.59	1.87	26.80	5.43
E7	28	8.00	3.43	15.58	2.30	18.91	0.64	4.27	1.23	7.90	1.20
E8	28	8.00	5.39	30.53	1.22	15.36	0.46	1.82	0.82	9.30	3.41
E9	29	7.80	4.08	19.43	2.89	21.67	0.72	6.41	1.49	12.20	1.40
E10	28	7.10	5.22	10.67	3.82	58.70	0.77	8.66	2.16	45.80	3.44
E11	29	7.50	5.39	3.63	2.40	68.94	0.77	11.65	3.08	26.30	8.46
E12	30	7.70	6.04	2.78	6.56	27.97	1.16	6.98	5.71	71.20	20.17
E13	29	7.80	4.08	18.79	2.45	67.76	0.68	6.21	1.55	18.80	2.35
E14	29	7.00	5.39	8.75	5.19	100.80	0.96	6.34	3.59	30.40	4.90
E15	31	7.60	5.06	3.42	3.57	49.64	1.01	12.10	5.29	25.90	16.91
E16	29	7.40	5.22	8.75	3.43	78.39	0.63	6.75	2.53	24.90	5.98
C1	29	8.20	6.28	35.01	1.37	11.03	0.35	1.33	1.15	26.00	2.20
C2	29	8.20	5.49	34.16	0.98	12.61	0.22	1.34	0.70	27.40	4.86
C3	30	8.20	5.34	34.16	1.57	10.24	0.29	0.86	0.86	23.10	11.15
C4	29	8.20	5.65	34.16	1.27	19.70	0.13	0.86	0.61	23.00	3.77
C5	29	8.20	5.49	34.16	4.99	33.88	1.03	BDL	0.82	37.70	9.68
C6	29	8.20	6.59	35.01	0.83	5.91	0.11	0.31	0.57	26.30	3.16
C7	30	8.20	5.49	35.01	1.96	4.33	0.41	0.14	0.88	40.30	3.23
C8	29	8.20	5.65	34.16	4.26	20.48	0.98	BDL	0.98	60.40	1.90
C9	29	8.20	5.97	35.86	0.54	3.55	0.18	0.12	0.57	12.00	1.98
C10	29	8.30	6.28	35.86	0.64	0.79	0.09	0.66	0.75	10.60	3.47
C11	29	8.20	6.28	35.01	0.54	2.76	0.17	0.10	0.58	7.80	2.34

BDL Below Detectable Limits

Appendix 7 Distribution of general sedimentary parameters in the Cochin estuary and its adjacent coast during pre-monsoon

Stations	Temperature, ^{0}C	pH	Eh, mV	Sand %	Silt %	Clay %	TC %	TP %	TN %	TS %
E1	28	6.15	-227	2.53	41.34	56.13	2.55	0.97	0.31	1.08
E2	28	6.99	-253	91.79	0.82	7.39	0.19	0.78	0.02	0.04
E3	28	6.9	-175	89.76	0.52	9.72	0.88	0.61	0.06	0.10
E4	28	6.89	-177	47.27	23.51	29.22	1.90	1.25	0.19	0.54
E5	28	6.75	-232	5.82	53.15	41.03	2.62	0.99	0.27	1.11
E6	28	6.73	-225	0.73	43.42	55.85	2.74	1.00	0.36	1.02
E7	29	6.84	-285	68.61	9.53	21.86	0.45	0.38	0.03	0.20
E8	28	7.51	-240	92.42	0.58	7.00	0.15	0.34	0.00	0.05
E9	28	6.06	-200	63.37	10.53	26.10	0.86	0.64	0.07	0.23
E10	29	7.08	-256	55.70	13.30	31.01	1.55	0.62	0.14	0.53
E11	28	7.05	-103	93.36	0.61	6.02	0.16	0.49	0.03	0.05
E12	28	6.94	-227	3.97	45.16	50.87	2.42	1.02	0.25	1.46
E13	29	6.89	-256	87.42	0.46	12.12	0.29	0.31	0.02	0.23
E14	29	6.97	-130	0.62	53.79	45.59	2.75	1.22	0.30	1.42
E15	28	6.74	-262	2.86	48.18	48.95	2.44	1.38	0.31	0.93
E16	29	7.01	-227	3.93	48.43	47.64	2.60	1.41	0.29	1.10
C1	27	6.73	-227	10.99	39.39	49.62	2.85	0.97	0.34	1.88
C2	27	7.03	-116	63.08	28.82	8.10	0.40	0.54	0.04	0.25
C3	27	7.42	25	92.40	0.59	7.01	0.20	0.41	0.01	0.01
C4	28	6.68	-212	0.44	42.96	56.60	3.05	1.43	0.34	1.68
C5	28	6.57	-194	0.21	38.19	61.60	3.04	1.33	0.35	1.04
C6	27	6.83	-88	39.32	41.48	19.20	1.88	0.79	0.18	0.75
C7	27	6.7	-154	61.45	18.40	20.15	1.12	0.63	0.03	0.83
C8	28	6.83	-199	37.83	37.71	24.45	1.78	0.84	0.19	0.69
C9	28	7.14	-213	57.67	21.10	21.22	2.35	0.50	0.03	0.40
C10	28	6.15	-227	2.53	41.34	56.13	2.55	0.97	0.31	1.08
C11	28	6.99	-253	91.79	0.82	7.39	0.19	0.78	0.02	0.04

Appendix 8 Distribution of general sedimentary parameters in the Cochin estuary and its adjacentcoast during monsoon

Stations	Temperature, ^{0}C	pH	Eh, mV	Sand %	Silt %	Clay %	TC %	TP %	TN %	TS %
E1	28	6.67	-406	30.10	30.71	39.19	1.73	0.95	0.22	0.93
E2	28	6.85	-490	69.69	13.98	16.33	0.51	0.51	0.06	0.29
E3	27	6.45	-183	48.50	23.10	28.40	1.43	0.95	0.15	0.62
E4	28	6.56	-537	44.34	22.45	33.21	1.21	0.89	0.19	0.64
E5	29	6.99	-510	28.91	43.37	27.72	1.26	0.89	0.16	0.64
E6	28	6.87	-90	3.42	50.84	45.74	2.24	1.26	0.36	1.61
E7	28	6.69	-643	11.15	27.71	61.14	1.91	1.54	0.29	1.15
E8	28	6.84	-587	12.03	37.38	50.58	1.98	1.38	0.26	1.14
E9	27	6.87	-491	0.51	56.40	43.09	9.98	1.23	0.25	1.33
E10	28	6.99	-512	52.61	22.99	24.40	1.11	0.61	0.10	0.60
E11	28	6.69	-485	86.55	0.41	13.04	0.23	0.35	0.04	0.02
E12	29	6.99	-396	73.30	8.78	17.92	0.81	0.66	0.06	0.37
E13	29	6.87	-467	8.10	39.34	52.56	2.06	1.60	0.22	1.09
E14	28	7.25	-477	83.92	4.03	12.05	0.48	0.33	0.04	0.23
E15	28	6.99	-520	72.22	8.87	18.90	0.83	0.36	0.12	0.33
E16	28	6.99	-284	47.80	28.74	23.46	2.36	0.71	0.16	0.60
C1	27	6.80	-299	34.57	36.45	28.98	1.46	0.95	0.18	0.93
C2	27	6.90	-284	30.96	45.88	23.16	1.07	0.77	0.07	0.92
C3	28	6.80	-160	52.34	34.93	12.73	0.25	0.39	0.01	0.13
C4	27	7.50	-85	46.14	22.85	31.02	1.44	0.83	0.09	0.42
C5	28	6.50	-407	0.40	31.73	67.87	2.47	1.65	0.36	1.41
C6	28	6.50	-373	0.34	42.45	57.21	2.54	1.32	0.33	1.07
C7	27	6.50	-435	0.54	42.66	56.80	2.56	1.36	0.30	1.19
C8	27	6.80	-299	0.58	34.73	64.69	2.63	1.30	0.38	1.21
C9	28	7.30	-350	4.94	50.17	44.88	2.70	1.17	0.25	1.47
C10	27	6.90	-448	57.85	22.26	19.89	1.10	0.51	0.08	0.36
C11	28	7.10	-304	18.53	45.80	35.68	1.65	0.70	0.21	1.04

Appendix 9 Distribution of general sedimentary parameters in the Cochin estuary and its adjacent coast during post-monsoon

Stations	Temperature, °C	pH	Eh, mV	Sand %	Silt %	Clay %	TC %	TP %	TN %	TS %
E1	30	7.40	-360	9.34	41.67	48.98	2.04	1.00	0.25	1.02
E2	29	7.30	-344	68.27	5.30	26.43	0.90	0.75	0.10	0.46
E3	29	7.80	-194	92.79	0.10	7.10	0.44	0.55	0.02	0.09
E4	30	7.20	-374	43.08	19.38	37.54	1.37	0.79	0.14	0.58
E5	28	7.50	-460	7.97	45.34	46.69	2.39	0.88	0.26	1.42
E6	29	7.20	-360	0.59	60.22	39.20	2.77	0.67	0.32	1.65
E7	29	7.60	-396	3.05	41.84	55.10	2.53	1.04	0.31	1.14
E8	28	7.40	-436	6.86	46.14	47.00	2.53	1.70	0.33	1.00
E9	29	7.60	-407	46.56	17.86	35.59	1.27	0.77	0.17	0.65
E10	28	7.40	-377	69.74	8.39	21.86	0.64	0.39	0.07	0.29
E11	30	7.50	-355	77.79	2.94	19.27	0.32	0.27	0.04	0.06
E12	29	7.60	-407	53.32	10.78	35.90	1.46	0.83	0.18	0.50
E13	29	7.60	-407	9.12	38.36	52.53	2.47	1.20	0.29	0.94
E14	29	6.90	-285	86.66	0.33	13.01	0.24	0.33	0.03	0.02
E15	30	7.40	-372	3.53	62.52	33.95	2.63	0.70	0.32	1.46
E16	29	7.70	-342	92.20	0.31	7.48	0.09	0.18	0.03	0.07
C1	29	7.60	-344	27.55	48.29	24.16	1.05	0.50	0.10	0.62
C2	29	7.40	-383	4.29	56.95	38.75	2.19	1.14	0.24	1.17
C3	29	7.80	-376	71.58	14.42	14.01	0.68	0.36	0.04	0.18
C4	29	7.30	-436	3.88	53.13	43.00	2.23	1.20	0.26	1.76
C5	29	7.10	-428	0.06	45.13	54.81	2.82	1.52	0.37	1.19
C6	30	7.20	-115	0.23	40.42	59.35	2.78	1.47	0.30	1.07
C7	29	7.40	-449	0.27	49.16	50.57	2.86	1.66	0.34	1.12
C8	29	7.40	-450	1.28	44.91	53.80	2.87	1.57	0.31	1.05
C9	30	7.60	-481	26.99	36.80	36.21	1.63	0.74	0.13	0.89
C10	30	7.30	-462	27.65	29.56	42.79	2.13	0.99	0.23	0.61
C11	30	7.50	-489	39.58	31.36	29.07	1.40	0.99	0.15	0.58

