# HYDROGEOCHEMICAL EVALUATION OF INORGANICS AND BIOORGANICS IN SELECTED AQUATIC ENVIRONMENTS

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**Cochin University of Science and Technology**

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in
Environmental Chemistry
*Under the Faculty of Marine Sciences*

**By**

**Resmi T.R.**

**DEPARTMENT OF CHEMICAL OCEANOGRAPHY**
**SCHOOL OF MARINE SCIENCES**
**COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY**
**KOCHI – 682 016**

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*Dedicated to My Beloved Parents*

# *Certificate*

*This is to certify that this thesis entitled "Hydrogeochemical evaluation of inorganics and bioorganics in selected aquatic environments" is a bonafide record of the research work carried out by Smt. Resmi T.R. under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the degree of Philosophiae Doctor of the Cochin University of Science and Technology and no part thereof has been presented before for any other degree, diploma, associateship, fellowship or any other similar title or recognition.*

Dr. Jacob Chacko
Supervising Guide

Kochi -16
July 2004

# *Declaration*

*I hereby declare that this thesis entitled "Hydrogeochemical evaluation of inorganics and bioorganics in selected aquatic environments" is an authentic record of research work carried out by me under the supervision of Dr. Jacob Chacko, Professor, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology in partial fulfilment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and that no part of it has previously formed the basis for the award of any degree, diploma, associateship, fellowship or any other similar title or recognition in any University.*

*Resmi T.R.*

*Kochi -16*
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# Chapter 1

# Introduction

## 1.1 Introduction

The hydrosphere represents a colossal system remaining in an astonishingly dynamic equilibrium between the saline solution, the land input, the atmospheric fallouts, the aquatic organisms, and sediments. Because of their exceptional complexity and multifaceted nature, the study of the hydrosphere essentially requires a fusion of different disciplines of ocean science. One such integrational science is hydrogeochemistry, which embraces the frontiers of chemistry, physics, geology and biology. Organisms and organic matter assume the principal role in biogeochemical processes occurring in the hydrosphere; and hydrogeochemistry is essentially aimed at assessing the transformations, cycling and fate of various forms of nutrients, organic matter and toxic pollutants. The study of hydrogeoorganics include investigations on the sources of these compounds, the pathways along which they enter the aquatic environment, the pattern of accumulation in the biotic and abiotic components of the ecosystem, the mechanisms and rate of migration, their transformations and other processes which determine the fate of these compounds in the environment.

The water bodies of our planet earth are quite unique and much varied. The largest of them, the oceans, carry the most dense, high saline water; while, the arteries of the continents, the rivers have the purest form. The meeting place of the two often creates yet another arena, the estuaries, which are brackish in nature.

Estuaries are complex systems, which receive chemical inputs from a variety of sources. River runoff contributes dissolved species derived from chemical weathering of rocks, suspended material from mechanical weathering of terrigenous matter and dissolved and particulate organic matter of biogenic origin. Superimposed on these natural sources are inputs resulting from anthropogenic activities. Biogeochemical characteristic of each element determine the type of behaviour exhibited in its passage through the estuarine system. The balance between the input and output of these elements, together with physical flow regiment determine the overall chemistry of the estuary. Penetrated by the sea through the recurring tides and flushed by the freshwater outflow of the lotic systems an estuary is indeed a dynamic ecotone where freshwater meets seawater witnessed by the lush verdure of mangroves in this area.

Rivers are the chief sources of water, salt, organic matter and mineral particles from land to sea. They are open-ended discharge systems. This contrasts with lake basins, which tend to accumulate materials. Rivers are ecologically important as transport agents, scouring the earth, moving loose soils downstream and depositing them on the flood plains or into the sea.. Since civilizations have flourished on the banks of rivers, man has interfered with this system for centuries to such an extent that practically none of them remain undefiled. All major industries have developed near the rivers and these discharge loads of toxic substances daily into them. These organic and inorganic-solute dynamics involve physical (dilution, sedimentation, adsorption/desorption), chemical (oxidation, reduction, dissolution) and biological (algal and microbial uptake, microbial oxidation and reduction) processes. Much chemical transformation takes place before the elements are discharged into the sea/estuary.

Mangroves are nature's own ecological balancers with wide singularities both in the biotic and abiotic compartments. Situated between the land and the sea, they are influenced by marine and terrestrial factors. Nutrients accumulate in mangroves as a result of inputs from nearby water bodies, recycling between the sediment and water column, inputs from anthropogenic activities such as modified land use, effluent disposal, aquaculture etc.

Obviously, therefore, mangroves are highly productive ecosystems. The principal form of energy is mainly derived from the lush vegetation so special to it. Each falling leaf is an energy increment. Death and decomposition of this plant biomass leads to a highly anoxic environment both in the sediment and in the water column. Development of this anoxia, in turn, paves the way to special chemical reactions. Identification and characterization of these reactions are vital as the importance of this valuable ecosystem is manifold.

## 1.2 Importance of mangrove habitats

Mangroves form one of the most extraordinary ecological formations. Mangroves, as tropical rainforests and saline-tolerant tidal forest, represent an open ecosystem. Plant litter, mainly leaves, represents about one-third of primary production in the mangroves and up to half this quantity can be exported *via* creeks to adjacent waters (Robertson *et al.*, 1992). The export of this large quantity of organic matter has a recognizable effect on food webs in coastal waters (Odum and Heald, 1975; Alongi *et al.*, 1989; Alongi, 1990). Coastal outwelling of dissolved and suspended organic matter and nutrients from mangrove swamps can also affect considerably the biogeochemical cycles of marine environments. The extent to which mangroves exchange dissolved and particulate nutrients with adjacent waters depends on several factors, including geomorphology, tidal regime and climate (Alongi, 1996).

A large fraction of the organic matter produced in the mangroves are deposited on sediment surfaces and is degraded and remineralized by early diagenetic processes near the sediment-water interfaces (Henrichs, 1992; Canuel and Martens, 1996). The degradation is mediated by an array of aerobic and anaerobic microbial processes in the dynamic interface with a concurrent release of inorganic nutrients (Mackin and Swider, 1989; Canfield, *et al*, 1993). Thus mangroves can be a rich source of food for the aquatic organisms including the microbial community. To a wide range of animals, the litter is a valuable food either as such or after microbial degradation. The debris also serves as a spawning ground and nursery beds for several most economic marine or offshore prawn and fish species. The roots of the mangroves serve as a good shelter for a large number of organisms including mosses, lichens, algae, fungi, bacteria, nematodes, etc.

The undisturbed mangrove forests can act as the seaward barrier and check the coastal erosion considerably and minimize the tidal thrust or strong storm hit arising from the sea. On the other hand, the well-developed mangrove forests may also accelerate the siltation and accretion processes by arresting the water transport of silt and clay particles, which ultimately extend the coastal zone. Mangrove coverage, again, may act as a buffer agent and protect or minimize the natural cyclone or surges of the bay. The commercial and subsistence demand for mangrove products have largely been for energy purpose in the form of firewood, charcoal, fodder and to some extent, in the form of food for coastal community.

## 1.3 Mangroves of Kerala coast

Kerala has a long narrow coastal line of ~ 560 km, punctuated by long patches of backwaters, which consists of a series of lagoons running parallel to the sea and separated from it by a strip of land varying in width from a few hundred meters to several kilometres. The entry of tidal waters regularly from the sea, the enrichment of 30 estuaries and backwaters with regular supply of freshwater flowing from the 44 perennial rivers creates a peculiar ecological environment leading to the development of unique mangrove vegetation on the fringes of the backwaters, estuaries and creeks. This unique flora with their specialized ecological characters affords suitable environment for a set of peculiar fauna living on their own in this highly specialized ecosystem.

According to Basha (1991), Kannur district in Kerala is the richest in mangrove vegetation (~755 ha). Besides Kannur, Kozhikode and Ernakulam districts have higher proportions of mangroves. At present, approximately an area 15 km$^2$ i.e. 88 percentage of total mangroves of Kerala are under private ownership. Patches of varying extent exist along the sides of Railway line especially in the Ernakulam-Alappuzha, Thiruvananthapuram-Kollam and Thanur-Kasarkode sectors. In most places, the vegetation is in a very narrow linear strip. Bigger bits are available in some parts on the sides of the line from Mahe to Dharmadom, Pazhayangadi, Ezhimala, Payyannur, Edakad and so on. Kumarakom, which is a bird sanctuary, supports a narrow belt of approximately one kilometre long mangrove vegetation along the fringes of Vembanad Lake varying in width from 10-20 m. This area comes approximately to 4 ha including vacant marshy places. Patches of mangroves are also seen in places such as Pathiramanal Island, Alappuzha and near Vikram Sarabhai Space Centre, Thiruvananthapuram.

An extent of 101 ha of land supporting mangrove vegetation in patches exists in Puthuvypu, Cochin. The entire area is marshy containing natural basins, sand pits, crevices and canals and support good mangrove vegetation, which are still in the successional stage. At present, the mangrove vegetation consists primarily of *Avicennia*, which is growing gregariously on the western side with *Rhizophora* and *Bruguiera* constituting occasional growth. This is the biggest mangrove area available on the Kerala coast. Around 3.44 ha of mangrove area is located in the heart of Cochin City and is known as Mangalavanam, which is also a bird sanctuary. The main species found here are *Avicennia officinalis, Excoecaria agallocha, Acanthus illicifolius* etc. However. According to Ramachandran *et al* (1986), Kerala once supported about 700 $km^2$ mangroves along its coast and, hence, what is seen today are only relics of the great past.

Despite the increasing observations on the distribution of chemical species in mangroves, estuaries or rivers, the chemistry of these systems has conspicuously lacked the coherence and the capacity to systematize further approaches, which are provided by unifying concepts. Hence, in an attempt to understand fully, the functioning of these exceptional water bodies, constituents such as nutrient and organic compounds along with their most unwanted associates, the toxic trace metals form the subject of evaluation in this study.

### 1.4 Nutrient compounds

The productivity of an aquatic system depends mainly on two conditions, the supply of fresh nutrients and their effective regeneration. The assimilation of dissolved nutrients by primary producers causes a decline in the inorganic form by converting it to dissolved organic form. The particulate organic forms are usually transported in suspension and are ultimately mineralized or settled in the bottom sediments. The distribution and concentration of nutrients are controlled by variations in physical, chemical, biological and geological processes. A successful understanding of the role of various aquatic systems as nutrient traps, filters and exporters require the knowledge of the distribution of these compounds as well as their rates of inputs, loss and accumulation in coastal waters.

The important species of nitrogen involved in the biogeochemical processes are nitrate, nitrite and ammonium ion. In well-oxygenated water bodies, the most abundant and stable form of nitrogen is nitrate. The regeneration of nitrate is manly done by bacterial oxidation of organic matter. When the cells die, they undergo rapid autolysis, releasing nitrate and phosphate. The decomposition of organic nitrogen compounds also takes place but a small percentage of particulate organic nitrogen is resistant to bacterial attack and can be accumulated in sediments. Nitrite is an intermediate in the nitrification-denitrification process. Nitrite enters the aquatic environment through the effluents from industries using nitrite as corrosion inhibitors and certain biologically purified water, which may also have large amounts of nitrite. Ammonium-N is the first inorganic product formed during the regeneration of nitrogen from organic compounds. This is the most abundant nitrogen species after nitrate in surface waters, where greater part of nitrate has been removed by phytoplankton growth. In the anoxic waters of mangroves, denitrification along with mineralization highly favours replenishment of this ion.

Phosphate is the major nutrient regulating the growth and production of phytoplankton. Its concentration levels are useful to predict the total biomass of phytoplankton. The major contributors of phosphate are the rivers with enormous loads of weathering products they carry. Phosphate exists in myriad forms in the hydrosphere. Abiotic regulation of soluble phosphate concentration in fresh waters is mainly through adsorption-desorption or through precipitation-solubilization reactions. Estuaries normally mediate phosphors-transfer from land to the ocean. Flocculation of inorganic and organic colloids takes place largely in estuaries, contributing to the removal of soluble inorganic phosphorus. In regions of higher salinity, they can behave as sources or sinks of soluble phosphorus. This non-conservative behaviour indicates that biogeochemical processes and recycling are acting within the estuary, as opposed to a conservative behaviour, where only dilution is operative. Mangrove sediments have significant ability to process and recycle phosphate and are important sources of inorganic and organic nutrients for adjacent coastal waters or function, alternatively, as a sink.

In an aquatic system, sediments act as reservoirs of nutrient materials in water. The replenishment of these nutrients in time of need and their subsequent removal generally aids the biological cycle of the system. Wetlands have been shown to trap, store, transform and release nutrients, thus significantly modifying the chemistry of water flowing through them. Thus the reactivity of the nutrient elements shows remarkable variations in accordance with the changing physical environment prevailing in each biotope. Identifying these vibrations are useful to understand the nutrient cycle in this river-estuary-mangrove system.

## 1.5 Bioorganic compounds

Organic matter provide a nutritional base for micro and macro organisms and exert a major influence on the speciation of many organic constituents through such processes as complexation and adsorption and are precursors of fossil fuels. Dissolved organic matter is an extremely complex and dilute mixture of compounds such as resistant humic substances, lignin etc. and more labile compounds from major biochemically important compound classes such as carbohydrates, proteins, steroids, alcohols, amino acids, hydrocarbons and fatty acids. The massive reserve of organic matter in various aquatic systems is significant since its presence in surface water makes an even more perfect nutrient medium than its content of inorganic nutrients would suggest.

Dissolved organic carbon in estuarine and coastal waters is supplied largely by input from rivers. This dissolved organic carbon pool represents a large potential energy source and fate of dissolved organic carbon will have consequences on the carbon budget of the entire ecosystem. In coastal sediments, where much organic matter remineralization is carried out under anoxic condition, the concerted action of many microbial communities is required to convert organic matter to $CO_2$ and $CH_4$. Heterotrophic bacteria utilize the hydrolysed substrates for cellular carbon and energy and excrete organic transformation product. The terminal members of the food chain utilize the simple substrates such as sugars, proteins, short chain fatty acids etc.

Carbohydrates and their derivatives are the most essential organic compounds in the biosphere. Most carbohydrates are unstable outside the living organisms and undergo degradation to (various) end products. This causes a drop in the pH and Eh of the surrounding environment and affects the metabolic processes in aquatic organisms. Large amounts of carbohydrates are liberated to the water by primary producers as a result of autolytic division of normally functioning cells, extracellular metabolites of low molecular weight compounds and other specific activities. Carbohydrate content in the sediments is enhanced by the action of the detritus feeders. Proteins constitute about 70-85 percentage of the nitrogenous substances in marine organisms. As a result of metabolism of living organisms and post humus organic matter decay, amino acids and peptides of various degrees of polymerisation are released into the water. These proteinaceous material have a slower rate of decomposition in the water mass and their destruction, resynthesis and incorporation into non-extractable complexes occur in such proportions that they maintain a relatively high level in the organic matter content. This process terminates mainly in the water-sediment interface and within several centimetres of the upper sediments. At the sediment-water interface, the proteinaceous compounds are main source of energy for the benthos. In the sedimentary column, they are markers of the microbial organic matter degradation processes.

The sources of lipids in the environment are the auto and heterotrophic organisms. A certain portion also reaches the aquatic environment with allochthonous organic matter comprising neutral lipids and the oil constituents. All forms of lipids in this environment like dissolved and colloidal, particulate, those contained in the bottom sediments and interstitial waters are interrelated and can be converted to one another. The magnitude of bioturbation, the quantity of the particulate matter arriving the system and its burial rates plus the environment arising largely under the effect of these factors and the gaseous regime of the sediment determine the concentration of lipids and their content in the organic matter. As the suspended materials pass into the sediments, the composition of the lipids undergoes restructuring as a result of catalytic reactions in the living organisms. The decomposition of the lipids and their condensation in the upper water layers gain a new momentum in the sediments and are accompanied by a change in the relationship between the lipid components and other organic matter classes.

Tannin and lignin are high molecular weight organic compounds widely distributed throughout the plant kingdom. These compounds are highly resistant to degradation and have the potential to damage the aquatic environment. Tannins can influence the cycles of metals and other elements and can react with proteins inhibiting the performance of many enzymes. The break down of terrestrial as well as mangrove plant tissue produces considerable variety of these compounds.

## 1.6 Trace metals

Natural waters are dispersed multielemental and multispecies systems that derive their composition from natural processes and that are affected by or the result of human activity. Over the past few years industry has released more wastes into the natural environment than overall the preceding centuries. Agricultural, chemical, textile or metallurgical industries consume large amounts of water, which subsequent to processing, is released into the environment together with dissolved toxic substances, which are prejudicial to the coastal environment. The fate of trace metals in the aquatic environment is of extreme importance because of their impact on the ecosystem. The distribution of metals and their reactivity vary in the estuaries depending on environmental factors such as hydrodynamic residence times, mixing patterns and transport processes. Trace metals may be bound to various forms of organic matter, living organisms, detritus and coatings on mineral particles etc. Trace metal partitioning between dissolved and particulate phases depends on a number of factors including pH, salinity, temperature, redox conditions, dissolved organic carbon and composition of suspended particulate matter.

At low concentration of trace metals, microchemical phenomena, including interactions on phase boundaries and colloid chemistry, may become very significant and must be taken into account. Chemical reactions with trace metals are therefore much more difficult to predict than those involving macroelements, and thus concentration levels often show large temporal and spatial variations even within specific aquatic systems. Metal toxicity may be influenced by the presence of other toxins capable of acting in synergistic or antagonistic fashion. Mangroves play an important role in the abatement of metal pollution. Trace metals enter into mangroves with incoming tide associated with suspended particles, Fe and Mn oxyhydroxides. When these entities meet with the reducing condition, dominant in mangroves, these oxyhydroxides are reduced, dissolved, and release their trace metal load into the water column. Due to the permanent anoxic condition of the mangroves sediments and high sedimentation rates, trace metals suffer rapid accumulation and burial in the sediment column. Thus mangroves can act as biogeochemical barriers to the transport of trace metals to coastal waters.

The intensity of research efforts expended in elucidating the physical, biological and chemical characteristics of Cochin backwater system during the last three decades are indicative of the economic and social importance enjoyed by it. Extensive studies have been carried out in this estuary especially on the physical, chemical and biological aspects. Trace metal chemistry has received particular attention among the various chemical constituents analyzed. Venugopal *et al.* (1982) studied the levels of Cu, Mn, Co, Ni and Zn in the northern sector of this backwater system. On the other hand, Nair *et al.* (1991) observed that the metal concentration in recently deposited sediments showed different behaviour and are influenced by natural as well as anthropogenic origin. The different forms in which trace metals existed in this estuary have been investigated by many researchers (Shibu *et al.*, 1990; Nair *et al.*, 1991; Nair and Balchand, 1993). Nutrient compounds in the estuarine waters have been estimated by Anirudhan (1992), while the biogeoorganics of the estuarine sediments were analysed by Vasudevan (1992). The study revealed that distribution of biogeoorganics in Cochin environment is influenced by the increasing human activities, waste discharge from major industrial establishments, river runoff and by sewage through the network of large and small canals. However, only the organics of the sedimentary environment was investigated in this study. Studies on the Chitrapuzha River are very few except the work done by Babu (1999) and Joseph (2001).

Studies on the mangroves on the Cochin area have received attention only recently. The different factors that are responsible for the colonization of the predominant vegetation in the mangrove areas of Cochin were investigated by Muraledharan and Rajagopalan (1993). A preliminary survey on the fauna of Cochin mangroves was carried out by Sunilkumar and Antony (1994). Assessment of the heavy metal concentration on the mangrove flora and sediments was carried out by Thomas and Fernandez (1997). Badarudeen (1997) studied the Sedimentology and geochemistry of mangroves around Cochin. In a study by Shaly (2002), inter variability of phosphorus speciation in the mangroves around greater Cochin was addressed. Biogenic organic compounds and their derivatives in the Cochin mangroves were estimated by Rini (2002). Many of these studies have concentrated on the sediment chemistry of the mangroves and only a few paid attention to the overlying water. Moreover, none of these studies have attempted a comprehensive estimation of the ecologically pivotal nutrients and organic compounds. Estimation of inorganic nutrients alone is inappropriate as the organic compounds can be the most favourable form for aquatic biota in certain extreme conditions. Thus, hydrogeochemical evaluation of both inorganic and bioorganic compounds in the three main, yet varied coastal water bodies becomes necessary to understand the functioning of these ecosystems completely.

The present study is an investigation to address relevant chemical aspects of the three varied aquatic environments, such as mangroves, river and the estuary. The sampling locations include a thick mangrove forest with high tidal activity, a mangrove nursery with minimal disturbances and low tidal inundation, a highly polluted riverine system and an estuarine site, as reference. Nutrients and bioorganic compounds in the water column and surface sediment were estimated in an attempt to understand the regeneration properties of these different aquatic systems. Assessment of the trace metal pollution was also carried out. The main objectives of the study were:-

- to determine the spatial/ temporal variations of nutrients, bioorganic compounds and trace metals in the major reaction phases
- to understand the role played by diverse aquatic systems in the processing of vital nutrients
- to determine the quality of organic matter in each systems
- to understand the pathways of diagenetic processes occurring in diverse aquatic systems
- to gain insight into the transport/transformations processes of metals in different compartments of the aquatic systems
- to comment on the relative ability of aquatic systems in abatement of trace metal pollution

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# Chapter 2

# Analytical techniques and General hydrography

## 2.1 Introduction

A brief description of the study area, sampling protocols and various analytical methods employed are presented in this chapter. Results of investigation on the variation of prime hydrographical parameters such as salinity, dissolved oxygen, pH and temperature, grain size analysis are also presented in this chapter.

## 2.2 The study area

The Cochin backwater system ($9^0 28' - 10^0 10'$ N and $76^0 13' - 76^0 31'$ E) is the largest estuarine system on the southwest coast of India and it runs almost parallel to the west coast of India. It has all the characteristics of a tropical positive estuary. Lying between Azhikode in the north and Alappuzha in the south, this estuary extends over an estimated length of ~60kms and an area of ~ 21,050 ha. The Cochin backwater system is connected to the Arabian Sea through a permanent opening, the Cochin bar mouth, which, is about 450m wide and 8-13 m deep. Here, the depth is maintained by dredging as this opening is used for navigational activities. The bar mouth is also responsible for the tidal flux of the Cochin backwater system and is the only source of seawater intrusion to the estuary. Tides are semidiurnal type, showing substantial range and time. The average tidal range near the mouth of the estuary is ~ 0.9m.

The Cochin estuary is fringed by patchy mangrove vegetations and near the metropolis of Kochi, is situated Mangalavanam, which has recently been declared as a protected zone. This is station 1 in the present study (Figure 2.1). Mangalavanam is a small shallow mangrove system situated between approximately $9^0 59' - 9^0 60'$ N and $76^0 16' - 76^0 18'$ E. It is connected to the main backwater by a feeder canal and has an area of 2.8 ha. It resembles a shallow muddy pond of average depth <1m and with a small green island at the centre and periphery. During low tide, part of the muddy substratum is exposed. The dominant species are *Avicennia officinalis*, *Acanthus illicifolius* and a few *Rhizophora mucronata*. Decaying roots, stem and fallen leaves of the macrophytes add up considerably to the detritus of this ecosystem.

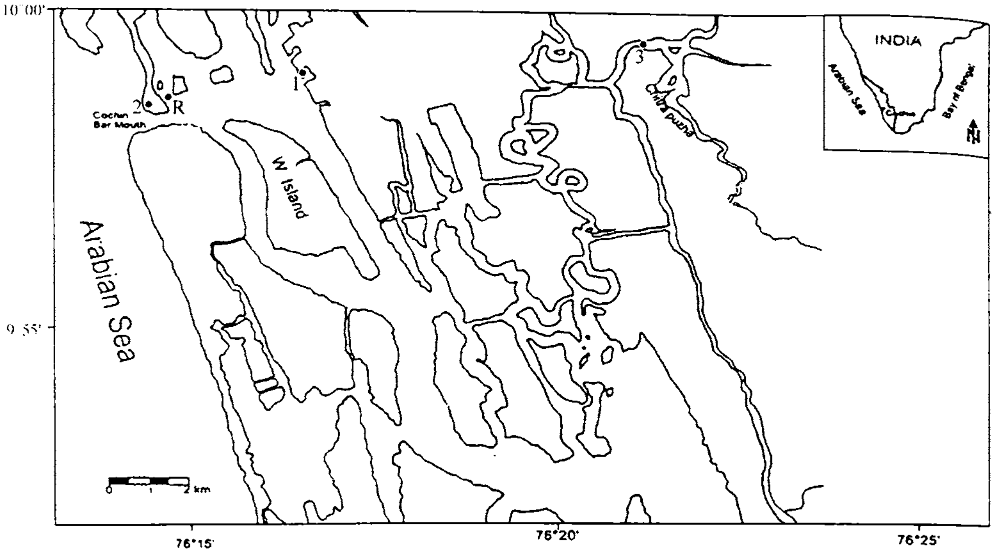

**Figure 2.1 The Investigated area with sampling stations**

Station 2 is located between latitude 9°58'N and longitude 76°11'E at Puthuvypu, on the southern tip of the Vypin island located on the northwestern bank of Cochin Bar mouth (Figure - 2.1). Since there is not much of destruction from outside and little disturbances, the succession of mangrove vegetation is progressing unhindered. At present, the mangrove vegetation consists primarily of *Avicennia*, which is growing gregariously on the Western side with *Rhizophora* and *Bruguiera* recording occasional growth. More extensive and highly developed mangroves are found on the Vypin Island (Basha, 1991). The sampling site was located at the terminus of a canal, which extends for about 1.5 km from open waters into the Kerala Agricultural University campus. This area is used by the University for the research in shrimp farming. The University maintains a 'mangrove nursery' and the samples were collected from the creeks running through it.

Chitrapuzha, station 3, (9°52′-10°00′N, 76°15′-76°25′E) is a tidal river, which forms part of the Cochin estuary. The river hosts diverse aquatic organisms and much area has been transformed into breeding pools so as to increase fish production. Numerous industrial units including a diesel power project, fertilizer manufacturing unit and a petrochemical unit, are located along the riverbanks. There are enduring local complaints about water pollution causing fish mortality and serious damage to agricultural crops. The river has thus considerable social, commercial and economic relevance.

## 2.3 Sampling Procedures

Samples were collected on a monthly basis from April 2000 to March 2001. All the glassware and plastic lab ware used were thoroughly cleaned with appropriate wash solutions. Surface water samples were collected using a clean plastic container, which was rinsed several times with collecting water before adequate amount was taken. Samples were then transferred to acid washed low-density plastic bottles. Temperature was determined immediately using a sensitive thermometer ($\pm 0.05^0$). 50 ml of the water sample was fixed in situ with Winkler reagents for the estimation of dissolved oxygen levels. Salinity and pH were determined immediately after returning to the laboratory. Sample for nutrient analysis were taken in low-density plastic bottles cleaned with dilute hydrochloric acid. Ammonium was preserved in situ using the phenol reagent and was kept in an icebox through its transport to the laboratory.

Surface sediment samples were collected using clean plastic scoops and the samples were transferred to clean plastic covers and kept in iceboxes till their transport to the laboratory. Only surface sediment samples were collected, as they are most important for the benthic organisms. After return to the laboratory, a portion of the samples was air-dried, and made into fine powder using an agate mortar and pestle. The dried samples were stored for subsequent analysis.

## 2.4 Analytical Techniques

All glassware used in the analyses were washed and soaked in appropriate wash solutions for 48 hours and rinsed several times with de-ionised water. They were finally rinsed with Milli-Q water and were dried at $150^0$C. Reagents used solutions were prepared using Milli-Q water. A Spectronics Genesis-10 spectrophotometer was used for the colourimetric determinations and for trace metals Perkin Elmer (Model 3110) atomic absorption spectrophotometer was used. The analytical procedures employed are discussed below.

### 2.4.1 Physico-chemical parameters

Common hydrographical parameters such as salinity, dissolved oxygen, pH and temperature were determined using standard procedures. Salinity was estimated argentometrically (Grasshoff, 1983a). Oxygen dissolved in water was fixed with Winkler reagents and were estimated chemically by Winkler method. Temperature and pH were determined at the time of sampling.

### 2.4.2 Sediment texture analysis

Texture analysis was carried out by the method of wet sieving and pipette analysis. A known weight of wet sediment was dispersed overnight in 0.025N sodiumhexametaphosphate (calgon) solution after the removal carbonates and organic matter. The sand fraction of the sediment was separated by wet sieving using a 63µ ASTM sieve (Carvar, 1971). The remaining portion containing silt and clay sediments was subjected to pipette analysis (Krumbein and Pettijohn, 1938; Lewis, 1984).

### 2.4.3 Dissolved nutrient compounds

For the analysis of dissolved nutrient compounds, the water samples were filtered using Whatman GF/C filter papers immediately after return to the laboratory. The filtered samples were stored in acid cleaned plastic bottles and were preserved under refrigeration until analysis.

### ➢ Ammonium

Ammonium, which was preserved in situ with phenol reagent, was analyzed immediately using the standard procedure given by Grasshoff (1983c). The compound was determined by measuring the absorbance of the molybdenum blue complex it forms using a spectrophotometer.

### ➢ Nitrite and Nitrate

Both nitrite and nitrate were determined colourimetrically by the method of Grasshoff (1983c). The absorbance of the azo dye was determined to estimate the concentration of the compound. Nitrate was determined after the reduction of the compound to nitrite by passing through the cadmium column. The reduced compound was determined the same way as above.