Appendix 10 Spatial and seasonal distributions of biochemical components of organic matter in the estuarine and coastal surface sediments

Stations	TOM %			CHO (%)			LPD (%)			PRT (%)			TAN & LIG (%)		
	Pre-M	Mon	Post-M	Pre-M	Mon	Post-M	Pre-M	Mon	Post-M	Pre-M	Mon	Post-M	Pre-M	Mon	Post-M
E1	1.12	2.07	3.27	0.39	0.20	0.32	0.26	0.13	0.19	0.12	0.06	0.03	0.07	0.06	0.10
E2	0.15	0.58	1.01	0.05	0.10	0.23	0.01	0.05	0.07	0.01	0.04	0.02	0.01	0.04	0.08
E3	0.29	1.52	0.19	0.18	0.30	0.07	0.07	0.12	0.03	0.01	0.04	0.01	0.00	0.04	0.01
E4	2.04	1.93	1.70	0.44	0.26	0.30	0.19	0.14	0.10	0.07	0.05	0.06	0.02	0.04	0.03
E5	3.84	1.95	3.38	0.48	0.17	0.37	0.29	0.17	0.15	0.13	0.10	0.08	0.04	0.08	0.09
E6	4.62	3.62	4.30	0.13	0.35	0.41	0.24	0.26	0.22	0.21	0.15	0.11	0.15	0.07	0.05
E7	0.46	3.24	3.79	0.22	0.48	0.29	0.04	0.16	0.20	0.03	0.09	0.09	0.03	0.05	0.06
E8	0.21	3.16	3.82	0.14	0.18	0.48	0.01	0.23	0.14	0.01	0.07	0.06	0.01	0.04	0.09
E9	1.20	3.95	1.58	0.29	0.23	0.28	0.16	0.23	0.08	0.09	0.10	0.03	0.06	0.05	0.03
E10	1.03	1.67	0.71	0.20	0.19	0.13	0.15	0.15	0.05	0.08	0.09	0.02	0.07	0.05	0.05
E11	0.25	0.26	0.35	0.05	0.06	0.04	0.01	0.05	0.04	0.03	0.02	0.01	0.01	0.02	0.02
E12	3.94	1.05	1.84	0.28	0.08	0.22	0.37	0.03	0.09	0.12	0.06	0.04	0.07	0.05	0.07
E13	0.30	3.47	3.44	0.06	0.37	0.50	0.05	0.10	0.13	0.03	0.07	0.09	0.02	0.03	0.13
E14	3.96	0.52	0.25	0.07	0.09	0.03	0.15	0.02	0.04	0.09	0.04	0.01	0.06	0.06	0.02
E15	4.17	1.18	3.67	0.15	0.18	0.29	0.29	0.05	0.13	0.10	0.08	0.13	0.04	0.03	0.13
E16	2.86	1.98	0.10	0.22	0.20	0.01	0.17	0.05	0.01	0.10	0.08	0.01	0.09	0.07	0.04
C1	3.90	1.92	0.89	0.44	0.32	0.24	0.00	0.11	0.07	0.14	0.04	0.02	0.03	0.03	0.02
C2		0.94	3.37		0.08	0.33		0.05	0.14		0.03	0.07		0.02	0.03
C3	0.22	0.16	0.30	0.09	0.06	0.13	0.00	0.02	0.02	0.02	0.01	0.00	0.01	0.01	0.01
C4	0.08	1.52	3.43	0.02	0.26	0.56	0.00	0.11	0.19	0.01	0.06	0.05	0.02	0.03	0.04
C5	5.12	1.73	4.23	0.44	0.38	0.43	0.00016	0.15	0.15	0.14	0.10	0.06	0.03	0.04	0.05
C6	5.13	4.28	4.48	0.43	0.37	0.47	0.00021	0.21	0.21	0.16	0.08	0.06	0.03	0.04	0.04
C7		4.37	4.74		0.32	0.38		0.15	0.20		0.09	0.05		0.04	0.04
C8	2.29	4.50	4.63	0.32	0.23	0.26	0.00016	0.18	0.21	0.07	0.09	0.04	0.02	0.05	0.04
C9	0.87	4.05	1.87	0.23	0.34	0.15	0.00013	0.18	0.08	0.05	0.08	0.02	0.01	0.05	0.03
C10	1.87	0.66	2.77	0.20	0.14	0.33	0.00016	0.08	0.15	0.09	0.03	0.05	0.02	0.02	0.04
C11	0.25	1.98	1.73	0.15	0.30	0.31	0.00006	0.13	0.11	0.01	0.04	0.02	0.01	0.03	0.03

Appendix 11 Distribution of heavy metals in the surface waters of the study area during pre- monsoon

Station	Cd, nM/L	Pb, nM/L	Cr, nM/L	Ni, nM/L	Co, nM/L	Cu, nM/L	Zn, nM/L	Mn, nM/L	Fe, nM/L
E1	19.57	6.03	47.12	122.67	112.42	42.10	142.61	9.10	BDL
E2	21.13	2.41	47.60	137.58	99.26	38.95	164.02	3.19	BDL
E3	19.79	14.48	50.48	127.36	63.21	32.26	21.41	5.92	BDL
E4	20.91	9.65	56.25	141.41	102.66	24.00	20.65	1.37	BDL
E5	21.13	16.89	49.52	149.93	81.02	37.37	50.08	6.37	BDL
E6	20.46	9.65	58.18	145.67	79.75	36.98	96.35	6.37	1172.89
E7	19.13	15.69	55.77	151.21	81.87	57.83	181.99	10.47	2502.46
E8	17.12	20.51	57.22	153.77	66.18	33.44	465.29	8.19	389.47
E9	17.35	21.72	56.74	152.49	93.33	314.34	62.32	2.73	67.15
E10	19.35	21.72	58.18	143.12	87.81	26.36	24.47	BDL	564.06
E11	19.57	21.72	57.70	137.58	109.87	31.47	26.76	11.38	452.14
E12	18.90	12.07	53.37	138.86	89.93	31.87	94.43	3.19	BDL
E13	21.13	12.07	60.10	141.84	74.66	28.72	24.09	2.73	850.57
E14	17.35	13.27	66.83	132.04	92.48	26.36	35.17	9.10	31.34
E15	17.57	26.54	62.99	143.97	125.99	24.39	26.38	10.47	BDL
E16	19.35	8.45	62.99	139.71	109.87	37.77	29.82	10.01	BDL
C1	10.45	1.21	BDL	44.72	2.97	24.39	79.91	2.73	183.54
C2	9.79	BDL	3.85	44.72	2.55	31.47	43.58	9.10	156.68
C3	5.56	10.86	11.54	95.41	10.18	56.26	109.34	10.47	420.81
C4	8.45	12.07	16.83	106.49	BDL	39.34	63.08	25.03	443.19
C5	10.90	BDL	27.41	104.36	BDL	26.75	26.76	3.19	170.11
C6	10.45	8.45	21.64	100.10	BDL	24.00	3452.36	0.91	183.54
C7	15.57	18.10	34.14	114.15	BDL	23.21	19.50	4.10	76.10
C8	15.35	2.41	29.33	97.97	BDL	31.87	38.61	4.10	98.49
C9	16.24	4.83	37.98	120.97	BDL	29.51	60.79	5.01	143.25
C10	14.01	3.62	41.83	120.54	BDL	24.39	26.00	4.10	183.54
C11	16.01	9.65	42.31	125.23	BDL	30.29	160.19	9.10	134.30

BDL Below Detectable Limits

Appendix 12 Distribution of heavy metals in the bottom waters of the study area during pre- monsoon

Station	Cd, nM/L	Pb, nM/L	Cr, nM/L	Ni, nM/L	Co, nM/L	Cu, nM/L	Zn, nM/L	Mn, nM/L	Fe, nM/L
E1	20.91	BDL	50.97	129.49	84.42	55.47	402.58	8.65	BDL
E2	25.35	9.65	46.16	144.39	87.39	71.21	1080.06	7.74	8.95
E3	20.91	BDL	57.22	138.01	101.81	37.37	48.94	5.01	BDL
E4	21.13	10.86	54.81	146.95	53.45	29.11	26.00	3.64	BDL
E5	20.46	9.65	63.95	124.38	75.93	40.52	73.02	5.46	BDL
E6	20.46	4.83	55.77	149.51	95.45	34.62	76.08	8.65	1911.54
E7	18.68	4.83	60.10	156.32	67.45	30.29	62.70	3.64	1168.41
E8	17.79	8.45	56.74	152.06	94.17	27.15	35.94	5.01	1101.26
E9	19.35	19.31	53.85	166.12	91.20	104.26	469.11	2.73	BDL
E10	18.68	20.51	62.50	151.21	72.54	25.57	40.91	10.92	367.09
E11	18.24	2.41	62.02	126.50	105.20	26.36	40.91	12.29	568.54
E12	16.46	12.07	56.74	155.04	95.02	53.50	419.02	6.37	BDL
E13	22.68	7.24	61.54	127.36	95.02	25.18	26.00	13.20	649.12
E14	15.35	3.62	57.70	130.76	75.93	35.41	71.11	13.65	49.24
E15	20.02	BDL	60.10	156.75	96.72	31.87	62.32	10.92	BDL
E16	17.57	12.07	57.22	141.84	82.72	24.79	74.55	6.83	BDL
C1	7.34	BDL	BDL	51.96	14.42	21.64	45.88	6.83	120.87
C2	9.34	BDL	9.14	72.84	7.21	32.65	43.20	6.83	125.35
C3	8.45	1.21	3.85	75.39	BDL	40.13	42.44	2.28	322.32
C4	8.01	3.62	14.90	84.34	BDL	123.53	3430.57	1.37	58.20
C6	12.68	9.65	27.41	128.63	BDL	61.37	128.08	14.56	111.92
C7	16.90	BDL	32.21	91.15	BDL	36.19	63.08	4.55	156.68
C8	14.23	3.62	33.18	122.25	BDL	37.77	86.40	BDL	201.45
C9	14.68	3.62	37.98	104.36	BDL	29.51	52.38	6.83	170.11
C10	20.02	20.51	39.43	138.43	BDL	25.97	44.35	5.01	188.02
C11	15.79	6.03	37.98	152.49	BDL	31.08	116.61	6.83	196.97