### ➢ Inorganic and total dissolved phosphate

Inorganic phosphate was determined colourimetrically according to the procedure put forward by (Grasshoff, 1983c). The various forms of dissolved phosphorus compounds that may be present in natural waters were converted to inorganic phosphates by oxidation with acid persulphate Grasshoff (1983c). The resulting inorganic phosphate ions were determined colourimetrically.

## 2.4.4 Sedimentary nutrient compounds

### ➢ Exchangeable ammonium

Nutrients adsorbed on the sediments were extracted with 2 N potassium chloride solution (Agemian, 1997). The dry powdered sediment samples were shaken with KCl for one and a half hours and centrifuged. The centrifugate was used for the analysis of exchangeable ammonium colourimetrically, using the indophenol method, in which it reacts with phenate in presence of hypochlorite and nitroprusside as catalyst.

### ➢ Total sedimentary nitrogen

In this study, sediments were collected from aquatic systems of distinct characteristics and hence the composition and geochemical behaviour of the sediments will be unique. Agemian (1997) has pointed out that some sediment may require stronger oxidants, such as potassium peroxodisulphate for the complete conversion of nitrogenous compounds into nitrate. Keeny and Nelson (1982) in their comparative study on the sensitivity of different detection methods for nitrogen have shown that colourimetric techniques are by far the most sensitive. Hence in this study, total digestion of the sediment sample with $K_2S_2O_8$ was done and the resulting nitrate was reduced to nitrite by the method described by Jones

(1984). In this method, spongy cadmium was used as the reducing agent. Spongy cadmium was prepared by dipping pure metallic zinc rods overnight in a cadmium sulphate solution. The spongy cadmium produced was separated from the zinc sticks and first washed with dilute hydrochloric acid. It was subsequently washed several times with double distilled water and finally with Milli-Q water. About 1g of this spongy cadmium was shaken with the centrifugate for one hour. The nitrite so produced by reduction was then colourimetrically determined.

### ➢ Total organic carbon

Total organic carbon in the sediments was determined by the wet oxidation method of Walkley and Black (1934) as modified by El Wakeel and Riley (1957). This involved the oxidation of organic matter by a known amount of chromic acid. The amount of acid used for the oxidation was determined by back titration with 0.5 N Mohr's salt solution with ferroin as indicator. Since chlorides may pose interference, correction for this was done using silver sulphate.

## 2.4.5 Bioorganic compounds

Biochemically important compounds such as carbohydrates, proteins, lipids and tannin and lignin both in the soluble form and those adsorbed onto the sediments were estimated in this study.

### ➢ Carbohydrate

Carbohydrate was determined by the complexation reaction between phenol and sulphuric acid (Dubois *et al.*, 1956). In this method, aliquots of water sample were made to react with concentrated sulphuric acid and 5% phenol. The resulting compound was estimated spectrophotometrically using D-glucose as the standard. For the sedimentary carbohydrates, the sediment was leached with 1N sulphuric acid at $100^0$C for one hour (Burney and Sieburth, 1977). The extract was cooled and the carbohydrates were determined after colour development.

### ➢ Protein

Protein in the sediments was estimated by the method proposed by Lowry *et al.* (1951). By this method proteins were dissolved in 1N NaOH solution at $80^0$C for 30 minutes. The extract was then cooled and aliquots were taken to which 5ml copper reagent (2ml each of 2 % copper sulphate and 4% sodium potassium tartrate and 96 ml 3 % sodium carbonate in 0.1N NaOH) and Folin-Ciocateu phenol reagent were added. After 40 minutes, proteins were estimated colourimetrically using bovine albumin as standard.

➢ **Total lipids**

Lipids were extracted from the sediments by the method suggested by Bligh and Dyer (1959). A 2:1 mixture of chloroform and methanol was used as the extractant. Extraction was repeated several times to ensure complete dissolution of lipids in this solvent mixture. The extracts were pooled together and dried in a dessicator. To this concentrated sulphuric acid was added and boiled at $60^0$ C in a water bath. After cooling phosphovanilin reagent (0.2% vanillin in 80% v/v orthophosphoric acid) was added. The absorbance of the resulting complex was determined spectrophotometrically using cholesterol as the standard.

➢ **Tannin and Lignin**

The hydroxylated aromatic compounds, tannin and lignin were also estimated spectrophotometrically. The method adopted was sodium tungstate-phosphomolybdic acid method (APHA, 1985). The aromatic hydroxyl groups in these compounds reduce the Folin-Ciocalteu reagent producing the blue coloured molybdic acid. The effects of Ca and Mg hydroxides and/or bicarbonates present in the sample were suppressed by the addition of trisodium citrate solution (Nair *et al.*, 1989). Tannic acid was used as the standard.

Tannin and lignin were batch-extracted from the sediments with 0.05M NaOH solution for 72 hours and the extract were pooled together and reagents were added for colour development, which was measured spectrophotometrically.

### 2.4.6 Trace metals

In this study, trace metals distributed in the three major fractions such as dissolved, particulate and sedimentary were estimated. The glassware and the plastic containers used for trace metal analysis was soaked in 5% nitric acid for one week and was washed with deionised water several times and finally rinsed with

Milli-Q water. The glassware were dried in an air-oven at $150^0$ C. the plastic containers were rinsed several times with the sampled water prior to sampling.

### ➤ Dissolved trace metals

Dissolved trace metals were separated from the particulate by filtration using 0.45µm cellulose nitrate filter paper. The filtrate was collected in acid-cleaned low-density plastic bottles and was preserved with $HNO_3$. Since the concentration of dissolved metals was low in natural waters, they required pre-concentration prior to analysis. Furthermore, since this study covers the entire salinity gradient, the analytical technique has to take into account the variable and complex matrix. One solution to this analytical predicament was to allow the dissolved metal to form complexes with organic chelating agents, extract the organo-metallic complex into an organic medium and then back-extract the metal into an aqueous medium by decomposing the complex with inorganic acid. The method provides the pre-concentrated sample with a consistent matrix (Klinkhammer, 1980; Statham, 1985; Coffey and Jickells, 1995). After pre-concentration, the matrix effects are sufficiently small to allow samples to be run against aqueous standard calibrations without the need for the routine use of the standard addition method (Jickells *et al*, 1992; Coffey and Jickells, 1995). Dissolved metal was estimated by the method described by many authors (Danielsson *et al*, 1978, 1982; Martin *et al.*, 1993, Dai and Martin, 1995).

The chelating agents used were ammonium pyrrolidine dithio carbamate and diethyl ammonium diethyl dithio carbamate. The metal was extracted with chloroform in several successions and were pooled together and back-extracted with $HNO_3$ and concentrated. The residue was then re-dissolved in warm 1M $HNO_3$ and made up to suitable volume. Metal concentrations were determined using graphite furnace atomic absorption spectrophotometer (Perkin-Elmer, Model 3110). Ultra pure metal nitrate solutions were used as standards.

### ➤ Particulate trace metals

Particulate trace metals were separated from its dissolved counterparts by filtration using Whatman 0.45µm cellulose nitrate fibre filters. The filter papers were cleaned by soaking overnight in dilute $HNO_3$, were washed thoroughly with deionised water, dried at $60^0$C and weighed. After filtration the particulate matter collected on the paper was dried at $60^0$ C in an oven and re-weighed. The metal was then leached in triple acid mixture of $HNO_3$, HCl and $HClO_4$. The residue was redissolved in dilute acid and made up to a definite volume. Metal concentration was determined using Perkin-Elmer atomic absorption spectrophotometer.

### ➢ Sedimentary metals

Metals adsorbed onto sediments were extracted similar to particulate metals. The residue was washed and centrifuged several times and the centrifugate was collected and made up. The absorbance was determined using ultra pure metal nitrate solutions as standards in an atomic absorption spectrophotometer using air-acetylene gas mixture.

### 2.4.7 Statistical analysis

Monthly variations in nutrients, bioorganics and trace metals were determined to identify the unique characteristics of the diverse aquatic environments under study. The calendar year was divided into three seasons, premonsoon (February-May), monsoon (June-September) and postmonsoon (October-January) since the heavy southwest and northeast monsoon periods are prime climatic determinants in this area. Seasonal averages of the monthly data are presented in tables and figures.

Simple correlation analysis was used to understand the inter-dependence of the determined variables with each other. Correlation coefficients are indices that measure the strength of a relationship between variables. The emphasis is on the degree to which two sets of values vary together around their respective means and on the direction of co-variation of the variable. In order to find out the cumulative effect of physico-chemical parameters on the trace metal concentrations, canonical regression analysis was also conducted.

### ➢ ANOVA

Analysis of variance was conducted in order to find the significance level of variance of the parameters with respect to month and with respect to sites. Two-way ANOVA was done using Microsoft Excel.

### ➤ Principal component analysis

Several papers (Meglen, 1992; Lee and Yi, 1999) proposed an integral approach to the examination of large environmental databases, based on the application of multivariate statistical methods such as Principal Component Analysis (PCA) and Cluster Analysis (CA). These methods resulted in wide and comprehensive analysis of the information contained in the database such as the general distribution of the data including clusters of similar groups, the significant parameters for the characterization of the systems and the source of micropollutants.

Principal component analysis or factor analysis was carried out for trace metals to find the 'latent variable' that, in numbers smaller than the original ones, could explain the variance and simultaneously reduced the dimensionality of the problem. By extracting the eigen values and eigen vectors, the number of significant factors, the percentage of variance explained by each of them and the participation of the old variable in the new 'latent ones' can be known (Hopke, 1983). The explained variance of some factors can be defined as the percentage of the sum of variance of these factors in the total variance. Davis *et al.* (1973) and Meglen (1992) have specified that factor number corresponding to a percentage value of 85-95% must be selected. Thus in this study, for trace metals, two factors or principal components with eigen value >1 was selected. The composition of the two principal components, referred to as factor 'loadings', is reported in the tables. Thus PCA analysis helps to evaluate the variation in spatial distribution of heavy metals, to identify any 'hot spots' of contamination and to determine the possible sources of the pollutants. The analysis was conducted using a software package 'Statistica' (version, 5.0) for windows.

### ➤ Cluster analysis

Since the present study encompassed three different aquatic environments such as mangroves, river and an estuary, their hydrogeochemistry may be significantly different. However, as the three systems are subjected to severe anthropogenic perturbations, the natural geochemical processes are astonishingly altered. Hence cluster analysis was carried out to identify any analogous behavioural patterns between the different sites. The clusters were joined together by tree diagrams. 'Statistica' (version, 5.0) for windows was used for the analysis and the plots were presented also.

## 2.5 General hydrographical parameters

Physico-chemical parameters such as salinity, dissolved oxygen, pH and temperature are the key parameters, which determine the status of each ecosystem. These environmental parameters can play a vital role in the prime ecosystem functioning and organic matter production. Hydrographical parameters are highly influenced by the local environmental regime and the hydrodynamic characteristics of the system. Since the southwest monsoon determines the major climatic variations in the study area, these parameters were found to change accordingly.

### ➤ Salinity

Salinity or salt concentration plays an important role in sustaining the aquatic life. Physical processes occurring in the systems affect surface salinity. The principal natural processes, which lead to change in salinity, are those, which bring about the removal or addition of freshwater. Salinity is increased by evaporation processes and reduced by the atmospheric run-off, increased river discharge and tidal intrusions etc.

Salinity varied distinctly at each of the sampling site. Spatial and monthly variation of salinity is depicted in Table A.1.The two mangrove sites varied in their salt concentration with station 2 exhibited higher salinity in all seasons. At station 1, salinity varied from freshwater condition to intermediate salinity values. Here, the salt concentration ranged between 0.29 to 14.56 ‰. At station 2, the variation was between 2.49 ‰ and 25.62‰. In the river water, salt concentration was very much low. In many months concentration was below detectable limit. The maximum range was 8.15 ‰ in the month of March. At the estuary, salinity varied between 0.87 to 22.13 ‰. Seasonally monsoon period was characterized by lowest salt concentration and the peak was observed in the premonsoon period (Figure 2.2). ANOVA statistics showed highly significant variation in salinity both among the sites and between months (Table B. 1).

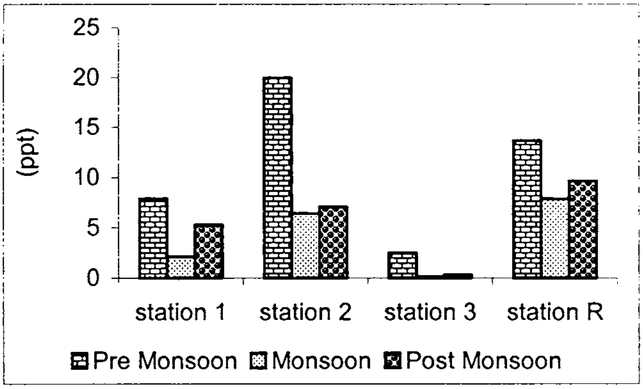

**Figure 2.2:- Seasonal mean variation of salinity**

Station 2 (fisheries station) dominated in salt concentration over that at station 1. Geographical setting and the varying hydrodynamic regime of the two sites could be the reason for this observed behaviour. Mangalavanam (station 1) was located very close to the estuary and tidal inundation was regular on semi-diurnal basis. The tidal activity has remarkable effects on the salt concentration. During flood tide, estuarine water covered the entire forest and diluted the waters, which might have got concentrated during the ebb tide. Since sampling was conducted only during the time of high tide, salinity may be low. However, at station 2, tidal activity was minimal as the entrance of floodwater to the creeks was limited to support the aquaculture practices. Hence water salinity would always be high at this site. Monsoon season recorded lowest salinity at both the sites clearly showing the dilution of the creek water with heavy monsoon showers coupled with increased land runoff. Intense evaporation was responsible for the high salt concentration observed during premonsoon. Concentration of the creek water by evaporation brought significant changes at station 2. Here, during premonsoon, salinity peaked up to 25.62 ‰. The intense summer condition together with the isolated nature of the site may be responsible for this observed hike in concentration. Correlation analysis revealed a co-variance of temperature with salinity, though less significantly (Table C. 1).

At station 3, salinity was very low and typical of a river site. High salinity was observed only during premonsoon and especially in the month of March. In the summer season, river flow was considerably reduced and saline water from the

At the riverine site the range observed was between 0.85 and 3.57ml/l. Seasonal variation at the estuarine site was relatively low and the variation was between 2.56 and 7.59ml/l. Seasonally, monsoon period recorded lowest concentration at all sites except station R (Figure 2.3). At the estuarine site monsoon and premonsoon values were similar. Premonsoon season exhibited peak in concentration at station 2 and 3. At station 1, postmonsoon period showed highest concentration.

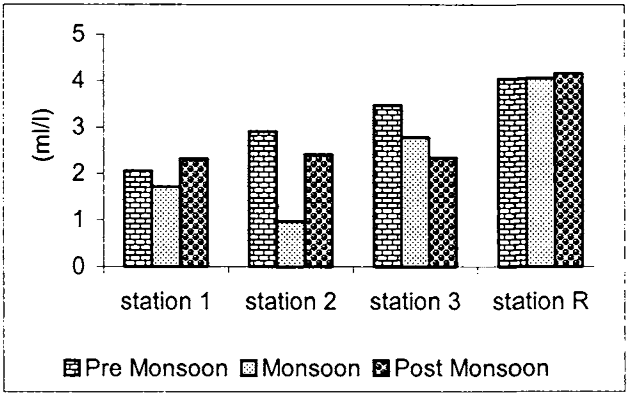

**Figure 2.3:- Seasonal mean variation of dissolved oxygen**

Biological decomposition of organic matter is the primary pathway in which oxygen is removed from an aquatic system. In mangrove habitats enormous quantities of organic matter are continuously added to the water column from the indigenous flora itself. About two third of mangrove production is litter, decomposition of which require substantial amounts of oxygen. Other than litter, plant parts like twigs, roots, shoots etc are also added to the overlying water. Mangrove-associated fauna includes diverse microorganisms and macrobenthic creatures. Respiration of these organisms again consume large amount of oxygen. Thus, by the microbial oxidation of organic matter, oxygen soon becomes limiting and an anoxic situation develops in the sediment and water column. Hence the observed low dissolved oxygen levels in this study can be considered as a characteristic of mangrove systems. Since mangroves are shallow systems, heavy influx of fresh water can disturb the sediment facilitating resuspension. The creek waters are turbid during monsoon season and organic production is considerably reduced. Thus, despite the low temperature of the monsoon season, which favours the dissolution of oxygen, dissolved oxygen levels were low during this period. Another reason is the high amount of terrestrially driven organic matter associated with the monsoon runoff. Oxidation of this additional amount of organic matter might have consumed oxygen in the water.

At the riverine site dissolved oxygen levels were significantly higher during the premonsoon season. The increased light penetration would have promoted primary production, which subsequently resulted in elevated levels of dissolved oxygen in the water column. Here, monsoon and postmonsoon periods recorded lower concentration. This can be related to the addition of organic matter by the heavy influx of runoff waters.

The estuarine site displayed almost similar levels of dissolved oxygen in all the three seasons. The substrate was mainly sand at this site, which has a poor coefficient of adsorption. Thus, by the action of tides and waves, the sediments were constantly washed and accumulation of organic matter may be minimum here. This leads to a uniform distribution of dissolved oxygen.

### ➢ pH

Many of the life processes are dependent on the hydrogen ion concentration in the surrounding medium. The pH of the medium depends on many factors like photosynthetic activity, precipitation, nature of dissolved materials, discharge of effluents etc. pH determines the solubility of many materials in natural waters. Photosynthesis, denitrification and sulphate reduction increase pH, whereas processes like respiration and nitrification decrease pH (Zhang, 2000). When photosynthetic reactions take place, carbon dioxide is reduced to carbohydrates increasing the pH of the system. Reduction in hydrogen ions occurs when respiration and degradation of organic matter take place, which add $CO_2$ to the water.

Hydrogen ion concentration did not vary significantly at any site in this study (Figure 2.4). River water showed distinctly lower pH values than other systems in all months. Since dissolution of ions increases the pH of the system, freshwater has pH value close to the neutral pH. However, in this study, a slight shift from the neutral pH was observed at the riverine site. Here, pH varied from 5.84 to 7.00 (Table A.3). This can be attributed to the influence of the effluent discharges of variable nature from industries located on the banks of this river. Though seasonal variation was minimum at this site, monsoon season recorded slightly higher values probably as the result of dilution of the system by the heavy influx of freshwater.

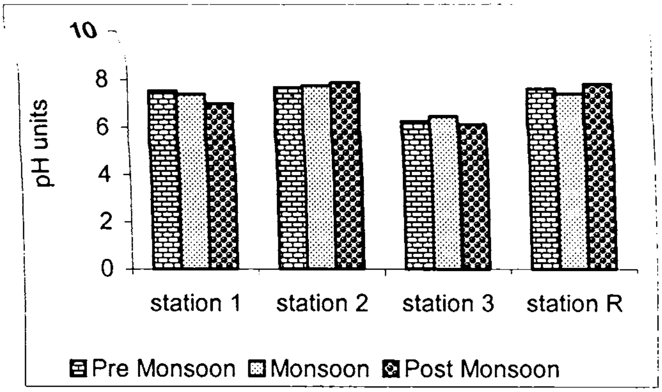

**Figure 2.4:- Seasonal mean variation of pH**

In the mangrove habitats, seasonal averages of pH did not show much variation from the neutral value. At station 1, pH ranged between 6.85 and 8.13 whereas at station 2, the variation was from 7.38 to 8.54. Though the intense remineralization of organic matter was expected to reduce the pH of the system, denitrification and sulphate reduction reactions are found to increase the pH (Zhang, 2000). Thus, in these mangroves, denitrification and sulphate reduction may be the dominating processes. The estuarine waters showed pH in the range 6.69 to 8.27. Here, monsoon season recorded the lowest values due to the influx of freshwater. Higher values were observed due to the influence of seawater. ANOVA statistics also showed highly significant variation between the aquatic systems (Table B.1).

## ➢ Temperature

Temperature is the prime hydrographical parameter, which can influence the chemistry of many compounds in natural waters. In this study, temperature showed highly significant variation between months whereas between sites, the variation was not significant (Table B. 1). At all the stations premonsoon season recorded highest temperature, which is a reflection of the increased atmospheric temperature.

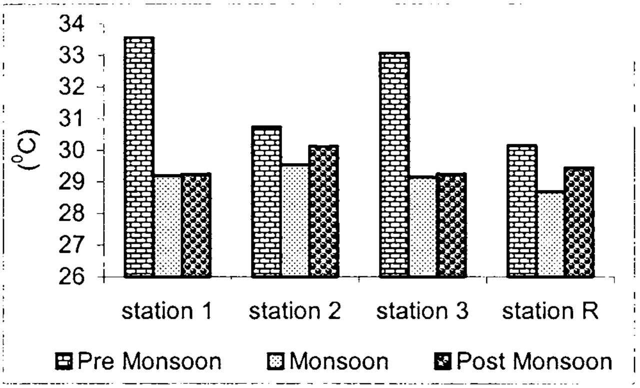

**Figure 2.5 Seasonal mean variation of temperature**

The seasonal mean variation of temperature at the different sites is depicted in Figure 2.5. At the mangrove station 1, temperature varied from $28^0$C to $36.5^0$C in the surface waters, whereas at station 2, the variation was from $28^0$C to $32^0$C. Between the mangrove sites, station 2 exhibited relatively lower temperature in all months during the study. At the riverine station, temperature varied from $28^0$C to $34.5^0$C. At the estuarine site, temperature varied from $28^0$C to $31.5^0$ C (Table A.4). Monsoon season was characterized by lowest temperature at all sites.

## ➢ Grain size analysis

Sediments are complex deposits of inorganic particles, organic matter, and adsorbed and dissolved constituents. With increased interest in monitoring and measurement of aquatic effects in the receiving environment due to industrial and domestic activities, it is imperative to understand the nature and character of the sediment. Quantitative analysis of the size distribution of particles can reflect mineralogical partitioning and thus act as an indicator of variation in physicochemical properties of sediments (DiLabio, 1995; Shilts, 1995). In addition, spatial and temporal variability of trace metal concentration in sediments has been attributed, in part, to particle size (Forstner and Wittman, 1981; Barbanti and Bothner, 1993). Further, it was observed that organic carbon, known to bind different concentrations, is inversely related to the proportions of sand-sized and directly proportional to the silt-and clay-sized sediment particles (Barbanti and Bothner, 1993). Hence determination of the particle nature in sediments is highly useful in understanding the sediment chemistry of nutrients, organic matter an trace elements.

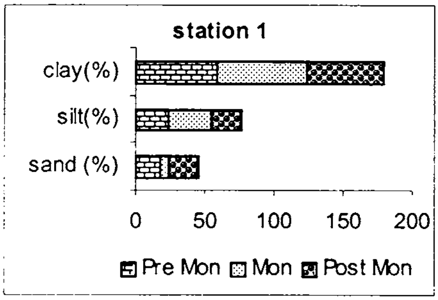

**Figure 2.6:- Percentage composition of sand, silt and clay at station 1**

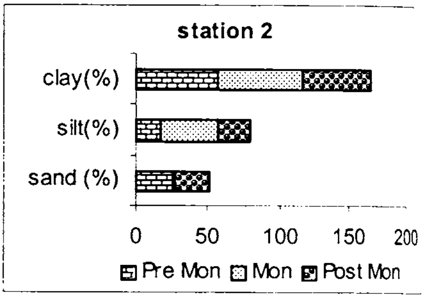

**Figure 2.7:- Percentage composition of sand, silt and clay at station 2**

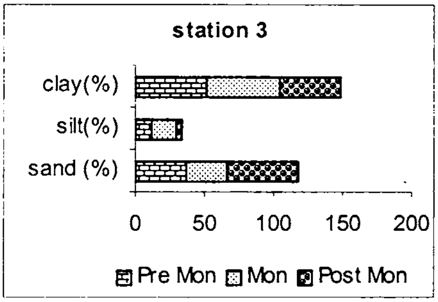

**Figure 2.8:- Percentage composition of sand, silt and clay at station 3**

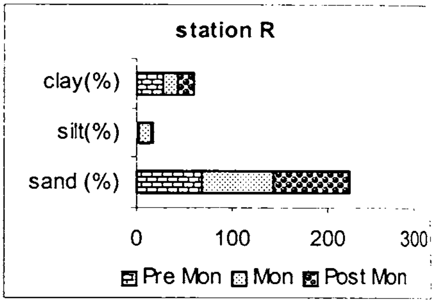

**Figure 2.9:- Percentage composition of sand, silt and clay at station R**

The variation in percentage composition of sand, silt and clay in sediments from the different aquatic systems are depicted in Figures 2.6, 2.7, 2.8 and 2.9. The aquatic systems under study were subjected to distinct hydrological regimes, and with unique environmental setting, composition of the sediment was exclusive for each system. However, the mangrove systems were found to be muddy substrates with the clay fractions dominating. At station 1, both the silt and clay fractions were dominating over the sand proportion in all seasons. Sand proportion was highly variable at station 2, which is also a mangrove site. Here, sand fraction was almost nil during the monsoon season reflecting the heavy influx of finer sediments associated with monsoon runoff. At both the stations monsoon season recorded highest proportion of silt and clay. Thus, in this study, sediments of mangroves were found to be of muddy nature.

The riverine and estuarine sediments exhibited a higher proportion of sand. In the river sediments, silt fraction contributed least to the particle composition in all seasons. Here, clay and sand fractions were found to be dominating alternatively in the three seasons. Clay content was high in the sediments as sediments were collected near the banks. The high proportion of the sand and silt fraction observed during the monsoon period might be due to the increased amount of finer particles in the runoff waters. In the estuary, sand was the prime fraction of the sediments. After sand, clay was the major component at this site. Sand fraction was found to be highest during the postmonsoon season. Thus in this study, mangroves habitats were identified as composed of muddy finer sediments while, the river sediments had variable dominance of sand and clays. The estuarine sediments were mainly composed of sandy sediments.

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# Chapter 3

# Nutrient dynamics

## 3.1 Introduction

Nitrogen and phosphorus are elements essential to a variety of biological and chemical processes, both at the organism level and on the scale of ecosystems. They can be considered as the 'back bones' of any ecosystem function. Nutrients are made available to the hydrosphere from precipitation and dry atmospheric fallouts and from weathering of rocks and soil minerals. The productivity of an aquatic system depends mainly on two conditions, the supply of fresh nutrients and their effective regeneration on rapid time scale. The assimilation of dissolved nutrients by primary producers cause a decrease in inorganic forms by converting them into particulate and dissolved organic forms. The particulate organic forms are usually transported in suspension and are ultimately remineralized or settled to the bottom sediments.

The distribution of nutrients in aquatic systems is controlled by variations in physical, chemical and biological processes. These dynamic processes being different in each aquatic realm, a successful understanding of the role of these systems as nutrient traps, filters and exporters require knowledge of the distribution of nutrients as well as of the rate of inputs, loss and accumulation in these environments. The three major aquatic environments (mangrove, river and estuary) analyzed in this study process nutrient compounds in distinct ways depending upon the physico-chemical condition existing there.

Mangroves are usually rich in nutrients due to their high productivity. Plant litter, mainly leaves, represents about one-third of primary production in mangroves and up to half this quantity can be exported via creeks to adjacent waters (Robertson *et al.*, 1992). Due to the regular tidal flushing, nutrients of different kinds are brought into the interior of the mangroves. Extremely anox conditions prevail inside the mangroves due to the anaerobic degradation proces In this anoxic environment, nutrient compounds undergo many chemic transformations and the water that leaves the mangroves during the ebb tide h characteristics peculiar to them, acquired during their long residence time in t swamps. They contain large amounts of dissolved organic matter in the form nutrient salts, like nitrates, ammonium, nitrites, phosphates and also silicates. Th export of these large amounts of organic material has a recognizable effect on foo webs in coastal waters (Odum & Heald, 1975; Alongi *et al.*, 1989; Alongi, 1990 Coastal outwelling of dissolved and suspended organic matter and nutrients fro mangrove swamps can also affect considerably the biogeochemical cycles o marine environments.

Most rivers carry low concentrations of dissolved inorganic nitrogen and phosphorus, which are actively taken up by plants and soil microbes and retained on land (Schlesinger, 1997a). Rivers are the major sources of phosphorus input to estuaries in the form of phosphate minerals in suspended detritus and as dissolved phosphate. Freshwater systems have been shown to trap, store, transform and release nutrients, thus significantly modifying the chemistry of water flowing through them (Hemond and Benoit, 1988; Whigham *et al.*, 1988). Effective regeneration of nutrients is found to occur in rivers. A single nutrient ion is found to have recycled many times within the river before it is finally transported downstream. The global transport of nitrogen and phosphorus has increased greatly as a result of human activities, such as the widespread use of nitrogen fertilizers and phosphorus detergents. Since one of the study sites is identified as a polluted river, determination of nutrient levels is important in assessing the pollution levels.

The distribution of nutrients in estuarine waters is controlled by the nature of estuarine circulation, mixing, and other physical processes, together with biological, sedimentological, and chemical effects. Nitrogen is supplied in elemental and chemically combined forms to estuaries. The most important forms of nitrogen for biogeochemical processes in estuaries are the dissolved inorganic species and organic nitrogen compounds in dissolved and particulate forms. Nitrogen supply to estuaries is important for primary production and the biological removal from estuarine waters may be achieved by sedimentation and burial. This process provides a nutrient-rich detrital resource for benthic productivity, and stimulates bacterial growth at the sediment-water interface. Phosphate can act as a regulator for estuarine phytoplankton biomass and is considered as a limiting nutrient in many situations. Generally, phosphate behaves in a conservative manner due to the buffering capacity of the estuarine waters. However, variation from this was often observed and the determination of estuarine concentration of nutrients is very important.