BDL Below Detectable Limits

Appendix 13 Distribution of heavy metals in the surface waters of the study area during monsoon

Station	Cd, nM/L	Pb, nM/L	Cr, nM/L	Ni, nM/L	Co, nM/L	Cu, nM/L	Zn, nM/L	Mn, nM/L	Fe, nM/L
E1	BDL	13.27	BDL	48.56	16.12	35.41	176.63	10.47	135.64
E2	BDL	9.65	BDL	46.43	42.42	35.41	546.34	4.10	343.81
E3	0.44	BDL	BDL	41.32	BDL	27.54	92.52	4.10	68.94
E4	BDL	BDL	BDL	BDL	50.06	31.47	43.58	7.28	141.46
E5	BDL	BDL	BDL	BDL	7.21	15.74	77.61	12.29	196.53
E6	BDL	BDL	BDL	BDL	13.15	31.47	51.23	166.55	144.60
E7	BDL	BDL	BDL	55.37	33.09	19.67	5.73	111.03	132.96
E8	BDL	7.24	BDL	BDL	14.42	31.47	BDL	75.54	54.17
E9	BDL	10.86	BDL	BDL	40.30	31.47	74.94	62.80	64.91
E10	BDL	8.45	BDL	BDL	10.61	19.67	BDL	31.40	95.80
E11	BDL	BDL	BDL	11.07	BDL	27.54	231.30	BDL	127.14
E12	BDL	1.21	BDL	BDL	5.51	19.67	BDL	BDL	51.48
E13	BDL	BDL	BDL	BDL	BDL	15.74	BDL	BDL	68.94
E14	BDL	22.92	BDL	BDL	18.24	23.60	BDL	BDL	111.02
E15	BDL	BDL	BDL	20.87	25.03	23.60	BDL	BDL	108.34
E16	BDL	BDL	BDL	BDL	36.48	27.54	BDL	BDL	155.79
C1	5.34	12.07	BDL	55.37	BDL	169.17	141.08	4.10	31.78
C2	6.45	18.10	BDL	50.69	15.70	27.54	43.58	8.19	107.89
C3	BDL	BDL	BDL	66.02	BDL	35.41	64.23	6.37	BDL
C4	BDL	13.27	BDL	73.26	10.61	23.60	41.29	4.10	107.89
C5	BDL	16.89	BDL	27.69	BDL	27.54	32.50	16.84	99.83
C6	BDL	BDL	BDL	48.13	7.21	11.80	BDL	11.83	48.80
C7	0.44	10.86	BDL	74.97	1.70	31.47	43.58	6.37	198.76
C8	BDL	10.86	BDL	66.02	4.67	27.54	72.64	24.12	1216.31
C9	0.22	12.07	BDL	71.56	33.94	23.60	6.50	16.84	168.32
C10	BDL	BDL	BDL	41.32	33.51	27.54	10.71	8.19	115.50
C11	BDL	6.03	BDL	49.41	BDL	23.60	14.15	8.65	107.44

BDL Below Detectable Limits

Appendix 14 Distribution of heavy metals in the bottom waters of the study area during monsoon

Station	Cd, nM/L	Pb, nM/L	Cr, nM/L	Ni, nM/L	Co, nM/L	Cu, nM/L	Zn, nM/L	Mn, nM/L	Fe, nM/L
E1	BDL	4.83	BDL	36.63	27.57	27.54	245.83	16.84	96.25
E2	BDL	BDL	BDL	28.11	42.00	11.80	4.21	5.92	167.88
E3	BDL	BDL	BDL	BDL	41.57	23.60	82.96	7.74	100.28
E4	BDL	1.21	BDL	BDL	36.06	11.80	BDL	13.65	97.59
E5	BDL	2.41	BDL	BDL	11.45	31.47	492.81	169.28	987.11
E6	BDL	BDL	BDL	BDL	6.36	27.54	42.44	96.47	99.38
E7	BDL	BDL	BDL	22.57	17.39	23.60	42.82	125.60	129.38
E8	BDL	BDL	BDL	BDL	7.21	27.54	26.00	72.81	110.57
E9	BDL	BDL	BDL	BDL	18.24	31.47	60.41	68.71	111.92
E10	BDL	18.10	BDL	BDL	5.51	19.67	BDL	13.20	107.44
E11	BDL	8.45	BDL	BDL	34.36	27.54	BDL	BDL	83.27
E12	BDL	BDL	BDL	BDL	22.48	35.41	154.08	BDL	77.89
E13	BDL	6.03	BDL	BDL	32.66	23.60	32.12	BDL	70.73
E14	BDL	7.24	BDL	BDL	BDL	27.54	57.35	BDL	72.97
E15	BDL	BDL	BDL	BDL	9.76	35.41	65.76	BDL	179.51
E16	BDL	BDL	BDL	BDL	23.33	31.47	30.20	1.37	171.46
C1	4.89	15.69	BDL	48.13	31.39	19.67	51.23	10.01	78.79
C2	4.23	27.75	BDL	77.10	9.76	11.80	158.66	4.55	45.66
C3	BDL	12.07	BDL	96.26	BDL	27.54	82.96	12.29	61.78
C4	3.34	14.48	BDL	58.35	20.79	27.54	150.25	7.28	130.27
C5	BDL	15.69	BDL	40.46	4.67	19.67	103.61	9.56	148.63
C6	BDL	7.24	BDL	89.45	15.70	23.60	1.53	10.47	85.06
C7	BDL	4.83	BDL	BDL	8.06	27.54	BDL	9.56	216.67
C8	BDL	7.24	BDL	55.80	BDL	23.60	4.21	6.83	128.03
C9	BDL	BDL	BDL	41.32	987.56	15.74	BDL	232.08	927.57
C10	BDL	BDL	BDL	49.41	19.09	19.67	1.91	2.28	87.74
C11	BDL	21.72	BDL	39.61	42.85	35.41	316.94	7.28	100.73

BDL Below Detectable Limits

Appendix 15 Distribution of heavy metals in the surface waters of the study area during post-monsoon

Station	Cd, nM/L	Pb, nM/L	Cr, nM/L	Ni, nM/L	Co, nM/L	Cu, nM/L	Zn, nM/L	Mn, nM/L	Fe, nM/L
E1	11.79	BDL	BDL	42.17	31.39	8.26	679.77	5.01	42.53
E2	15.79	32.58	BDL	52.82	10.61	10.62	1425.29	4.10	BDL
E3	1.33	BDL	BDL	6.39	19.09	1.97	75.32	5.46	BDL
E4	1.78	8.45	BDL	23.43	22.91	4.72	73.02	9.56	BDL
E5	3.11	8.45	BDL	48.98	77.63	4.72	168.99	2.28	BDL
E6	BDL	BDL	BDL	48.98	90.36	1.97	36.70	10.47	BDL
E7	BDL	8.45	BDL	43.87	56.42	12.20	21.41	6.37	BDL
E8	0.67	BDL	BDL	60.48	25.03	14.95	30.97	10.47	76.10
E9	BDL	8.45	BDL	13.63	45.39	19.67	21.03	6.37	217.12
E10	2.67	2.41	BDL	52.82	5.94	14.95	12.23	10.47	380.97
E11	BDL	7.24	BDL	71.56	17.82	11.80	BDL	12.29	13.43
E12	2.00	BDL	BDL	68.58	10.18	8.26	BDL	8.19	BDL
E13	BDL	3.62	BDL	71.56	50.91	35.41	3.06	5.92	13.43
E14	1.11	20.51	BDL	84.76	30.12	5.51	BDL	10.92	BDL
E15	BDL	BDL	BDL	44.30	75.09	6.29	BDL	3.64	110.57
E16	BDL	19.31	BDL	108.62	48.36	6.29	BDL	5.92	41.63
C1	3.78	BDL	BDL	105.21	BDL	12.20	89.08	2.73	187.57
C2	2.45	4.83	BDL	BDL	BDL	4.72	BDL	3.19	BDL
C3	3.34	BDL	BDL	80.08	BDL	11.80	15.29	3.64	128.48
C4	0.67	13.27	BDL	73.26	BDL	9.05	16.82	4.10	BDL
C5	8.23	13.27	0.48	118.84	BDL	5.90	BDL	1.82	103.41
C6	1.56	6.03	BDL	94.56	58.54	7.08	14.15	5.92	32.68
C7	7.12	14.48	BDL	87.32	69.15	5.51	10.71	6.83	BDL
C8	3.11	20.51	BDL	160.15	37.75	5.90	8.41	2.73	2.69
C9	2.45	10.86	BDL	61.34	51.33	2.75	7.65	1.82	BDL
C10	0.89	13.27	BDL	91.58	9.76	3.93	8.79	6.83	2.69
C11	2.89	BDL	BDL	42.17	25.45	1.57	BDL	4.55	BDL

BDL Below Detectable Limits

Appendix 16 Distribution of heavy metals in the bottom waters of the study area during post-monsoon

Station	Cd, nM/L	Pb, nM/L	Cr, nM/L	Ni, nM/L	Co, nM/L	Cu, nM/L	Zn, nM/L	Mn, nM/L	Fe, nM/L
E1	9.79	16.89	BDL	37.48	BDL	4.72	359.38	2.28	BDL
E2	8.67	4.83	BDL	25.98	18.24	10.23	436.04	6.37	BDL
E3	BDL	BDL	BDL	58.35	44.97	5.11	15.68	2.28	BDL
E4	4.89	BDL	BDL	74.11	44.54	3.93	40.53	15.47	BDL
E5	10.23	BDL	3.37	29.39	72.54	3.93	213.34	10.47	BDL
E6	BDL	BDL	BDL	65.17	36.91	5.90	27.53	6.83	BDL
E7	BDL	24.13	BDL	50.69	50.48	1.18	BDL	7.74	85.06
E8	BDL	BDL	BDL	27.69	42.42	7.08	BDL	5.46	77.00
E9	BDL	2.41	BDL	42.59	43.69	5.90	BDL	2.73	BDL
E10	BDL	9.65	BDL	77.95	36.91	7.47	0.38	12.74	BDL
E11	0.22	16.89	BDL	87.32	16.54	9.84	3.44	5.92	BDL
E12	BDL	2.41	BDL	74.97	2.12	10.23	BDL	6.37	BDL
E13	BDL	BDL	BDL	120.12	57.27	9.84	4.97	10.92	364.85
E14	2.00	BDL	BDL	68.58	52.60	11.02	BDL	8.19	396.19
E15	BDL	13.27	BDL	99.67	49.21	3.54	BDL	4.55	71.63
E16	BDL	1.21	BDL	92.86	35.63	8.26	3.82	1.37	199.66
C1	0.22	9.65	BDL	23.00	BDL	6.29	6.50	4.55	53.72
C2	7.78	13.27	BDL	49.84	BDL	12.20	24.47	13.20	91.77
C3	9.56	4.83	BDL	106.91	3.39	4.72	BDL	25.03	BDL
C4	3.11	BDL	BDL	100.95	20.79	8.66	BDL	13.65	BDL
C5	1.11	9.65	8.17	72.41	41.57	BDL	BDL	0.46	772.23
C6	4.45	2.41	BDL	92.43	30.12	1.97	3.44	12.74	BDL
C7	2.00	3.62	BDL	124.38	35.21	5.11	11.09	6.83	48.80
C8	4.67	25.34	BDL	98.82	47.09	4.33	BDL	10.92	BDL
C9	4.00	12.07	BDL	93.28	24.18	6.69	BDL	3.64	42.53
C10	2.89	36.20	BDL	85.61	28.00	2.75	0.38	8.19	13.43
C11	BDL	1.21	BDL	54.52	40.30	2.36	BDL	7.74	BDL