## 3.2 Dissolved nutrient compounds

Among the dissolved nutrients, forms of nitrogen selected for study were ammonium, nitrite, nitrate and urea. Dissolved inorganic phosphorus and total dissolved phosphorus was determined in order to assess the phosphate compounds in these aquatic systems. ANOVA calculations were conducted to determine the significant level of variation of these compounds in the different environments studied.

### ➤ Ammonium

Ammonium is the most abundant form of inorganic nitrogen in the surface water layers after a period of productivity when phytoplankton blooms have removed the greater part of nitrate and phosphate. In the assimilation process of phytoplankton, ammonium is preferentially used for synthesizing protein. When organisms decompose as a result of oxidative bacterial action they release nitrate and phosphate. As the water approaches anoxic conditions, bacteria use the nitrate ions to continue the oxidation process. This denitrification leads to the production of molecular nitrogen and ammonium. At the onset of sulphate reduction, ammonium and hydrogen sulphide are often produced, sometimes in high concentrations. The concentration of ammonium shows considerable variations and can change rapidly. In oxygenated, unpolluted waters, the amount of ammonium rarely exceeds 5µmol/l, but in anoxic stagnant water, the amount of ammonium can be as high as 100µmol/l.

In this study, ammonium exhibited highest concentration at the riverine site. However, this was closely followed by station 1, the mangrove site. The estuarine site displayed lower levels in all seasons (Table A.6). The order of abundance of ammonium-N in the various aquatic systems were, station 3 > station 1 > statio > station R. At station 1, ammonium varied from 23.38 to 161.6 μmol/l. Howe at the other mangrove site, station 2, the concentration was in the range 20.1 85.24 μmol/l. Ammonium ranged from 10.44 to 225.75 μmol/l at the riverine s The estuarine site displayed much lower ammonium levels compared to the oth three sites. At this site, ammonium ranged from 4.57 to 13.37 μmol/l.

Seasonally, all the sites exhibited a monsoon hike in concentratio (Figure 3.1). At the mangrove environments and at the riverine site lowe concentration was observed in the post monsoon period while premonsoon seaso was characterized by the minimum at the estuary. However the difference i concentration in the non-monsoon periods was only marginal. ANOV calculations showed significant difference in concentration among the aquati systems analyzed (Table B.2).

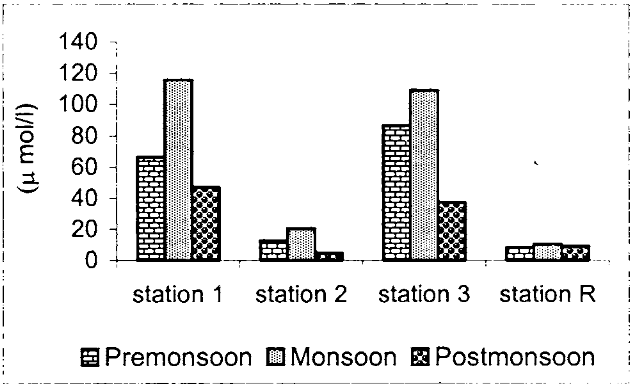

**Figure 3.1:- Seasonal mean variation of dissolved ammonium**

The elevated concentration levels of $NH_4^+$ in mangroves can be related to the increased rate of mineralization processes taking place there. Since oxygen is depleted in the water column due to the enormous load of organic matter degradation, anoxic conditions prevail in the sediment and water column. The mineralization process releases assimilated nitrogen compounds in the dead mangrove flora and associated fauna to the environment. $NH_4^+$ is the most preferred form since the other oxidized compounds of nitrogen are highly unlikely to form in this oxygen-deficient soils. Other studies done elsewhere on the mangroves also reported the dominance of $NH_4^+$ in the dissolved inorganic nitrogen (DIN) pool (Dittmar, 1999; Stribling and Cornwell, 2001; Konovalov *et al.*, 2001; Fourqurean *et al.*, 1993; Davis *et al.*, 2001).

In highly anoxic sediments, porewater contains large amounts of $NH_4^+$. Diffusion of porewater $NH_4^+$ further contributes to the dissolved $NH_4^+$ in the overlying water. Another important pathway for $NH_4^+$ in the anoxic sediments is the denitrification process. As Knowless (1982) states, denitrification relies on the presence of $NO_3^-$ as a precursor and organic compounds to provide electrons for denitrifying heterotrophs to form $N_2$ and $N_2O$. If nitrogen inputs were dominated by ammonia and nitrate levels were inadequate, direct denitrification would not be the favoured process (Smith *et al.*, 2000). Instead, a coupled process of nitrification-denitrification was a more likely pathway for denitrification within the ammonia-dominated system. This process has been found particularly important within the sediment rhizome matrix where macrophyte-release of dissolved oxygen within the anoxic sediments facilitates this transformation (Reddy *et al.*, 1989; Caffrey and Kems, 1992). Denitrifying bacteria plays an important role in the carbon cycle of the aquatic systems by oxidizing organic matter. Up to 50 percentage of carbon mineralized in euphotic freshwaters has been attributed to denitrifying activity (Anderson *et al*, 1977). Thus, by the increased rate of organic matter mineralization, amount of $NH_4^+$ produced also increases (Seitzinger, 1988). Many researchers have found a strong relationship between sedimentary organic carbon content and denitrification rates (Seitzinger, 1988; van Luijin *et al.*, 1999; Sander and Kalff, 1993). Hence denitrification can be a reason for the observed elevated concentration for $NH_4$-N in the mangrove waters.

Sediment resuspension and bioturbation both are found to increase the mineralization rate (Kristensen *et al.*, 1985). Organisms living in the sediment indeed modify the physical structure of the sediment by constructing burrows, by mixing, sorting and aggregating small particles into pellets and pumping water into and out of the bed. The activity of benthic organisms increases the amount of water in the sediment and these sediments are easily resuspended (Rhoads, 1974). Water soaking causes leaching of labile materials and promotes leaf conditioning by microbes (Chale, 1993). Since the mangrove sediments are organic and nutrient-rich, the potential for degradation is high (Fenchel *et al.*, 1998). Furthermore, retention of leaf litter by crabs in the sediments, which increase the leaching and mineralization rates within the forest, leads to high nutrient and organic matter concentration in porewater (Benner and Hodson, 1985; Boto and Willington, 1988; Smith *et al.*, 1991). Since bioturbation was high in the mangroves of the present study, increased rate of mineralization might have led to elevated levels of $NH_4^+$.

Of the two mangrove sites, station 1 recorded higher concentration than station 2. This can be due to two reasons. At station 1, bird droppings are very high in all seasons since this site is a bird sanctuary. The excreta of the birds are rich in ammonia and urea and this might have contributed substantially to the dissolved $NH_4^+$ pool. Another reason may be the characteristic hydrodynamic feature of this habitat. This site is an open system with regular flushing of tidal water. Stribling and Cornwell (2001) have shown that more frequently flooded sites contained higher $NH_4^+$. Since station 2 is of isolated nature, exchange with estuarine waters was minimal reducing the probability of build up of $NH_4^+$ in surface water.

Seasonally, monsoon period was characterized by peak concentration. This can be related to the increased runoff of $NH_4^+$-rich freshwater into the creeks. The heavy influx of freshwater can also disturb the sediment, and diffusion of $NH_4^+$ into the overlying water can take place. In the mangroves of Andhra Pradesh, Boillon *et al.* (2002) observed highest $NH_4^+$ levels during monsoon. In a previous study by Shaly (2002) a monsoon-hike and a postmonsoon minimum in the Cochin mangroves was reported. At both the mangrove sites, minimum was noted during the post monsoon period. After the turbulent monsoon period, as the temperature is raised during the postmonsoon period, mineralization processes occur at faster rates. $NH_4^+$ ions are found to have a natural affinity for negatively charged organic compounds in sediments and suspended particles (Seitzinger *et al.*, 1991). In the low salinity period of the post monsoon season, adsorption of $NH_4^+$ on particulates is favoured, which reduces the concentration of the compound in the dissolved fraction. However, as salinity increases in the premonsoon season, competition from seawater cations (primarily $Na^+$ and $Mg^{2+}$) also increases resulting in a higher molecular competition with $NH_4^+$ for the negative binding sites. Thus significant exchange of adsorbed $NH_4^+$ with other positive ions is to be expected with increasing salinity. In an experimental study by Rysgaad *et al.* (1999), it was observed that increasing salinity from zero to 10 ppt introduced large amount of

$Na^+$ ions, which removed all the adsorbed $NH_4^+$ ions. In addition to the ion exchange effect, increasing salinity also resulted in an increased number of anions in the porewater, which may ion pair with $NH_4^+$ and result in further reduction of $NH_4^+$ adsorption to particle surfaces (Gardner *et al.*, 1991).

Correlation analysis showed an inverse relationship of $NH_4^+$ with dissolved oxygen (Table C.2). In addition to this, nitrate also exhibited highly significant negative correlation with $NH_4^+$. These inverse relationships clearly show that $NH_4^+$ is produced in the anoxic mangrove water by the rapid reduction of nitrate that might have formed in the oxidizing microenvironments in the vicinity of plant roots. At both these mangrove sites, correlation exhibited by $NH_4^+$ and total dissolved nitrogen indicated the dominance of $NH_4^+$ among the DIN compounds.

The riverine site, Chitrapuzha recorded highest annual mean concentration of $NH_4^+$ among the aquatic systems under study. Though oxygenated water bodies contain low levels of $NH_4^+$, the abundance of the compound in this river points to some external supply. A cluster of industries (of which one is a fertilizer factory) is located on the banks of this river. Leachates from this industry may have contributed to the $NH_4^+$ pool at this site. Among the hydrographical parameters, temperature as well as pH was found to co-vary with $NH_4^+$ (Table C.2). Mineralization processes are found to increase at elevated temperature as a consequence of increased bacterial activity.

Stanley and Hobbie (1981), in a study on the Chowan River, US, found that dissolved organic nitrogen, which accounted for 69 percentage of the total annual inflow into this river, after assimilation by bacteria was regenerated in the form of $NH_4^+$. Smith *et al.* (2000) has shown that freshwater systems act as sinks for natural and anthropogenic nitrogen. In the present study, seasonal distribution of $NH_4^+$ showed peak concentration in the monsoon period. This can be related to the increased land runoff containing leachates from the effluent discharge points of the nearby industries. $NH_4^+$ was correlated significantly with total dissolved nitrogen at this site (Table C.2) pointing to the major proportion in which it present in the total dissolved nitrogen pool.

In the estuary, remarkably low concentration of $NH_4^+$ was observed. Here also, monsoon season recorded the maximum concentration. The hike concentration during this period can be related to the heavy influx of freshwa coupled with increased rate of runoff from various industries, waste disposal a fisheries industries. Furthermore, Savidge and Jhonston (1987) have shown th remineralization rate was highest when salinity was lower. As the salini increases, mineralization processes were found to decrease. Among th hydrographical parameters, salinity and temperature were found to correla inversely with $NH_4$-N as well as with nitrite (Table C.2).

### ➢ Nitrite

Nitrite occurs in aquatic systems as an intermediate compound in th microbial reduction of nitrate or in the oxidation of ammonia. In addition, nitrite can be excreted by phytoplankton especially during periods of luxury feeding. I unpolluted coastal surface water, $NO_2^-$ is generally below 1 μmol/l.

Nitrite, in this study, showed distinct distribution pattern in each of the systems analyzed. Generally, the concentration was lower in the mangroves. At station 1, $NO_2^-$ varied between 0.79 to 2.776μmol/l whereas at station 2, it ranged between 0.28 to 2.54μmol/l. Exceptionally high values of this compound was observed at station 3, the polluted river site. At this site, $NO_2^-$ varied from as low as 1.12 to as high as 31.02μmol/l. In the estuary, $NO_2^-$ ranged from 0.53 to 1.36μmol/l (Table A.7). Seasonally, the two mangrove stations recorded maximum concentration in the monsoon season, while at the river and estuary, concentration hike was observed in the premonsoon period (Figure 3.2). At station 1, minimum $NO_2^-$ was noted during the premonsoon season, whereas postmonsoon exhibited the lowest at station 2. Premonsoon and monsoon concentration levels varied only marginally at the riverine site. Estuarine site displayed lower concentration during the monsoon period. ANOVA calculations showed significant variation among the systems analyzed (Table B.2).

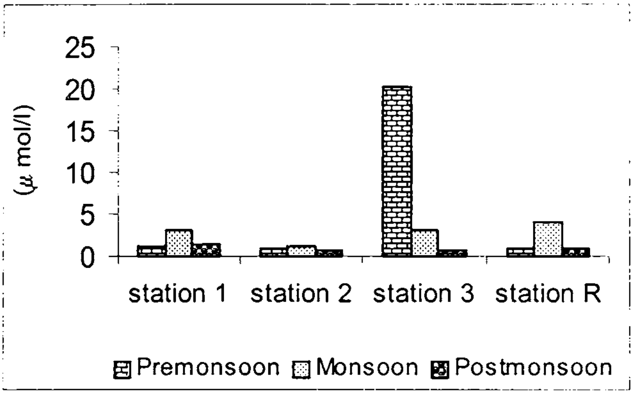

**Figure 3.2:- seasonal mean variation of dissolved nitrite**

Generally, $NO_2^-$ concentrations are very low in the anoxic mangroves forests. In this study also mangrove waters recorded very low nitrite content. However, among the two mangrove sites, station 1 showed higher values in all seasons than station 2. This may be due to the regular tidal flushing at this site. At the flood tide, oxygen-rich estuarine waters enter the forest and oxidation of ammonia might have enhanced leading to higher $NO_2^-$ content in surface water. At station 2, regular tidal flushing was not possible as the entry of floodwaters was manually restricted to support the prawn farming.

Though, oxidization of mineralized ammonium at the micro-environments in the rhizosphere of the mangrove sediments is possible, Yamada and Kayama (1987) through an experimental study have shown that concentration of $NO_2^-$ in the interstitial water was lower even in the warmer months. It is supposed that $NO_2^-$ is not liberated from sediments by diffusion. However, by the bioturbative forces, greater amount of oxygen is available in the sediments and $NO_2^-$ formed may diffuse to the upper layer through the disturbed sediment. The presence of high sulphide in the sediments is found to have a negative impact on nitrifying bacteria. Bacterial action is inhibited by sulphides (Furumai, *et al.*, 1988). Hence insufficient supply of dissolved oxygen and associated elevated levels of sulphides may be the reason for hampering oxidation of mineralized ammonium in these mangrove creeks.

Monsoon season was characterized by peak $NO_2^-$ levels at both mangrove sites. Increased rate of bacterial activity of the surface water may be reason for this observed concentration hike. The minimum values observed in premonsoon season can be related to the increased evapo-transpiration rate in t season leading to highly anoxic condition, which may have limited the formati of $NO_2^-$. Hydrographical parameters were found to have no influence on the N distribution in these mangroves as evidenced from their non-correlation with t compound (Table C.2). However, at station 1, nitrate was inversely correlated w $NO_2^-$. The observed concentration levels of $NO_2^-$ in the mangroves were similar those reported in previous studies (Shaly, 2002; Shriadah, 2000; Davis, 2001).