BDL Below Detectable Limits

Appendix 17 Distribution of heavy metals in the surface particulates of the study area during pre-monsoon

Station	Cd, µM/g	Pb, µM/g	Cr, µM/g	Ni, µM/g	Co, µM/g	Cu, µM/g	Zn, µM/g	Mn, µM/g	Fe, µM/g
E1	0.10	BDL	0.45	BDL	0.53	0.39	1.28	9.87	319.76
E2	0.91	BDL	BDL	BDL	8.74	BDL	0.93	60.67	447.67
E3	0.05	0.30	1.28	BDL	1.67	0.49	0.66	44.92	680.25
E4	BDL	BDL	1.11	0.83	1.35	0.19	0.99	63.07	558.43
E5	0.18	BDL	1.47	BDL	5.54	BDL	BDL	185.06	752.08
E6	0.08	BDL	0.99	2.04	1.99	0.25	0.60	15.10	623.06
E7	0.17	BDL	1.58	3.28	2.17	0.43	0.59	20.10	733.06
E8	BDL	0.27	1.61	0.84	0.78	0.52	1.64	13.24	768.38
E9	BDL	0.28	0.93	1.41	0.36	11.85	0.11	18.15	813.48
E10	BDL	BDL	0.92	BDL	3.73	BDL	BDL	16.04	288.92
E11	BDL	BDL	1.44	0.06	1.72	0.22	0.76	19.61	597.89
E12	0.14	0.44	2.82	0.04	3.89	0.47	0.04	8.60	217.67
E13	BDL	BDL	1.55	BDL	0.81	0.21	0.98	27.71	586.33
E14	0.01	BDL	1.86	2.04	1.11	0.10	0.41	6.22	650.98
E15	0.16	BDL	0.72	1.25	1.27	BDL	0.45	5.72	490.99
E16	0.02	BDL	0.79	BDL	3.17	BDL	BDL	9.47	499.40
C1	0.01	BDL	1.34	0.63	2.02	0.08	0.59	10.95	404.08
C2	0.05	BDL	1.78	0.73	0.90	0.18	0.99	6.46	527.16
C3	0.07	BDL	1.88	0.54	1.07	0.30	1.66	6.62	621.50
C4	0.28	BDL	0.25	BDL	5.22	BDL	5.11	9.01	598.46
C5	0.12	0.45	0.71	3.81	2.67	2.53	BDL	11.60	486.35
C6	0.12	0.22	0.12	BDL	1.78	BDL	BDL	10.89	315.03
C7	BDL	BDL	0.23	0.42	1.55	0.15	0.65	16.48	354.32
C8	BDL	BDL	0.84	2.88	3.05	BDL	0.36	9.84	442.07
C9	0.33	1.60	0.57	1.00	3.18	BDL	BDL	13.12	256.75
C10	BDL	BDL	0.09	BDL	2.58	BDL	BDL	2.01	132.00
C11	0.15	BDL	0.52	BDL	3.10	0.17	8.92	2.93	201.13

BDL Below Detectable Limits

Appendix 18 Distribution of heavy metals in the bottom particulates of the study area during pre-monsoon

Station	Cd, µM/g	Pb, µM/g	Cr, µM/g	Ni, µM/g	Co, µM/g	Cu, µM/g	Zn, µM/g	Mn, µM/g	Fe, µM/g
E1	0.06	0.05	0.56	0.26	1.86	1.54	4.18	13.87	566.79
E2	7.23	18.10	3.61	BDL	194.08	13.77	201.67	924.91	8058.02
E3	0.01	0.15	1.91	0.43	1.15	0.61	1.54	9.10	624.78
E4	0.03	0.17	0.88	0.11	0.92	0.36	1.10	29.48	419.49
E5	0.16	BDL	2.36	1.06	1.73	1.38	2.64	57.48	744.93
E6	BDL	0.28	1.92	1.64	0.48	0.44	1.42	8.87	745.29
E7	0.02	BDL	1.94	2.03	0.84	0.48	3.32	15.24	823.39
E8	BDL	0.24	1.75	1.16	0.51	0.42	1.66	10.72	640.61
E9	0.05	0.22	1.99	0.27	1.57	2.60	5.80	17.40	825.65
E10	0.09	0.23	1.32	0.26	2.26	0.27	1.19	13.19	652.99
E11	0.27	0.19	2.26	0.46	1.62	0.35	1.82	16.20	760.52
E12	0.04	0.31	2.51	0.96	0.74	0.77	5.39	9.43	695.01
E13	0.12	0.45	2.33	0.87	1.01	0.27	1.33	18.75	692.36
E14	0.06	BDL	1.62	0.71	0.90	0.40	2.56	5.69	588.65
E15	0.01	BDL	2.10	0.99	1.04	0.38	2.04	6.54	649.86
E16	0.05	BDL	2.60	0.74	3.65	0.45	1.90	15.59	585.56
C1	0.04	BDL	2.84	1.64	0.79	0.53	2.22	9.63	624.18
C2	0.08	BDL	2.22	1.19	0.81	0.58	1.81	10.33	558.05
C3	0.02	0.12	2.91	0.69	0.53	1.01	3.18	11.17	707.12
C4	BDL	1.31	0.64	1.09	2.90	0.41	45.43	6.59	588.80
C6	BDL	BDL	3.29	1.50	0.71	0.91	2.83	11.32	738.46
C7	0.05	0.21	1.71	BDL	0.76	0.89	3.01	6.99	758.31
C8	0.09	BDL	1.96	2.04	1.74	1.05	4.07	6.94	639.25
C9	0.33	0.74	2.99	1.35	2.42	0.55	3.76	14.21	816.80
C10	0.12	1.62	0.45	BDL	2.31	BDL	1.30	1.54	143.99
C11	0.06	0.65	5.16	0.96	0.59	1.26	6.34	13.38	654.68

BDL Below Detectable Limits

Appendix 19 Distribution of heavy metals in the surface particulates of the study area during monsoon

Station	Cd, µM/g	Pb, µM/g	Cr, µM/g	Ni, µM/g	Co, µM/g	Cu, µM/g	Zn, µM/g	Mn, µM/g	Fe, µM/g
E1	BDL	0.49	23.29	BDL	0.43	0.60	2.57	2.67	133.17
E2	0.15	1.91	38.50	BDL	1.13	0.66	6.88	11.57	161.91
E3	BDL	BDL	36.33	BDL	BDL	0.34	0.57	6.01	84.86
E4	BDL	0.30	36.14	BDL	BDL	0.66	1.85	6.11	155.19
E5	0.52	0.65	28.38	BDL	BDL	BDL	1.09	5.53	61.55
E6	BDL	0.08	25.58	BDL	BDL	0.26	3.34	8.13	128.33
E7	BDL	2.41	96.48	BDL	BDL	1.31	BDL	18.20	428.27
E8	BDL	1.41	57.62	BDL	BDL	1.31	3.25	12.97	242.49
E9	BDL	0.27	BDL	0.49	0.43	0.74	2.77	15.62	82.39
E10	BDL	0.27	BDL	BDL	BDL	0.89	3.18	17.27	755.13
E11	BDL	0.20	BDL	BDL	1.18	0.66	2.52	14.80	632.78
E12	BDL	0.59	BDL	BDL	0.39	0.58	3.42	12.16	400.93
E13	BDL	BDL	BDL	BDL	4.12	1.82	4.14	100.87	1538.65
E14	0.32	0.80	BDL	BDL	1.58	0.87	3.32	15.85	822.24
E15	BDL	0.49	BDL	BDL	BDL	0.45	2.67	19.25	866.09
E16	BDL	BDL	BDL	BDL	0.34	0.40	2.90	12.42	618.19
C1	0.46	BDL	BDL	BDL	BDL	1.56	5.04	16.97	275.35
C2	BDL	BDL	BDL	BDL	0.48	0.79	1.44	10.17	168.25
C3	0.81	0.96	11.32	BDL	BDL	0.70	2.13	17.24	212.35
C4	BDL	0.16	10.57	BDL	1.93	0.26	0.60	5.48	77.75
C5	BDL	BDL	14.73	BDL	0.71	0.31	0.24	6.73	154.00
C6	BDL	1.13	17.65	BDL	1.19	0.61	0.39	8.18	112.62
C7	BDL	BDL	18.26	BDL	BDL	0.82	1.04	7.81	105.70
C8	0.41	BDL	17.82	0.85	BDL	0.58	1.41	5.55	74.39
C9	BDL	0.45	17.17	0.96	0.03	BDL	0.57	6.19	38.37
C10	0.32	BDL	17.60	BDL	BDL	BDL	0.69	5.63	46.18
C11	BDL	BDL	22.90	BDL	0.37	0.35	0.60	5.43	48.30

BDL Below Detectable Limits

Appendix 20 Distribution of heavy metals in the bottom particulates of the study area during monsoon

Station	Cd, μM/g	Pb, μM/g	Cr, μM/g	Ni, μM/g	Co, μM/g	Cu, μM/g	Zn, μM/g	Mn, μM/g	Fe, μM/g
E1	BDL	0.37	36.02	BDL	1.90	0.24	3.19	3.85	256.24
E2	0.16	0.94	19.48	BDL	0.02	0.41	3.13	5.47	242.02
E3	0.45	0.23	24.59	BDL	1.83	BDL	BDL	0.89	22.67
E4	0.10	0.29	18.20	BDL	BDL	BDL	0.47	2.94	287.34
E5	0.15	0.59	17.28	BDL	0.71	1.19	12.66	10.59	90.08
E6	BDL	0.68	22.30	BDL	0.24	0.25	1.70	5.40	113.04
E7	0.31	0.10	24.99	2.57	BDL	BDL	2.37	3.61	71.78
E8	BDL	0.42	18.06	BDL	1.59	9.24	1.36	6.49	101.99
E9	BDL	0.46	BDL	1.72	0.92	0.68	2.99	11.62	8.73
E10	0.10	0.37	BDL	BDL	BDL	0.99	3.23	12.82	12.59
E11	0.06	1.08	BDL	BDL	BDL	0.88	2.98	13.24	675.52
E12	BDL	0.21	BDL	BDL	1.15	0.53	3.20	9.81	153.14
E13	BDL	0.88	BDL	BDL	2.72	1.20	2.77	15.09	676.96
E14	BDL	0.41	BDL	2.48	0.91	0.78	3.89	12.96	12.63
E15	BDL	0.74	BDL	BDL	BDL	0.56	2.74	9.94	655.80
E16	BDL	0.54	BDL	BDL	1.35	1.05	3.65	9.84	2.90
C1	0.11	0.90	BDL	0.14	0.19	0.50	1.55	5.13	494.24
C2	0.08	0.74	4.44	BDL	1.13	0.49	0.99	4.99	410.36
C3	BDL	0.15	6.92	BDL	1.19	0.36	1.58	3.99	471.40
C4	BDL	0.43	3.64	0.48	1.26	0.53	2.84	4.47	76.30
C5	0.08	0.47	4.77	BDL	1.05	0.40	1.28	2.91	416.72
C6	BDL	0.34	3.70	0.52	0.25	0.35	1.42	3.05	36.05
C7	0.02	0.17	3.17	0.45	0.49	0.34	0.88	2.16	17.64
C8	0.27	0.39	9.14	BDL	0.60	0.63	1.15	3.95	398.90
C9	0.18	0.39	7.05	0.21	0.15	0.47	1.33	4.36	494.29
C10	BDL	0.46	11.14	0.75	0.21	0.37	1.07	4.64	448.37
C11	BDL	0.39	13.44	BDL	0.31	0.18	0.59	4.97	356.91

BDL Below Detectable Limits

Appendix 21 Distribution of heavy metals in the surface particulates of the study area during post-monsoon

Station	Cd, µM/g	Pb, µM/g	Cr, µM/g	Ni, µM/g	Co, µM/g	Cu, µM/g	Zn, µM/g	Mn, µM/g	Fe, µM/g
E1	0.30	6.48	10.98	BDL	4.88	0.29	33.27	105.55	1135.87
E2	0.98	4.23	5.68	BDL	0.88	1.07	35.85	63.47	780.22
E3	BDL	8.62	9.87	BDL	2.20	1.41	BDL	38.11	682.69
E4	BDL	12.07	11.54	BDL	9.76	1.34	68.59	28.49	733.28
E5	BDL	5.10	2.11	BDL	1.83	BDL	4.13	22.64	529.56
E6	0.32	6.30	3.79	BDL	4.15	0.13	BDL	35.55	499.90
E7	0.17	2.45	9.09	BDL	4.97	0.37	BDL	32.14	537.90
E8	BDL	3.89	6.04	5.40	2.64	0.79	1.40	44.14	887.87
E9	0.03	3.97	4.03	3.57	2.24	1.37	3.30	82.19	1482.86
E10	BDL	3.70	1.73	3.51	1.97	0.21	2.58	33.29	1425.08
E11	0.17	2.38	12.46	8.26	2.01	1.69	2.59	26.61	1407.67
E12	BDL	1.16	3.14	3.07	0.66	0.73	3.59	15.37	39.78
E13	BDL	2.34	3.49	4.31	1.88	3.29	3.20	163.05	1517.03
E14	0.28	2.76	8.81	3.87	1.33	0.45	1.77	69.09	70.12
E15	BDL	3.93	6.64	BDL	3.91	0.09	2.67	48.76	79.94
E16	0.07	5.50	9.66	BDL	4.70	0.43	2.20	61.50	88.20
C1	BDL	1.97	15.72	BDL	2.21	0.72	1.78	15.34	265.79
C2	BDL	1.95	10.80	BDL	1.24	0.91	1.09	12.43	249.66
C3	BDL	1.51	6.39	2.46	2.15	0.28	0.81	17.56	229.08
C4	BDL	2.57	2.58	2.48	4.56	0.33	0.11	9.06	194.82
C5	BDL	1.69	4.90	2.56	2.40	1.00	2.14	4.64	367.39
C6	BDL	2.99	5.30	2.28	6.39	0.04	0.04	0.89	BDL
C7	BDL	3.98	13.23	8.52	3.94	2.19	BDL	3.10	13.85
C8	BDL	1.87	29.71	8.21	5.05	BDL	BDL	4.93	3122.48
C9	BDL	6.03	7.70	BDL	5.06	BDL	BDL	0.21	1258.56
C10	0.20	5.02	9.81	BDL	5.71	0.51	1.29	1.31	1733.94
C11	BDL	2.68	BDL	2.79	2.78	BDL	0.47	10.28	182.38

BDL Below Detectable Limits

Appendix 22 Distribution of heavy metals in the bottom particulates of the study area during post-monsoon

Station	Cd, μM/g	Pb, μM/g	Cr, μM/g	Ni, μM/g	Co, μM/g	Cu, μM/g	Zn, μM/g	Mn, μM/g	Fe, μM/g
E1	BDL	2.36	10.23	2.85	1.83	0.16	10.41	45.84	1035.08
E2	0.16	4.79	8.62	0.00	1.28	0.34	17.23	44.39	757.48
E3	0.08	1.92	5.11	0.77	1.01	0.26	1.60	12.68	899.27
E4	BDL	5.76	BDL	BDL	7.60	BDL	BDL	0.48	1636.99
E5	BDL	1.78	2.29	BDL	0.94	0.07	3.86	6.42	798.83
E6	BDL	2.03	5.31	1.62	2.69	0.43	2.55	18.42	909.87
E7	BDL	4.12	5.05	BDL	1.99	BDL	BDL	3.86	97.47
E8	0.41	3.11	16.44	2.93	2.96	BDL	BDL	7.39	85.20
E9	BDL	3.16	5.99	6.84	1.70	0.71	3.01	91.79	1119.54
E10	0.01	1.19	5.14	2.07	0.62	0.52	1.87	17.89	53.66
E11	BDL	2.11	5.47	3.55	1.00	0.61	2.47	21.92	78.81
E12	0.20	1.10	10.13	7.24	1.25	0.60	2.81	8.68	134.68
E13	BDL	2.89	2.30	3.40	BDL	0.59	2.26	19.78	1180.60
E14	0.01	2.10	5.46	0.99	1.47	0.58	2.01	19.44	61.55
E15	0.03	2.10	7.78	2.11	4.36	0.73	2.54	26.28	34.05
E16	0.14	1.36	14.91	4.12	1.38	0.62	2.26	22.76	77.31
C1	0.12	1.07	3.05	BDL	1.35	0.48	1.50	5.02	559.76
C2	0.05	0.92	9.04	1.69	1.75	0.46	1.16	9.18	611.21
C3	0.01	2.30	5.12	4.19	1.27	1.14	1.26	6.58	569.18
C4	0.01	1.63	3.64	BDL	0.52	0.12	0.81	4.27	562.31
C5	0.02	0.74	4.67	2.47	1.01	0.28	1.01	4.67	642.53
C6	0.03	2.11	5.59	3.04	2.24	0.28	0.19	2.02	374.13
C7	BDL	1.17	5.17	2.30	1.27	0.23	0.71	4.00	406.79
C8	BDL	0.82	5.22	2.37	1.39	0.60	1.25	3.59	17.20
C9	BDL	2.21	7.57	BDL	2.26	0.13	0.00	1.78	214.88
C10	BDL	2.16	10.98	BDL	2.12	0.00	0.04	1.20	55.75
C11	BDL	5.10	2.90	BDL	3.86	1.21	BDL	BDL	74.61

BDL Below Detectable Limits

Appendix 23 Concentrations of sedimentary heavy metals in the study area during pre-monsoon

Station	Cd, mg/kg	Pb, mg/kg	Cr, mg/kg	Ni, mg/kg	Co, mg/kg	Cu, mg/kg	Zn, mg/kg	Mn, mg/kg	Fe, %
E1	9.39	48.8	34.56	149.15	35.36	40.84	1229.83	222.36	4.27
E2	1.73	8.13	10.53	49.1	9.77	9.11	110.32	83.78	0.71
E3	1.01	11.4	12.99	68.9	14.19	9.93	34.04	95.67	0.89
E4	1.39	25.62	53.21	146.77	27.14	21.12	81.84	158.71	3.1
E5	6.21	41.87	36.96	181.46	32.33	35.84	720.09	282.4	4.15
E6	2.97	41.92	37.48	208.83	36.6	35.68	134.23	295.16	5.06
E7	0.7	11.22	23.38	93.97	14.66	11.76	32.4	114.41	1.46
E8	0.26	5.63	21.92	75.12	7.93	6.04	11.42	76.27	0.59
E9	0.75	19.44	22.91	119.64	16.35	16.2	47.86	114.66	2.1
E10	1.99	27.92	22.41	148.31	24.63	22.33	71.04	154.79	3.03
E11	0.25	7.63	13.06	96.05	9.79	8.71	14.27	97.71	0.85
E12	2.89	43.16	40.22	204.84	33.88	32.76	114.77	235.03	4.26
E13	0.6	10.44	17.47	76.43	10.71	8.21	17.74	94.33	1.05
E14	2.75	45.7	40.63	200.8	34.49	38.31	145.6	268.73	4.54
E15	3.13	42.74	48.29	177.44	33.2	31.88	125.99	334.49	4.71
E16	2.62	39.98	124.85	158.44	34.72	33.79	112.78	269.74	4.58
C1	2.47	38.46	31.69	76.67	31.82	27.07	83.17	213.54	3.58
C3	0.65	12.91	19.79	32.03	17.73	7.2	29.29	256.21	0.16
C4	0.29	3.75	5.5	24.86	6.07	5.02	9.62	92.2	0.35
C5	3.15	41.38	49.41	114.97	34.66	28.34	89.69	172.7	3.59
C6	2.86	40.51	71.72	129.47	30.84	27.26	87.23	162.77	2.37
C8	2.97	31.9	32.68	108.67	28.79	18.05	70.54	277.17	2.97
C9	1.46	21.83	23.64	110.86	24.03	11.93	50.1	280.75	1.9
C10	2.05	27.45	32.76	94.56	29.12	15.99	50.15	255.74	2.89
C11	1.47	13.71	17.42	117.9	19.32	7.75	31.9	268.44	1.92