Highest annual mean concentration of $NO_2^-$ was observed at station 3, t riverine site. Exceptionally higher values were noted in the premonsoon season this site. Since many industrial establishments are located on the banks of th river, of which one is a fertilizer factory, effluents from their discharge points ca contaminate the river water. As the stream flow is highly reduced during th summer months, magnitude of the effluent discharges are higher as dilution wa minimized. Lower values recorded during the monsoon period also support th argument. Bacterial activity was higher in the summer months and due to increase mineralization, $NO_2^-$ content in the water column may have elevated. Furumai *et a* (1988) have shown that nitrification rates are increased in the freshwater system and they concluded that $NO_2^-$ oxidation was more sensitive at higher salinitie Correlation analysis showed significant correlation between $NO_2^-$ and dissolve inorganic phosphorus only (Table C.5). Mineralization processes are found t liberate inorganic phosphate and nitrogenous compounds to the surface water.

At the estuarine site $NO_2^-$ concentration did not vary much from that observed in the mangroves. This may due to the dilution of the estuarine water with nutrient-deficient marine water. At this site also premonsoon season recorded maximum concentration pointing to the elevated anthropogenic inputs in this season. The rivers draining into this estuary have many industries located on their banks, the effluents of which enhance the pollutant levels in this estuary. In the premonsoon period as the river inputs were considerably reduced, effluents discharge effects were more pronounced. In fact, $NO_2^-$ content in the non-monsoon season varied only slightly highlighting the anthropogenic sources of this compound.

Among the hydrographical parameters, salinity and temperature were found to have a negative impact on $NO_2^-$ in the estuarine water (Table C.2). This may be due to the decrease in nitrification rates as salinity increases (Furumai *et al.*, 1988). Among other nutrient elements, only ammonium-N showed significant inverse relationship with $NO_2^-$ (Table C.5) indicating that ammonium-N produced during the heterotrophic breakdown was biochemically oxidized to $NO_3^-$ *via* $NO_2^-$.

$NO_2^-$ reported in the present study was lower than those observed in the previous study by Shaly (2002). However, the levels were similar to those reported by Lakshmanan *et al.* (1987) in the bar mouth region. In the Mandovi estuary, Nasnolkar *et al.* (1996) observed very low levels of $NO_2^-$.

### ➢ Nitrate-N

Nitrate is the micronutrient that controls the primary production in aquatic systems. It is the final oxidation product of nitrogen compounds in aquatic system and is considered to be the only stable oxidation level of nitrogen in the presence of oxygen in seawater. If oxygen becomes depleted in water as a result of microbial remineralization processes, nitrate may be used as an alternative electron acceptor instead of oxygen. This process, called denitrification, leads to the reduction of a portion of the nitrate to molecular nitrogen. Nitrate as anions is not subjected to immobilization by the negatively charged soil particles (Atlas and Bartha, 1981) and is thus more mobile in solution.

Nitrate, in this study, exhibited extremely low concentration in the mangrove habitats. Mangalavanam (station 1) recorded higher values than station 2 (fisheries station). This variation was in accordance with that of nitrite. At station 1, nitrate ranged from 0.091 to 2.956μmol/l and at station 2, the concentration was in the range 0.051 to 2.900μmol/l (Table A.8). At both these sites postmonsoon season dominated in nitrate content and the lowest levels were observed during monsoon (Figure 3.3). Distinctly high values of nitrate were recorded at the riverine site. Nitrate varied between 7.518 to 32.26 μmol/l. Premonsoon exhibited highest concentration here, with a monsoon minimum. The estuarine site exhibited values that were intermediate between the mangroves and the river. In the estuary nitrate concentration as low as 2.579 to as high as 12.11 mol/l were observed.

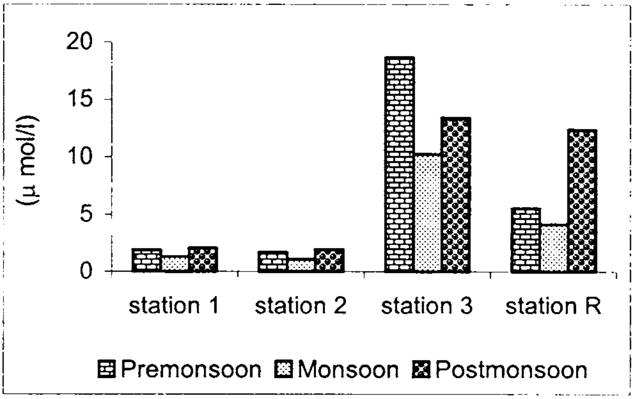

**Figure 3.3 : Seasonal mean variation of dissolved nitrate**

Of the two mangrove environments, station 1 was noted with higher nitrate content than station 2. This variation can be attributed to the regular flushing of the oxygenated estuarine water at station 1, whereas station 2 is of isolated nature. Hence, intense anoxic conditions might have developed in the creeks leading to increased mineralization. The general lower concentration of nitrate in mangroves can be due to the prevailing anoxic condition inside the forest. Since the decomposition process of enormous quantity of organic matter consumes available dissolved oxygen to meet with the oxygen requirement of the microbes, nitrate ions are used leading to the depletion of the compound in these environments.

The anoxic environment of the mangroves favours denitrification process. By this process, facultive anaerobic bacteria transform nitrate into nitrite and then to nitrogen gas (Knowles, 1982). Presence of nitrate as the precursor of the reaction and organic compounds to provide electrons is found to increase the rate of denitrification. The process has been found particularly important within the sediment-rhizome matrix where macrophyte-release of dissolved oxygen within the anoxic sediment facilitates this transformation (Reddy, *et al.*, 1989; Caffrey and Kemp, 1992). Hence, in the mangroves, all the conditions are highly conducive for this process, which removes nitrogen from these systems. In addition to this, Kristensen *et al.* (1998) have shown that nitrogen fixation is generally low in mangrove sediments, diminishing the potential for N-enrichment during decomposition.

However, Lakshmanaperumalsamy (1987) has reported very high population of nitrogen fixing bacteria, *Azetobacter* spp., in the mangrove sediments than in the marine backwaters and in estuaries. Halotolerant nitrogen fixing *Rhizobium* strains have been isolated from the root nodules of mangrove plants in Sunderbans (Sengupta and Chowdhary, 1990). Hence nitrate may have formed by the nitrification processes in the mangroves. Generally, higher concentration of organic carbon and nitrate in the mangrove sites is due to the high concentration of humic substances in sediments, which are known to have a high C/N ratio. High levels of phosphorus and nitrogen have been reported in sediments due to the decay of mangrove foliage (Sahoo *et al.*, 1991). Since humic substances are reported to be present in the Cochin mangroves, mineralization of these compounds may be the reason for the observed low nitrate levels in these mangroves.

Sediment resuspension and bioturbation both are found to cause increased mineralization and nitrification (Kristensen *et al.*, 1985). In an experimental study by Yamada and Kayama (1987) concentration of nitrate was found to increase by bioturbation. Since bioturbation was very high in these mangroves, nitrification reactions may have taken place, producing nitrate. Due to the intense mineralization processes ammonium-N is produced in plenty in these mangroves. Cifuentes *et al.* (1988) opined that no phytoplankton assimilation of nitrate would take place if the $NH_4^+$ concentration remained greater than 2μM. $NH_4^+$ observed in these mangroves were manifold greater than those of nitrate. Hence nitrate produced might be present in the water column itself.

Seasonally, post monsoon season recorded maximum concentration at both the mangrove sites. Minimum concentration was noted in the monsoon season and might be due to the turbulent condition in the creek water, causing sediment resuspension. Correlation analysis (Table C.5) revealed some interesting features of these mangrove systems. At both the stations, remarkably high inverse correlation of nitrate was observed with both nitrite and ammonium. This clearly shows that nitrate produced in these systems is immediately reduced to nitrite or ammonium. At station 1, dissolved oxygen exhibited high correlation with nitrate, augmenting this proposition.

Highest nitrate concentration was observed at the riverine station in this study. In freshwaters, since dissolved oxygen levels were generally high, formation of nitrate is highly favoured. However, the most probable source of this compound in this river is the effluents discharged from the nearby industries. Nitrate is used extensively in agriculture and a fertilizer factory is located on the banks of this river. Leachates from this might have significantly contributed to the nitrate pool of this river.

Seasonally, monsoon recorded lowest concentration while premonsoon recorded the highest. In the summer season, when the river flow is considerably reduced, effluents are discharged to this river without much treatment. Heavy influx of freshwater coupled with terrestrial runoff might have a dilution effect on the compound in the monsoon season. Correlation statistics revealed a temperature driven reaction pathway for this compound (Table C. 2). Nitrate did not correlate with any other nitrogeneous compounds (Table C. 5).

Similar to the nitrite distribution pattern, the estuarine site displayed nitrate concentrations intermediate of the mangroves and river. At this site also, postmonsoon season recorded higher values. Sources of nitrate to this estuary may include the industrial effluents, sewage outlets and the fishery wastes. Extremely low concentration levels observed in the monsoon season may be due to the dilution effect of the monsoon showers. Among the hydrographical parameters, dissolved oxygen and pH were found to regulate the nitrate dynamics in this estuary (Table C. 2).

### ➢ Urea

Urea is a low molecular weight organic compound and is used by marine phytoplankton as a source of nitrogen. Hydrolysis reaction of urea is weakly exothermic and so does not allow ATP synthesis from ADP and phosphate. Hence it is less attractive for the heterotrophic organisms than more complex organic compounds. On the other hand, it is a nitrogen compound easily hydrolysable for autotrophic organism, which are under nitrogen limiting conditions.

In this study, highest annual mean concentration of urea was observed at station 1, the mangrove station (Table A.9). The order of abundance of the compound in this study was, station 1 > station3 > station 2 > station R. At station 1, urea varied between 1.11to 69.13µmol/l whereas at station 2, also a mangrove site, recorded much lower values. Here, urea ranged from below detectable limit to 15.35µ mol/l. At station 3, urea varied from as low as 0.51 to 36.56µmol/l. The estuarine site displayed much lower values of urea ranging from 0.04 to 10.06µ mol/l. Except at station 3, all other sites exhibited highest concentration during the monsoon season (Figure 3.4). At station 3, premonsoon recorded the maximum concentration. The lowest concentration was observed in the postmonsoon season at all stations except at station R. Here, the non-monsoon period did not vary much in urea content. ANOVA showed significant variation within the stations analyzed and not between months (Table B. 2).

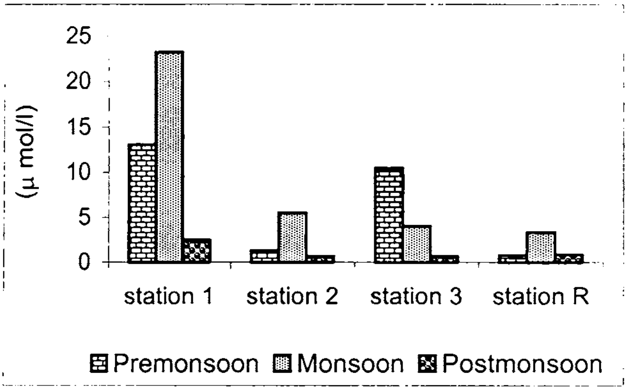

**Figure 3.4:- Seasonal mean variation of dissolved urea**

Mangalavanam (station 1) exhibited distinctly high urea concentration among the mangroves. Urea is excreted into the environment as an end product of nitrogen metabolism by many higher organisms and as a product of microbial action on amino acids, purins and pyrimidines. Station 1 is a bird sanctuary also and in all seasons local and some migratory birds inhabit here. Large amounts of bird excreta of which both urea and uric acid are the major fractions, were present at this site. Besides, this site is located very near to the urban area and sewage disposals also might have contributed significant amount of urea. Station 2 is a closed system with minimum human interference. The main source of urea in this system may be the excreta of the indigenous fauna. At both these sites, monsoon season recorded highest concentration may be due to the increased terrestrial inputs. Correlation analysis (Table C.5) showed significant correlation of urea with ammonia at station 1 indicating their common origin from the bird excreta. Highly significant inverse relationship with dissolved oxygen was also observed at this site (Table C.2).

Extremely high concentration of urea was observed at the riverine site in the month of April and July. Since many industries including a fertilizer-manufacturing unit are located on the banks of this river, substantial amounts of urea might have leached from the effluent discharge points. During April, as the stream flow was considerably reduced, the dimensions of the effluent discharges were most significant. Urea is extensively used for agricultural purposes and leachates from the fields may be the reason for the observed high concentration of the compound in the peak monsoon month, July. In the estuary also, concentration of urea was much lower except in July. In this month, maximum concentration of urea was observed. Runoff from land in the high-energy period of monsoon may be the reason for this observed high value. Effluents from industries located on the banks of the rivers draining to this estuary may also have contributed to the urea pool of this estuary. None of the hydrographical parameters correlated with urea point to an anthropogenic origin (Table C.2). In the non-monsoon period, concentration was significantly low in estuarine waters.

### ➢ Dissolved inorganic phosphorus (DIP)

The principal dissolved species of phosphorus in natural waters is the inorganic phosphate anion ($PO_4^{3-}$). In river water, phosphate is derived from natural weathering processes, from oxidation of urban and agricultural sewage and from the breakdown of polyphosphates used in detergents. The dissolved phosphorus is taken up by plankton and after death and decay of organisms, a proportion of this phosphorus is returned to water. The concentration of dissolved phosphorus in most unpolluted river water varies between 0.1 and 1μM (Meybeck, 1982) although higher values are not uncommon, particularly in rivers draining from industrial or agricultural watersheds (Meybeck, 1982; Alongi *et al.*, 1992).

Dissolved inorganic phosphorus showed higher concentration in the mangroves and in the river than the estuary. The order of abundance of the element was station 3 > station 1 > station 2 > station R. DIP ranged from 8.35 to 69.13µmol/l at station 1, from 7.17 to 30.55 µmol/l at station 2. The polluted river site showed highest annual mean concentration. Here, DIP varied from 10.23 to 110.0µ mol/l. Generally very low levels of DIP was noted in the estuarine waters. Here, it ranged between 0.59 to 10.06µmol/l (Table A.11). Seasonally, premonsoon season was found to be dominating in DIP concentration at stations 2 and 3, while monsoon period recorded highest concentration levels at station 1 and R (Figure 3.5).