Appendix 24 Concentrations of sedimentary heavy metals in the study area during monsoon

Station	Cd, mg/kg	Pb, mg/kg	Cr, mg/kg	Ni, mg/kg	Co, mg/kg	Cu, mg/kg	Zn, mg/kg	Mn, mg/kg	Fe, %
E1	5.93	36.6	60.08	137.2	30.13	31.75	1043.08	250.25	3.57
E2	2.56	16.03	45.24	83.83	18.74	15.78	221.15	169.13	1.59
E3	1.75	20.73	31.59	129.87	26.42	19.33	78.92	208.54	2.57
E4	1.56	27.81	34.26	132.82	28.55	22.47	91.86	211.27	2.62
E5	5.01	29.02	31.13	142.61	33.04	28.92	902.53	266.62	4.96
E6	3.05	46.67	39.97	152.18	31.13	40.12	185.95	277.81	4.35
E7	2.2	42.98	39.38	138.09	35.92	33.37	121.54	283.1	4.4
E8	1.94	36.53	68.29	146.62	33	31.49	88.97	309.39	3.95
E9	2.28	39.97	38.06	141.76	34.41	33.42	124.38	307.6	4.99
E10	1.62	22.18	32.28	120.64	22.31	21.09	77.27	207.88	2.85
E11	0.6	8.16	6.86	41.81	8.99	5.93	14.32	117.59	0.83
E12	0.82	15.81	16.49	64.75	16.69	16.03	46.11	142.64	2.02
E13	1.92	40.09	55.13	136.7	33.99	30.55	99.6	284.11	4.31
E14	0.48	9.97	9.23	59.67	13.26	9.36	28.26	145.11	1.39
E15	0.83	17.96	11.14	65.7	13.84	16	47.9	148.54	1.91
E16	1.16	24.43	27.3	87.12	24.14	20.76	72.06	279.62	2.89
C1	2.14	33.05	60.04	90.71	27.71	22.32	67.1	279.32	3.29
C2	1.15	26.64	56.55	88.4	27.99	18.97	53.78	236.3	2.66
C3	1.09	16.92	31.42	78.36	23.91	10.47	37.56	343.28	2.07
C4	1.87	26.37	70.17	102.49	26.02	21.44	65.92	178.86	2.57
C5	2.37	41.71	67.96	126.37	35.16	32.32	114.39	241.26	3.69
C6	2.06	41.29	57.74	142.79	32.86	29	94.53	187.81	3.61
C7	2.58	41.21	55.26	145.48	36.07	30.19	97.57	216.73	3.82
C8	2.42	39.13	52.27	139.33	34.87	29.56	90.23	189.43	3.74
C9	2.84	39.67	46.98	134.98	34.16	28.17	95.81	205.84	3.38
C10	1.57	36.35	32.3	120.52	27.91	13.5	55.78	427.04	2.91
C11	1.52	38.6	40.31	115.79	32.92	21.17	70.47	361.8	3.27

Appendix 25 Concentrations of sedimentary heavy metals in the study area during post-monsoon

Station	Cd, mg/kg	Pb, mg/kg	Cr, mg/kg	Ni, mg/kg	Co, mg/kg	Cu, mg/kg	Zn, mg/kg	Mn, mg/kg	Fe, %
E1	6.41	45.66	45.06	130.49	34.76	35.78	633.48	232.53	4.05
E2	4.47	20.98	152.77	67.43	22.05	19.68	709.04	184.32	2.59
E3	0.02	8.97	37.96	34.05	8.55	5.1	19.6	63.46	0.61
E4	2.9	28.22	70.1	96.15	25.92	21.38	168.58	233.02	2.94
E5	4.17	38.71	71.08	133.37	32.29	35.79	783.97	273.73	3.67
E6	2.75	48.2	74.78	119.63	31.04	42.88	203.3	267.98	3.55
E7	1.85	43.16	65.74	127.25	33.48	33.58	129.24	277.69	4.45
E8	2.12	40.46	192.36	169.33	36.51	39.24	113.14	278.47	5.23
E9	1.3	24.73	48.98	78.92	25.5	22.23	64.44	228.77	2.57
E10	0.62	15.87	39.56	49.36	16.07	19.27	42.91	151.04	1.79
E11	BDL	10.68	37.98	42.2	12.41	9.36	23.83	122.14	1.27
E12	1.07	26.2	47.95	47.41	22.26	24.48	73.35	195.86	3.15
E13	1.6	38.5	64	103.75	35.08	33.63	117	266	4.45
E14	0.03	7.99	49.02	25.97	10.09	8.99	55.59	91.54	0.94
E15	2.24	36.32	64.1	97.01	32.76	34.3	124.88	237.56	3.86
E16	BDL	4.97	31.97	11.92	6.08	7.28	7.28	74.01	0.49
C1	1.4	27.94	61.3	58.63	28.74	18.24	55.64	386.98	3.07
C2	2.84	39.92	60	91.07	33.68	28.99	85.33	231.79	3.82
C3	0.84	14.17	30.32	32.31	19.83	10.88	45.48	193.34	1.56
C4	1.69	37.39	65.1	93.97	31.61	26.92	97.21	205.13	2.98
C5	2.59	42.17	109.88	131.24	33.91	30.69	103.79	208.08	3.93
C6	1.82	42.29	68.41	129.35	35.07	29.28	87.06	168.91	3.79
C7	2.04	41.63	82.13	133.35	31.95	26.92	80.01	159.27	3.64
C8	2.62	38.67	66.82	123.75	32.91	27.57	77.84	165.92	3.71
C9	1.35	31.44	61	81.34	28.37	20.03	67.61	271.21	2.77
C10	1.72	29.13	45.44	79.43	30.98	18.13	58.52	233.81	2.66
C11	0.9	24.75	59.85	76	24.35	15.23	46.75	192.75	2.29

BDL Below Detectable Limits

Appendix 26 Enrichment factors of metals in the study area during pre-monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn
E1	95.05	3.34	0.28	2.70	1.49	1.65	19.16	0.31
E2	105.09	3.35	0.51	5.34	2.48	2.22	10.34	0.71
E3	49.16	3.76	0.50	6.00	2.88	1.94	2.55	0.65
E4	19.43	2.41	0.59	3.66	1.58	1.18	1.76	0.31
E5	64.61	2.95	0.31	3.37	1.40	1.49	11.53	0.41
E6	25.35	2.42	0.25	3.18	1.30	1.22	1.76	0.35
E7	20.59	2.24	0.55	4.95	1.80	1.39	1.47	0.47
E8	19.42	2.79	1.28	9.84	2.42	1.77	1.29	0.78
E9	15.41	2.71	0.37	4.40	1.40	1.34	1.52	0.33
E10	28.40	2.69	0.25	3.77	1.46	1.27	1.56	0.31
E11	12.64	2.62	0.53	8.72	2.07	1.77	1.12	0.69
E12	29.35	2.96	0.32	3.71	1.43	1.33	1.79	0.33
E13	24.63	2.91	0.57	5.63	1.84	1.35	1.13	0.54
E14	26.13	2.94	0.31	3.41	1.37	1.46	2.13	0.36
E15	28.75	2.65	0.35	2.91	1.27	1.17	1.78	0.43
E16	24.65	2.55	0.93	2.67	1.36	1.27	1.64	0.36
C1	29.86	3.14	0.30	1.65	1.60	1.31	1.54	0.36
C3	169.28	22.88	4.12	15.00	19.37	7.55	11.82	9.38
C4	35.81	3.16	0.54	5.53	3.15	2.50	1.84	1.60
C5	37.84	3.36	0.47	2.47	1.74	1.36	1.66	0.29
C6	52.02	4.98	1.04	4.21	2.34	1.98	2.44	0.41
C8	43.20	3.14	0.38	2.83	1.75	1.05	1.58	0.56
C9	33.27	3.35	0.43	4.50	2.28	1.09	1.75	0.89
C10	30.60	2.77	0.39	2.53	1.81	0.96	1.15	0.53
C11	33.08	2.08	0.31	4.74	1.81	0.70	1.10	0.84

Appendix 27 Enrichment factors of metals in the study area during monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn
E1	71.65	2.99	0.58	2.96	1.52	1.54	19.40	0.42
E2	69.71	2.94	0.98	4.07	2.12	1.72	9.25	0.64
E3	29.41	2.35	0.42	3.89	1.85	1.30	2.04	0.49
E4	25.75	3.09	0.45	3.90	1.96	1.48	2.33	0.49
E5	43.62	1.71	0.22	2.22	1.20	1.01	12.09	0.32
E6	30.32	3.13	0.31	2.70	1.29	1.59	2.84	0.39
E7	21.59	2.85	0.31	2.42	1.47	1.31	1.84	0.39
E8	21.22	2.70	0.59	2.87	1.51	1.38	1.50	0.47
E9	19.78	2.34	0.26	2.19	1.24	1.16	1.66	0.37
E10	24.56	2.27	0.39	3.27	1.41	1.28	1.80	0.44
E11	31.32	2.88	0.28	3.90	1.96	1.24	1.15	0.86
E12	17.47	2.29	0.28	2.48	1.49	1.37	1.52	0.43
E13	19.23	2.72	0.44	2.45	1.42	1.23	1.54	0.40
E14	14.93	2.09	0.23	3.30	1.71	1.16	1.35	0.63
E15	18.85	2.75	0.20	2.66	1.31	1.45	1.67	0.47
E16	17.32	2.47	0.32	2.32	1.50	1.24	1.66	0.58
C1	28.04	2.93	0.63	2.13	1.51	1.17	1.35	0.51
C2	18.58	2.92	0.73	2.56	1.89	1.23	1.34	0.54
C3	22.83	2.38	0.52	2.92	2.08	0.87	1.21	1.00
C4	31.36	3.00	0.94	3.08	1.82	1.44	1.70	0.42
C5	27.80	3.30	0.63	2.64	1.72	1.51	2.06	0.39
C6	24.69	3.34	0.55	3.05	1.64	1.39	1.74	0.31
C7	29.23	3.15	0.50	2.94	1.70	1.37	1.70	0.34
C8	27.93	3.05	0.48	2.87	1.68	1.37	1.60	0.31
C9	36.32	3.42	0.48	3.08	1.82	1.44	1.88	0.37
C10	23.32	3.65	0.38	3.20	1.73	0.80	1.28	0.89
C11	20.09	3.45	0.42	2.73	1.81	1.12	1.43	0.67

Appendix 28 Enrichment factors of metals in the study area during post-monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn
E1	68.45	3.29	0.38	2.49	1.55	1.53	10.40	0.35
E2	74.50	2.36	2.02	2.01	1.53	1.31	18.18	0.43
E3	1.17	4.27	2.12	4.28	2.51	1.44	2.12	0.62
E4	42.61	2.80	0.82	2.53	1.59	1.26	3.81	0.48
E5	49.08	3.08	0.66	2.80	1.58	1.68	14.19	0.45
E6	33.43	3.96	0.72	2.60	1.57	2.09	3.81	0.46
E7	17.91	2.83	0.51	2.20	1.35	1.30	1.93	0.38
E8	17.52	2.26	1.26	2.50	1.26	1.30	1.44	0.32
E9	21.86	2.81	0.65	2.37	1.79	1.50	1.67	0.54
E10	14.95	2.59	0.76	2.12	1.61	1.86	1.59	0.51
E11	0.00	2.46	1.03	2.57	1.76	1.28	1.25	0.58
E12	14.73	2.43	0.52	1.16	1.27	1.34	1.55	0.38
E13	15.52	2.52	0.49	1.80	1.42	1.30	1.75	0.36
E14	1.53	2.48	1.79	2.13	1.93	1.65	3.94	0.59
E15	25.06	2.75	0.57	1.94	1.53	1.54	2.15	0.37
E16	0.00	2.96	2.24	1.88	2.23	2.57	0.99	0.91
C1	19.66	2.66	0.68	1.47	1.69	1.03	1.20	0.76
C2	32.20	3.05	0.54	1.84	1.59	1.31	1.49	0.37
C3	23.37	2.65	0.67	1.60	2.29	1.20	1.94	0.75
C4	24.54	3.66	0.75	2.43	1.91	1.56	2.17	0.41
C5	28.51	3.13	0.96	2.57	1.55	1.35	1.75	0.32
C6	20.72	3.26	0.62	2.64	1.67	1.34	1.53	0.27
C7	24.25	3.34	0.77	2.83	1.58	1.28	1.46	0.26
C8	30.52	3.04	0.62	2.57	1.60	1.28	1.40	0.27
C9	21.00	3.31	0.75	2.26	1.84	1.25	1.62	0.59
C10	27.87	3.19	0.59	2.30	2.09	1.18	1.46	0.53
C11	17.01	3.16	0.90	2.56	1.92	1.15	1.36	0.51

Appendix 29 Contamination factors of metals in the study area during pre-monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe
E1	93.87	3.30	0.27	2.66	1.47	1.63	18.92	0.31	0.99
E2	17.25	0.55	0.08	0.88	0.41	0.36	1.70	0.12	0.16
E3	10.08	0.77	0.10	1.23	0.59	0.40	0.52	0.13	0.21
E4	13.93	1.73	0.42	2.62	1.13	0.84	1.26	0.22	0.72
E5	62.06	2.83	0.29	3.24	1.35	1.43	11.08	0.39	0.96
E6	29.69	2.83	0.30	3.73	1.53	1.43	2.07	0.41	1.17
E7	6.98	0.76	0.19	1.68	0.61	0.47	0.50	0.16	0.34
E8	2.65	0.38	0.17	1.34	0.33	0.24	0.18	0.11	0.14
E9	7.48	1.31	0.18	2.14	0.68	0.65	0.74	0.16	0.49
E10	19.94	1.89	0.18	2.65	1.03	0.89	1.09	0.22	0.70
E11	2.49	0.52	0.10	1.72	0.41	0.35	0.22	0.14	0.20
E12	28.94	2.92	0.32	3.66	1.41	1.31	1.77	0.33	0.99
E13	5.97	0.71	0.14	1.36	0.45	0.33	0.27	0.13	0.24
E14	27.47	3.09	0.32	3.59	1.44	1.53	2.24	0.38	1.05
E15	31.31	2.89	0.38	3.17	1.38	1.28	1.94	0.47	1.09
E16	26.16	2.70	0.99	2.83	1.45	1.35	1.74	0.38	1.06
C1	24.73	2.60	0.25	1.37	1.33	1.08	1.28	0.30	0.83
C3	6.45	0.87	0.16	0.57	0.74	0.29	0.45	0.36	0.04
C4	2.87	0.25	0.04	0.44	0.25	0.20	0.15	0.13	0.08
C5	31.47	2.80	0.39	2.05	1.44	1.13	1.38	0.24	0.83
C6	28.58	2.74	0.57	2.31	1.28	1.09	1.34	0.23	0.55
C8	29.66	2.16	0.26	1.94	1.20	0.72	1.09	0.39	0.69
C9	14.63	1.47	0.19	1.98	1.00	0.48	0.77	0.39	0.44
C10	20.46	1.85	0.26	1.69	1.21	0.64	0.77	0.36	0.67
C11	14.71	0.93	0.14	2.11	0.80	0.31	0.49	0.37	0.44

Appendix 30 Contamination factors of metals in the study area during monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe
E1	59.26	2.47	0.48	2.45	1.26	1.27	16.05	0.35	0.83
E2	25.64	1.08	0.36	1.50	0.78	0.63	3.40	0.24	0.37
E3	17.53	1.40	0.25	2.32	1.10	0.77	1.21	0.29	0.60
E4	15.64	1.88	0.27	2.37	1.19	0.90	1.41	0.30	0.61
E5	50.10	1.96	0.25	2.55	1.38	1.16	13.89	0.37	1.15
E6	30.54	3.15	0.32	2.72	1.30	1.60	2.86	0.39	1.01
E7	21.99	2.90	0.31	2.47	1.50	1.33	1.87	0.40	1.02
E8	19.38	2.47	0.54	2.62	1.38	1.26	1.37	0.43	0.91
E9	22.84	2.70	0.30	2.53	1.43	1.34	1.91	0.43	1.15
E10	16.20	1.50	0.26	2.15	0.93	0.84	1.19	0.29	0.66
E11	6.00	0.55	0.05	0.75	0.37	0.24	0.22	0.16	0.19
E12	8.16	1.07	0.13	1.16	0.70	0.64	0.71	0.20	0.47
E13	19.17	2.71	0.44	2.44	1.42	1.22	1.53	0.40	1.00
E14	4.82	0.67	0.07	1.07	0.55	0.37	0.43	0.20	0.32
E15	8.32	1.21	0.09	1.17	0.58	0.64	0.74	0.21	0.44
E16	11.60	1.65	0.22	1.56	1.01	0.83	1.11	0.39	0.67
C1	21.37	2.23	0.48	1.62	1.15	0.89	1.03	0.39	0.76
C2	11.45	1.80	0.45	1.58	1.17	0.76	0.83	0.33	0.62
C3	10.95	1.14	0.25	1.40	1.00	0.42	0.58	0.48	0.48
C4	18.66	1.78	0.56	1.83	1.08	0.86	1.01	0.25	0.59
C5	23.73	2.82	0.54	2.26	1.47	1.29	1.76	0.34	0.85
C6	20.65	2.79	0.46	2.55	1.37	1.16	1.45	0.26	0.84
C7	25.82	2.78	0.44	2.60	1.50	1.21	1.50	0.30	0.88
C8	24.18	2.64	0.41	2.49	1.45	1.18	1.39	0.26	0.87
C9	28.44	2.68	0.37	2.41	1.42	1.13	1.47	0.29	0.78
C10	15.69	2.46	0.26	2.15	1.16	0.54	0.86	0.60	0.67
C11	15.19	2.61	0.32	2.07	1.37	0.85	1.08	0.51	0.76

Appendix 31 Contamination factors of metals in the study area during post-monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe
E1	64.12	3.09	0.36	2.33	1.45	1.43	9.75	0.32	0.94
E2	44.71	1.42	1.21	1.20	0.92	0.79	10.91	0.26	0.60
E3	0.17	0.61	0.30	0.61	0.36	0.20	0.30	0.09	0.14
E4	28.97	1.91	0.56	1.72	1.08	0.86	2.59	0.33	0.68
E5	41.71	2.62	0.56	2.38	1.35	1.43	12.06	0.38	0.85
E6	27.47	3.26	0.59	2.14	1.29	1.72	3.13	0.37	0.82
E7	18.46	2.92	0.52	2.27	1.40	1.34	1.99	0.39	1.03
E8	21.23	2.73	1.53	3.02	1.52	1.57	1.74	0.39	1.21
E9	12.99	1.67	0.39	1.41	1.06	0.89	0.99	0.32	0.59
E10	6.20	1.07	0.31	0.88	0.67	0.77	0.66	0.21	0.41
E11	0.00	0.72	0.30	0.75	0.52	0.37	0.37	0.17	0.29
E12	10.73	1.77	0.38	0.85	0.93	0.98	1.13	0.27	0.73
E13	16.00	2.60	0.51	1.85	1.46	1.35	1.80	0.37	1.03
E14	0.33	0.54	0.39	0.46	0.42	0.36	0.86	0.13	0.22
E15	22.39	2.45	0.51	1.73	1.37	1.37	1.92	0.33	0.89
E16	0.00	0.34	0.25	0.21	0.25	0.29	0.11	0.10	0.11
C1	13.97	1.89	0.49	1.05	1.20	0.73	0.86	0.54	0.71
C2	28.44	2.70	0.48	1.63	1.40	1.16	1.31	0.32	0.88
C3	8.45	0.96	0.24	0.58	0.83	0.44	0.70	0.27	0.36
C4	16.95	2.53	0.52	1.68	1.32	1.08	1.50	0.29	0.69
C5	25.95	2.85	0.87	2.34	1.41	1.23	1.60	0.29	0.91
C6	18.16	2.86	0.54	2.31	1.46	1.17	1.34	0.24	0.88
C7	20.44	2.81	0.65	2.38	1.33	1.08	1.23	0.22	0.84
C8	26.20	2.61	0.53	2.21	1.37	1.10	1.20	0.23	0.86
C9	13.47	2.12	0.48	1.45	1.18	0.80	1.04	0.38	0.64
C10	17.18	1.97	0.36	1.42	1.29	0.73	0.90	0.33	0.62
C11	9.00	1.67	0.48	1.36	1.01	0.61	0.72	0.27	0.53