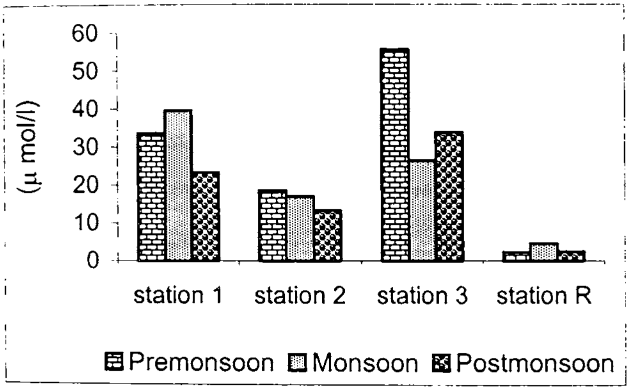

**Figure 3.5:- Seasonal mean variation of dissolved inorganic phosphate**

Mangroves are considered as exporters of nutrient elements to adjacent water bodies (Dittmar and Lara, 2001). They can act as source for nitrogen and phosphorus nutrients by the 'out welling' mechanism. In general, concentration of DIP was high in the mangroves. Results summarized by Alongi *et* al. (1992) show that DIP concentration in unpolluted mangrove waters can vary between <0.1 and 20 µM. Since enormous loads of organic matter are mineralized in the mangroves through microbial action, phosphates and ammonium are released in greater amounts into the system. The reducing conditions prevailing in the mangroves favours desorption of phosphate from sediments, particulate organic phosphate and/or dissolved organic phosphorus. However, local characteristics as well as intertidal position, season and time of sampling can account for wide range of concentration.

Phosphorus is shown to have a high affinity for ferric hydroxide adsorption sites in natural waters. Due to the intense anoxic condition prevailing in the mangroves, these oxyhydroxides are reduced and trigger the release of adsorbed phosphorus into the overlying water (Buccini, 1985, Smolders and Roelofs, 1993; Stribling and Cornwell, 2001). Another source of DIP in the water column is that released during the degradation of organic matter in aquatic sediments. Phosphate released from sediments is controlled by the sulphate reduction (Caraco *et al.*, 1989); as $S^{2-}$ produced from sulphate respiration may reduce the Fe-oxides in the sediment and thus promote the release of Fe-bound phosphorus (Jensen *et al.*, 1995; Howarth *et al.*, 1995). In addition to this, high amounts of sulphate may cause phosphate release due to the competition between sulphate and phosphate for anion adsorption sites (Caraco *et al.*, 1989; Beltman *et al.*, 2000).

In this study, Mangalavanam, station 1, recorded higher DIP in all seasons than station 2 among the two mangrove habitats. Due to the regular tidal inundation of estuarine waters, station 1 is flooded on a semidiurnal basis and Stribling and Cornwell (2001) have shown that nutrient elements were high at sites with regular flushing. Nutrient dynamics in creeks are significantly influenced by porewater inputs from the upper layers of sediment (Dittmar, 1999; Lara and Dittmar, 1999). The nutrient-rich water at low tide is not immediately exported from the mangroves, but transported back at the beginning of the flood tide. In the course of flood tide, it is mixed with nutrient-poor estuarine water and spread out in the mangrove at high tide. During the ebb tide, a comparatively well-mixed water body leaves the mangroves. Only when most water has already flowed out and the water body stagnates does the influence of porewater leads to elevated nutrient concentration. This water, enriched with nutrients and organic matter, is not directly exported. It first returns to the forest where it mixes with the estuarine water. Thus, due to the regular tidal activity, nutrient concentration in the creeks of station 1 may be elevated. Since station 2 is a closed system with minimum tidal activity, DIP concentration was low. Furthermore, station 1 can have an additional supply from the excreta of birds since this site is a bird sanctuary also.

Effluents from many shrimp farms could have contributed to the phosphate pool of mangroves. It has been reported that of the total quantity of formulated feed used in shrimp farms, 10 percent gets dissolved in water and 15 percent goes unbeaten (Diana *et al.*, 1994). The unbeaten compound gets decomposed by the microbes increasing the nutrient levels in water and sediment. Furthermore, other studies also emphasized the role of mangroves in processing the effluents from aquaculture areas. According to Alongi *et al.* (1992) and Boto (1992), aquaculture effluents or sewages enriched in nutrients added to mangrove areas may be sequestrated and processed by sediment bacteria. When the water from the shrimp farms is discharged into the natural water bodies during regular water exchange and along with sediments during harvest at the end, there are chances for nutrient enrichment when tidal flushing could not neutralize the impact through discharge. Since station 2 is located near the prawn farm, effluents from this would have significantly influenced the DIP load in this mangrove.

Monsoon season recorded peak concentration at station 1. Terrestrial runoff enhanced during the monsoon period may be the reason for this observed hike in concentration. At station 2, monsoon and premonsoon concentration differed only a little. However, premonsoon season exhibited higher values. This can be related to the increased bacterial activity in this season. At both mangrove habitats, postmonsoon recorded the minimum concentration. Relatively reduced runoff and low mineralization rates can be the possible cause for this decreased DIP concentration. Among the hydrographical parameters, dissolved oxygen was correlated inversely with DIP at station1 (Table C.2). As anaerobic decomposition was predominant in this oxygen-depleted water, enhanced rate of mineralization increases the DIP level in the surface water. At station 2, pH was found to regulate DIP concentration. At this site, both DIP and total dissolved phosphorus exhibited high correlation (Table C.5).

Highest concentration of DIP was observed at the riverine site in this study. Though, freshwater systems contain lower phosphorus levels than seawater (Garcia-Soto *et al.*, 1990), high concentration of DIP in this river points to anthropogenic inputs. Industrial effluents were found to be an important source of pollutants to this river. Emanations from these industries, in particular, the fertilizer factory may be the reason for the observed high DIP levels in this river. Premonsoon season recorded the highest concentration pointing to the increased dimensions of these effluent discharges at the time of reduced stream flow. Coupled with this, elevated rates of mineralization processes due to the increased bacterial activity in the summer months would have favoured release of DIP from sediments. Mulholland, (1992) has further shown that during river transport, phosphorus is adsorbed on sediments and suspended materials. Considerable dilution of the effluents would have occurred in the monsoon season as evidenced by low DIP concentration during this season. Correlation analysis (Table C.5) revealed that DIP co-varied with both nitrite and nitrate indicating their common source presumably the effluents.

Relatively lower concentration of DIP was observed at the estuarine site. Since the study site was located near the Cochin bar mouth, considerable dilution of the nutrient-rich estuarine water with nutrient-deficient marine waters might have occurred reducing the DIP concentration levels. In this estuary, DIP varied from as low as 0.59 to as high as 10.06µmol/l. This extremely high value was noted in the month of July, the heavy monsoon period. Thus, land runoff may be the most significant contributor of DIP in this estuary. The almost ubiquitous nature of phosphate pollution from detergents, fertilizers, and domestic/industrial effluents is identified in early studies. Cochin estuary receives large amount of effluents from industries located on the rivers draining into this. Moreover, urban sewage disposals and nutrient-rich effluents from aquaculture practices are released into this estuary without much treatment increasing the phosphate load of this estuary. According to Valdes and Real (1998), resuspension of sediments increases the DIP concentration. Regular dredging of the shipping channel was done every year in this estuary, which will promote the sediment resuspension. Since the site vas located near the Cochin bar mouth, tidal action by the waves also promotes esuspension. None of the hydrographical parameters exhibited any correlation vith DIP at this site augmenting its anthropogenic source (Table C.2).

### ➤ Total Dissolved Phosphorus (TDP)

Phosphorus exists in natural waters in a wide variety of forms including the norganic and organic fraction. Inorganic phosphates remain mainly in the form of [PO$_4^{2-}$ ions. Condensed phosphoric acids such as diphosphoric acids and olyphosphoric acids with P-O-P linkages are detected in the estuarine water. The rganic fraction mainly contains the decomposed and excreted compounds of dead ganisms and includes phospholipids, phosphonucleotides and their derivatives.

Determination of total phosphorus thus becomes very necessary to understand the nutrient dynamics of the aquatic systems completely.

In the present study, total dissolved phosphate showed wide variation in the various systems analyzed. The highest concentration was observed at station 3 in all seasons except monsoon. In the mangroves, TDP concentration varied between 10.02 to 74.01 µmol/l at station 1 and from 12.01 to 55.81 µmol/l at station 2. Station 3, the riverine site exhibited generally high values. TDP varied from 23 to 118.98 µmol/l at this station. Very low concentration levels of TDP were observed at the estuarine site. Here, TDP ranged from 4.94 to 29.64µ mol/l (Table A.12). Seasonally, postmonsoon season recorded the minimum concentration and monsoon the peak concentration at stations 1 and R (Figure 3.6). At the riverine site and at station 2 highest concentrations were observed during the premonsoon season while minimum concentration was recorded during the postmonsoon period.

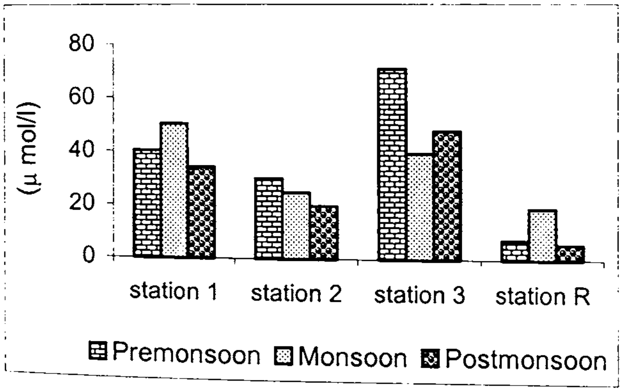

**Figure 3.6:- Seasonal mean variation of total dissolved phosphorus**

Similar to the trend with other nutrient compounds, Mangalavanam (station 1) recorded higher TDP levels than station 2. Regular flooding with estuarine water together with increased sewage inputs may be the reason for this observed high concentration. Station 1 is located near the metropolis of Cochin and large amount of urban sewage is released into this area. Polyphosphates are found to be a major component in phosphorus detergents and this would have contributed substantially to the TDP pool at this site.

Redox reactions are found to significantly regulate phosphorus dynamics in water bodies (Schlesinger, 1997b). Anoxic waters usually show high concentration of phosphorus. Anaerobic conditions in sediments can control the phosphorus solubility, through changes in the $Fe^{3+}/Fe^{2+}$ ratios. Furthermore, reductive dissolution of Fe(III) oxyhydroxides are found to release phosphorus adsorbed onto them along with Fe(II) ions. This promotes an increase in the dissolved phosphorus concentration in interstitial waters, with Fe being converted to soluble Fe sulphides (Krom and Berner, 1981; Caraco *et al.*, 1989). This process is catalyzed by enzymes released by nitrate and sulphate reducing bacteria and depends on the carbon source. In a phosphorus speciation study by Shaly (2002), Fe-bound phosphorus fraction was the major form of phosphorus in the mangrove sediments of Cochin area. Hence reductive dissolution of this fraction in the highly anoxic sediments is highly possible in these mangrove sites.

Seasonally, monsoon recorded high values at station 1 emphasizing large inputs of phosphates by the terrestrial runoff waters. Here, lower values were observed during the postmonsoon season. In contrast to this, premonsoon season dominated in TDP content at station 2. As the temperature increases in this period, bacterial action is enhanced releasing increased amount of phosphate to the surface water. Correlation analysis showed high correlation of TDP with DIP, nitrite and pH (Tables C.2 and C.5).

The riverine station exhibited highest annual mean concentration of TDP. This can be due to the high anthropogenic input of phosphate into this river through industrial effluents. High concentration observed in the premonsoon season clearly shows that the magnitude of these emanations increased during the reduced flow period. By the increased bacterial activity, remineralization of organic matter would also have contributed to the TDP pool of this river. Correlation analysis showed that both DIP and TDP co-varied in this river pointing to their common source (Table C.5). The estuarine distribution of TDP was different from that at the other sites. Relatively low concentration of TDP was observed here. Monsoon season exhibited highest TDP concentration, which can be related to increased runoff from land. Since this estuary is largely used as an urban and aquaculture waste disposal site, heavy influx of freshwater may contain leachates from these discharge points. None of the hydrographical parameters exhibited any correlation with TDP at this site confirming its anthropogenic sources (Table C.2).

### [illegible].2.1 N/P ratio

The N/P ratio (Redfield ratio) can be used to assess the nutrient status of a system. It is used to evaluate the major nutrient demand for production of phytoplankton biomass (Redfield, 1963). Nitrogen and phosphorus are assimilated in an approximately constant proportion of 16:1 (by atoms) by phytoplankton from seawater as they grow. Thus, N/P > 16 indicates than P is the limiting nutrient for algal growth and if N/P < 16 denotes an excess of P where nitrogen becomes the limiting nutrient.

In this study, the bioavailable forms of inorganic nitrogen i.e., ammonium, nitrite and nitrate were summed up to get the total dissolved nitrogen. This quantity was used to calculate the N/P ratio with dissolved inorganic phosphorus, DIP. The highest annual mean N/P ratio was noted at station R, the estuarine site and the lowest was detected in one of the mangroves, station 1. In fact, the river displayed N/P ratio close to that of the mangroves (Table A.13).

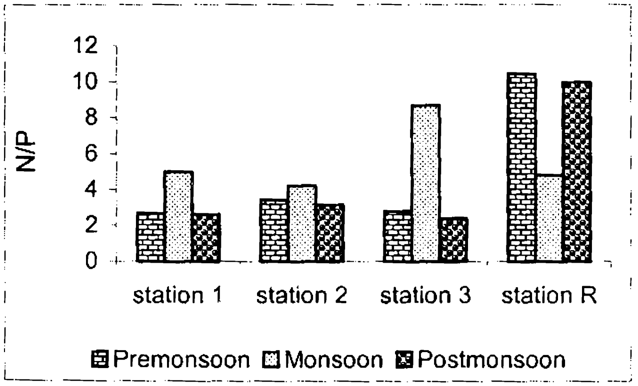

**Figure 3.7:- Seasonal mean variation of N/P ratio**

N/P ratio in this study exhibited significant seasonal variation. Monsoon season was characterized by the highest ratio at all stations except at the estuarine site where the lowest was observed in this season (Figure 3.7). At station 1, the annual mean ratio was 3.42 indicating that this site may be nitrogen limited. However, during the monsoon season the ratio was 4.99. The elevated nitrogen concentration during this period clearly shows its terrestrial origin associated with the monsoon runoff.

Marine algae are considered to be phosphorus limited when the N/P ratio is > 6 and nitrogen limited when the ratio is > 4.5. The two nutrients are near the assimilative proportion in the range 4.5 to 6. In the mangroves, in the peak monsoon month, July, the nutrients were in assimilative proportion. In the non-monsoon months the system is severely nitrogen limited. At station 2 also, monsoon season displayed higher N/P ratio. Here, N/P ratio varied between 1.39 and 6.61. However, the ratio was a little lower than the assimilable proportion, although, at this station it can be considered that nitrogen concentration is influencing the proportion.

At the riverine site, the non-monsoon period was severely nitrogen limited as evident from the low ratios (2.4 and 2.8). Exceptionally higher value (23.09) was observed in the monsoon period clearly showing that the main source of nitrogen in this river is the land runoff. During this period, heavy load of nitrogen was leached into the river water. The estuarine site displayed completely different seasonal distribution. Here, during the monsoon season, the ratio was the lowest. However, during this period, the ratio was in the assimilative proportion. Generally, in the non-monsoon periods N/P ratio was much higher and points to the increased rate of release of effluents containing the nitrogen fertilizers.