Appendix 32 Geoaccumulation index of metals in the study area during pre-monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe
E1	5.97	1.14	-2.45	0.83	-0.03	0.12	3.66	-2.27	-0.60
E2	3.52	-1.45	-4.17	-0.77	-1.88	-2.04	0.18	-3.68	-3.19
E3	2.75	-0.96	-3.86	-0.29	-1.34	-1.92	-1.52	-3.49	-2.87
E4	3.22	0.21	-1.83	0.81	-0.41	-0.83	-0.25	-2.76	-1.07
E5	5.37	0.92	-2.35	1.11	-0.16	-0.07	2.88	-1.93	-0.64
E6	4.31	0.92	-2.33	1.31	0.02	-0.07	0.46	-1.86	-0.36
E7	2.22	-0.98	-3.02	0.16	-1.30	-1.67	-1.59	-3.23	-2.15
E8	0.82	-1.98	-3.11	-0.16	-2.18	-2.63	-3.09	-3.82	-3.46
E9	2.32	-0.19	-3.04	0.51	-1.14	-1.21	-1.03	-3.23	-1.63
E10	3.73	0.33	-3.08	0.82	-0.55	-0.75	-0.46	-2.79	-1.10
E11	0.73	-1.54	-3.86	0.19	-1.88	-2.11	-2.77	-3.46	-2.93
E12	4.27	0.96	-2.23	1.29	-0.09	-0.19	0.24	-2.19	-0.61
E13	1.99	-1.09	-3.44	-0.14	-1.75	-2.19	-2.46	-3.51	-2.63
E14	4.19	1.04	-2.22	1.26	-0.06	0.03	0.58	-2.00	-0.51
E15	4.38	0.95	-1.97	1.08	-0.12	-0.23	0.37	-1.68	-0.46
E16	4.12	0.85	-0.60	0.92	-0.05	-0.15	0.21	-1.99	-0.50
C1	4.04	0.79	-2.58	-0.13	-0.18	-0.47	-0.23	-2.33	-0.86
C3	2.11	-0.78	-3.26	-1.39	-1.02	-2.38	-1.73	-2.07	-5.30
C4	0.94	-2.57	-5.10	-1.76	-2.57	-2.90	-3.34	-3.54	-4.22
C5	4.39	0.90	-1.94	0.45	-0.05	-0.40	-0.12	-2.64	-0.85
C6	4.25	0.87	-1.40	0.62	-0.22	-0.46	-0.16	-2.72	-1.45
C8	4.31	0.52	-2.53	0.37	-0.32	-1.06	-0.47	-1.95	-1.13
C9	3.29	-0.02	-3.00	0.40	-0.58	-1.65	-0.96	-1.94	-1.77
C10	3.77	0.31	-2.53	0.17	-0.31	-1.23	-0.96	-2.07	-1.17
C11	3.29	-0.70	-3.44	0.49	-0.90	-2.27	-1.61	-2.00	-1.75

Appendix 33 Geoaccumulation index of metals in the study area during monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe
E1	5.30	0.72	-1.65	0.71	-0.26	-0.24	3.42	-2.10	-0.86
E2	4.10	-0.47	-2.06	0.00	-0.94	-1.25	1.18	-2.67	-2.03
E3	3.55	-0.10	-2.58	0.63	-0.45	-0.96	-0.30	-2.36	-1.33
E4	3.38	0.32	-2.46	0.66	-0.33	-0.74	-0.09	-2.35	-1.30
E5	5.06	0.39	-2.60	0.76	-0.12	-0.37	3.21	-2.01	-0.39
E6	4.35	1.07	-2.24	0.86	-0.21	0.10	0.93	-1.95	-0.57
E7	3.87	0.95	-2.26	0.72	0.00	-0.17	0.32	-1.92	-0.56
E8	3.69	0.72	-1.47	0.80	-0.13	-0.25	-0.13	-1.80	-0.72
E9	3.93	0.85	-2.31	0.75	-0.07	-0.17	0.35	-1.80	-0.38
E10	3.43	0.00	-2.55	0.52	-0.69	-0.83	-0.34	-2.37	-1.18
E11	2.00	-1.44	-4.78	-1.01	-2.00	-2.66	-2.77	-3.19	-2.97
E12	2.44	-0.49	-3.52	-0.38	-1.11	-1.23	-1.08	-2.91	-1.68
E13	3.68	0.85	-1.78	0.70	-0.08	-0.30	0.03	-1.92	-0.59
E14	1.68	-1.15	-4.36	-0.49	-1.44	-2.00	-1.79	-2.89	-2.22
E15	2.47	-0.31	-4.08	-0.35	-1.38	-1.23	-1.03	-2.85	-1.77
E16	2.95	0.14	-2.79	0.05	-0.58	-0.85	-0.44	-1.94	-1.16
C1	3.83	0.57	-1.65	0.11	-0.38	-0.75	-0.54	-1.94	-0.98
C2	2.93	0.26	-1.74	0.07	-0.36	-0.98	-0.86	-2.18	-1.28
C3	2.87	-0.39	-2.59	-0.10	-0.59	-1.84	-1.38	-1.65	-1.65
C4	3.64	0.25	-1.43	0.29	-0.47	-0.81	-0.56	-2.59	-1.33
C5	3.98	0.91	-1.48	0.59	-0.03	-0.21	0.23	-2.15	-0.81
C6	3.78	0.90	-1.71	0.77	-0.13	-0.37	-0.04	-2.52	-0.84
C7	4.11	0.89	-1.77	0.79	0.00	-0.31	0.00	-2.31	-0.76
C8	4.01	0.82	-1.85	0.73	-0.05	-0.34	-0.11	-2.50	-0.79
C9	4.25	0.84	-2.01	0.68	-0.08	-0.41	-0.03	-2.38	-0.94
C10	3.39	0.71	-2.55	0.52	-0.37	-1.47	-0.81	-1.33	-1.16
C11	3.34	0.80	-2.23	0.46	-0.13	-0.83	-0.47	-1.57	-0.99

Appendix 34 Geoaccumulation index of metals in the study area during post-monsoon

Stations	Cd	Pb	Cr	Ni	Co	Cu	Zn	Mn	Fe
E1	5.42	1.04	-2.07	0.64	-0.05	-0.07	2.70	-2.21	-0.68
E2	4.90	-0.08	-0.31	-0.32	-0.71	-0.93	2.86	-2.54	-1.32
E3	-3.17	-1.31	-2.32	-1.30	-2.07	-2.88	-2.31	-4.08	-3.40
E4	4.27	0.35	-1.43	0.19	-0.47	-0.81	0.79	-2.20	-1.14
E5	4.80	0.80	-1.41	0.67	-0.16	-0.07	3.01	-1.97	-0.82
E6	4.19	1.12	-1.34	0.51	-0.21	0.19	1.06	-2.00	-0.87
E7	3.62	0.96	-1.52	0.60	-0.10	-0.16	0.41	-1.95	-0.54
E8	3.82	0.87	0.03	1.01	0.02	0.07	0.21	-1.95	-0.31
E9	3.11	0.16	-1.95	-0.09	-0.50	-0.75	-0.60	-2.23	-1.34
E10	2.05	-0.48	-2.26	-0.77	-1.16	-0.96	-1.18	-2.83	-1.85
E11	-	-1.06	-2.31	-0.99	-1.54	-2.00	-2.03	-3.14	-2.36
E12	2.84	0.24	-1.98	-0.83	-0.69	-0.62	-0.41	-2.46	-1.04
E13	3.42	0.79	-1.56	0.30	-0.04	-0.16	0.26	-2.01	-0.54
E14	-2.17	-1.47	-1.95	-1.69	-1.84	-2.06	-0.81	-3.55	-2.79
E15	3.90	0.71	-1.56	0.21	-0.14	-0.13	0.36	-2.18	-0.75
E16	-	-2.16	-2.56	-2.82	-2.57	-2.36	-3.74	-3.86	-3.72
C1	3.22	0.33	-1.62	-0.52	-0.32	-1.04	-0.81	-1.47	-1.08
C2	4.25	0.85	-1.66	0.12	-0.10	-0.37	-0.19	-2.21	-0.76
C3	2.49	-0.65	-2.64	-1.38	-0.86	-1.78	-1.10	-2.47	-2.05
C4	3.50	0.75	-1.54	0.16	-0.19	-0.48	0.00	-2.39	-1.12
C5	4.11	0.93	-0.78	0.64	-0.09	-0.29	0.09	-2.37	-0.72
C6	3.60	0.93	-1.47	0.62	-0.04	-0.36	-0.16	-2.67	-0.78
C7	3.77	0.91	-1.20	0.67	-0.17	-0.48	-0.29	-2.75	-0.83
C8	4.13	0.80	-1.50	0.56	-0.13	-0.44	-0.32	-2.69	-0.81
C9	3.17	0.50	-1.63	-0.05	-0.34	-0.90	-0.53	-1.99	-1.23
C10	3.52	0.39	-2.06	-0.08	-0.22	-1.05	-0.74	-2.20	-1.28
C11	2.58	0.16	-1.66	-0.14	-0.56	-1.30	-1.06	-2.48	-1.50

Appendix 35 Equilibrium adsorption data of heavy metals

Stations	Initial Concentration, mg/l	Adsorbed Concentration, mg/l				
		Cd	Pb	Co	Cu	Zn
C1	50	19.05	34.75	17.45	20.60	17.66
	100	28.15	69.75	23.75	29.05	27.03
	150	30.10	74.25	33.05	38.75	36.56
	200	28.00	72.00	35.30	35.10	41.25
	250	41.40	80.00	43.80	30.90	49.38
	300	47.00	133.25	53.10	53.40	52.19
C5	50	23.50	14.75	23.60	32.73	28.59
	100	39.00	82.50	32.40	38.40	47.03
	150	84.10	110.00	42.50	42.95	56.72
	200	57.40	120.75	56.60	44.90	66.56
	250	48.40	122.50	59.80	44.10	77.81
	300	57.40	161.00	73.30	130.80	86.88
C9	50	18.10	18.25	20.55	25.86	21.72
	100	26.80	78.50	30.00	27.70	28.13
	150	33.80	97.25	38.55	32.80	40.00
	200	38.00	100.75	49.80	41.40	53.75
	250	42.00	124.25	49.20	38.50	51.88
	300	45.60	142.50	59.70	58.60	56.56
E9	50	15.95	108.75	29.15	13.66	19.38
	100	29.20	57.50	29.85	21.75	33.44
	150	48.60	64.50	41.10	22.85	37.19
	200	31.20	70.00	35.60	31.90	44.69
	250	41.80	67.75	41.40	34.70	53.75
	300	51.20	114.75	44.30	46.80	62.19
E12	50	17.70	17.25	15.00	11.90	13.28
	100	27.70	57.25	24.15	17.80	19.38
	150	66.10	60.50	38.45	26.10	22.81
	200	48.20	65.25	33.50	33.50	26.56
	250	83.40	62.50	36.30	17.30	35.63
	300	64.20	118.50	47.30	53.60	38.75
E13	50	21.75	-30.00	32.75	19.14	20.16
	100	31.35	65.50	58.15	27.15	26.56
	150	43.90	81.25	34.35	27.40	27.66
	200	40.40	78.75	39.50	38.20	39.38
	250	74.00	70.75	46.50	31.40	35.31
	300	56.80	106.50	56.60	45.50	37.50

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