By the analysis of N/P ratio it can be concluded that though the nutrient levels were much lower in the estuary, it reflected an N/P ratio closest to the theoretical value. The river, which recorded the highest nutrient concentrations have the elements in the most assimilative proportion. The two mangrove habitats can be considered as severely affected by anthropogenic perturbations.

## 3.3 Sedimentary nutrients

In an aquatic system, the sediments act as storage reservoirs of nutrient materials in water. The replenishment of these elements in time of need and the consequent removal greatly helps in the biological cycle of the system. Carbon, nitrogen and phosphorus are the most significant macronutrients in aquatic ecosystems. In the aquatic environment, they are distributed between the water and sediment interface in both dissolved and particulate forms. In a specific aquatic system, nutrient dynamics partition these elements among water, sediment, and biota to attain a natural balance. This balance may change as nutrients are introduced from agricultural, industrial, and urban sources. Studies of nutrients in aquatic sediments are mainly related to the assessment of the effects of their increasing concentrations originating from different sources. A comprehensive understanding of nutrient behaviour in aquatic ecosystems requires their study in both water and sediments.

Nutrient elements are distributed in the sediments in various forms. Types of organic carbon found in sediments include different compounds, such as proteins, carbohydrates, and lipids (Fabiano and Danovaro, 1994). Of these, simple sugars, fatty acids and proteins are labile compounds and rapidly mineralize. Other compounds such as humic and fulvic acids and complex carbohydrates are refractory and break down slowly. The ecological significance of carbon as a nutrient is manifested through its organic forms. The concentration of organic carbon in marine surface sediments depends on the extent and supply of organic matter, preservation condition and dilution by mineral matter. The concentration of total organic carbon is often used in correlation with other elements. The carbon to nitrogen and carbon to phosphorus ratio is used to characterize the association of nitrogen and phosphorus in organic matter.

Nitrogen found in sediments in various forms dissolved in porewater, adsorbed on sediments and contained in particulate organic detritus and living organisms of various sizes. Some of the forms defined analytically as exchangeable ammonium, exchangeable nitrite, and total nitrogen. Ammonia is the most reduced form of inorganic nitrogen, and is the product of decomposition of organic matter. Bacterial oxidation in the nitrification cycle produces nitrite and nitrate. Phosphorus species in the environment include organic phosphorus compounds, inorganic phosphates and mineralized inorganic complexes with iron, calcium and aluminium. Phosphorus precipitates to form low solubility compounds and metallic complexes, and is relatively immobile compared to carbon and nitrogen. Bacteria and microorganisms play a significant role in the release, mobilization, and fixation of phosphorus in sediments through the synthesis of polyphosphates in biological cells. Thus benthic bacteria do more than just mineralize organic phosphorus compounds, by regulating the flux of phosphorus across the sediment-water interface and contribute to fixation in refractory phosphorus compounds.

The nutrient forms discussed in the present study are exchangeable ammonium, total nitrogen, total phosphorus and total organic carbon. Exchangeable nitrite, nitrate and urea were below micro-molar levels and are not included in the study.

### ➤ Exchangeable ammonium

Exchangeable ammonium exhibited highest concentration in the river sediments whereas the estuarine sediments recorded the lowest. Exchangeable ammonium ranged from 0.82 to 5.27 µmol/g at station 1, from 1.23 to 4.55 µmol/g at station 2, also a mangrove site. At station 3, the compound varied between 0.86 to 11.55 µmol/g. The estuarine site, station R recorded exchangeable ammonium in the range 0.72 to 1.81 µmol/g (Table A.14). The order of abundance of the compound in different systems analyzed were station 3 > station 1 > station 2 > station R. Seasonally, premonsoon period recorded highest concentration at all stations except at station 1 where monsoon recorded the highest. Postmonsoon season exhibited minimum concentration in the mangroves as well as in the estuarine sediments. Monsoon period was characterized by low exchangeable ammonium content in the river sediment (Figure 3.8).

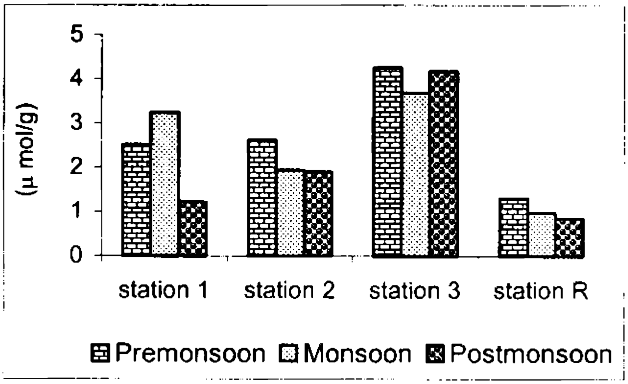

**Figure 3.8:- Seasonal mean variation of exchangeable ammonium**

Among the mangrove systems analyzed, station 1 recorded higher exchangeable ammonium than station 2. Station 1 is a bird sanctuary and the excreta of birds contain substantial portion of ammonia. According to Li (1997), in mangroves, nitrogen is originally from atmosphere and nitrogen fixation is carried out by prokaryotes mostly bacteria and cyanobacteria, which can fix gaseous nitrogen to form ammonia *via* nitrogenous activity. In mangroves, organic matter is produced in enormous quantity. Decomposition of freshly settled organic matter leads to nitrogen mineralization (ammonification). The increase in organic matter concentration in sediments can be interpreted as the predominance of organic matter in comparison with its mineralization in sediment, which subsequently leads to anoxic condition.

The studies by Wafer *et al.* (1997) and Ashton *et al.* (1999) have shown that decomposition of mangrove litter take place rapidly followed by low rates of accumulation of refractory materials. Nitrogen fixation is generally low in mangrove sediments, diminishing the potential for nitrogen enrichment during decomposition (Kristensen *et al.*, 1998), whereas the larger nutrient pools provides a potential for bacterial nitrogen incorporation directly from porewater pools (Kristensen *et al.*, 1998; Holmer *et al.*, 2001). In these anoxic sediments of mangroves, denitrification may play an important role in the nitrogen cycle. Denitrification primarily occurs in the sediments (Seitzinger, 1988) and the rates are highly variable both among systems (Seitzinger, 1988) and over time within systems (Christensen and Sorenson, 1986; Olsen and Anderson, 1994; Ahlgren *et al.*, 1994).

Several environmental factors influence denitrification. Bacterial activity is stimulated by an increase in water temperature (van Luijin *et al.*, 1999) and is disproportionately higher in warm littoral zones (den Heyer and Kalff, 1998). Both nitrate and organic matter supply can be rate limiting for denitrifiers (Seitzinger, 1988). Sediment redox potential has also been shown to affect denitrification rates, with higher rates in more reduced sediments (van Kessel, 1977). In addition, denitrification rates are typically higher in vegetated than unvegetated sediments (Christensen and Sorensen, 1986; Olsen and Anderson, 1994). Aquatic plants can serve as a direct source of organic carbon and as traps for particulate matter from the open waters. Furthermore, plant roots release oxygen into the sediments, thereby increasing the sediment redox potential and creating more favourable condition for nitrate production through nitrification (Christensen and Sorensen, 1986; Ottosen *et al.*, 1999). The increase in denitrification rates with increasing sedimentary organic carbon content has been previously reported for denitrifying bacteria (Seitzinger, 1988; van Luijin *et al.*, 1999). In general, heterotrophic bacterial activity in the summer months would have favoured release of DIP from sediments. Mulholland, (1992) has further shown that during river transport, phosphorus is adsorbed on sediments and suspended materials. Considerable dilution of the effluents would have occurred in the monsoon season as evidenced by low DIP concentration during this season. Correlation analysis (Table C.5) revealed that DIP co-varied with both nitrite and nitrate indicating their common source presumably the effluents.

Relatively lower concentration of DIP was observed at the estuarine site. Since the study site was located near the Cochin bar mouth, considerable dilution of the nutrient-rich estuarine water with nutrient-deficient marine waters might have occurred reducing the DIP concentration levels. In this estuary, DIP varied from as low as 0.59 to as high as 10.06µmol/l. This extremely high value was noted in the month of July, the heavy monsoon period. Thus, land runoff may be the most significant contributor of DIP in this estuary. The almost ubiquitous nature of phosphate pollution from detergents, fertilizers, and domestic/industrial effluents is identified in early studies. Cochin estuary receives large amount of effluents from industries located on the rivers draining into this. Moreover, urban sewage disposals and nutrient-rich effluents from aquaculture practices are released into this estuary without much treatment increasing the phosphate load of this estuary. According to Valdes and Real (1998), resuspension of sediments increases the DIP concentration. Regular dredging of the shipping channel was done every year in this estuary, which will promote the sediment resuspension. Since the site was located near the Cochin bar mouth, tidal action by the waves also promotes resuspension. None of the hydrographical parameters exhibited any correlation with DIP at this site augmenting its anthropogenic source (Table C.2).

### ➢ Total Dissolved Phosphorus (TDP)

Phosphorus exists in natural waters in a wide variety of forms including the inorganic and organic fraction. Inorganic phosphates remain mainly in the form of $HPO_4^{2-}$ ions. Condensed phosphoric acids such as diphosphoric acids and polyphosphoric acids with P-O-P linkages are detected in the estuarine water. The organic fraction mainly contains the decomposed and excreted compounds of dead organisms and includes phospholipids, phosphonucleotides and their derivatives.

wetlands (Reed *et al.*, 1988) indicating that wetlands are dominant in ammonia. Denitrification relies on the presence of nitrate as a precursor and organic compounds to provide electrons to the denitrifying heterotrophs to form nitrogen gas and $N_2O$ (Knowles, 1982). Thus ammonification processes might have facilitated the build up of ammonia in the sediments. Correlation analyses did not show any influence of hydrographical parameters on ammonium distribution at this site (Table C.3). Ammonium did not correlate with any other nutrient elements also (Table C.4).

Premonsoon season dominated in ammonium content at the estuarine site. However, the concentration was generally low at this site. Fluctuating salinity play a major part in controlling the ammonium adsorption capacity of the estuarine sediment (Boatman and Murray, 1982). It was reported that the amount of adsorbed $NH_4^+$ was lower in estuarine sediments compared to sediments from freshwater tidal rivers (Simon and Kennedy, 1987). With increasing salinity, desorption of ammonium from the adsorbed sediment sites was favoured and also ion-pair formation between ammonia and seawater anions partially neutralize the polarity of $NH_4^+$ ions, which reduces adsorption to sediment particles and hence lowers the residence time of $NH_4^+$ within the sediment (Gardner *et al.*, 1991).

The major source of ammonium in this estuary may be the rivers and the sewage from urban area/ aquaculture farms. Since ammonia is extensively used in fish processing, a substantial amount of the compound enter this estuary as numerous fish peeling centers and seafood exporting units are located on the banks of this estuary. Hydrographical parameters were found to exert no influence on the distribution of sedimentary ammonium reflecting its anthropogenic source (Table C.3).

### ➤ Total Nitrogen (TP)

The processes controlling distribution of various forms of nitrogen between coastal waters, estuarine waters, river waters and near-shore shelf waters are not well understood. The concentration of various forms of nitrogen in an aquatic system is the result of the input rates, the inter-conversion reactions occurring within the water column and the rate of loss by way of out flow, denitrification and sediment associated deposition. Though nitrogen cycling is of complex nature, characterization of its cycling in the riverine, estuarine and oceanic waters enable identification of the potential source, major pathways of losses as well as the internal processes. Unlike inorganic carbon, transformation between inorganic nitrogen species occurs almost exclusively through biological processes with physical equilibrium assuming minor role. Nitrogen enters the mangrove sediments primarily *via* autocthonously produced leaf litter, micro-algae and epiphytes. Other sources include nitrogen fixation by bacteria and cyanobacteria as well as possible particulate and dissolved nitrogen from adjacent coastal zone (Alongi, *et al.*, 1992). Due to the high content of nitrogen-poor structural carbohydrates in mangrove litter entering the sediment, the nitrogen content of the sediment detritus is relatively low (Kristensen *et al.*, 1988).

In this study, total nitrogen showed generally high concentration in the mangrove and river sediments compared to the estuarine sediments (Table A.15). At station 1, TN varied from 1.10 mg/g to 3.900mg/g, from 1.11 to 6.71mg/g at station 2. In the river sediment, the variation was from 0.81 to 5.72 mg/g, while the estuarine sediments recorded TN in the range 0.74 to 2.64mg/g. Monsoon recorded highest concentration at all stations while premonsoon exhibited minimum concentration at all stations except station 2 (Figure 3.9). Here, variation between non-monsoon periods was though very low, postmonsoon season recorded relatively lower TN levels.

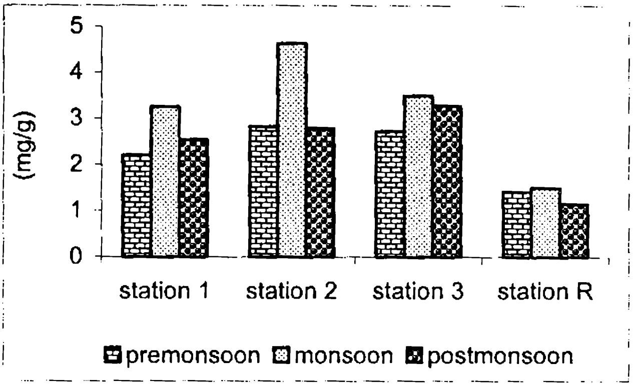

**Figure 3.9:- Seasonal mean variation of total nitrogen**

In contrast to all other nutrient forms under study, station 2 exhibited higher TN content than station 1. This showed that mangrove sediment at this station was nitrogen-rich than at station 1. Effluents from the adjacent shrimp farm, which may be rich in organic nitrogen compounds, may be the reason for this elevated concentration. It was well established that nitrogen fixation by cyanobacteria and heterotrophic bacteria are the important nitrogen transformation processes in mangrove forests (Alongi *et al.*, 1992). According to Holmer (2001) there was a significant immobilization of nitrogen during the degradation of nitrogen-poor mangrove detritus. The larger loss of carbon compared to nitrogen in the mangrove leaves led to an overall decrease in the C/N ratios of mangrove detritus. The decrease in C/N of detritus is usually attributed to colonization by bacteria (Steinke *et al.*, 1993; Wafer *et al.*, 1997; Pedersen *et al.*, 1999). Bacteria incorporated nitrogen from the indigenous particulate organic nitrogen pool, whereas the detritus served as an energy source.

Seasonally, monsoon recorded high TN content at both the stations. This monsoon hike can be related to the increased terrestrial runoff, which is characteristic of this season. Among the hydrographical parameters, both salinity and dissolved oxygen were inversely related to total nitrogen (Table C.3). Nitrogen was found to be enriched in the finer fraction of sediment at this site.

Highest annual mean concentration of total nitrogen was recorded at station 3. Here, TN varied between 2.736 to 3.501mg/g. Monsoon season was found to be dominating in TN content. The elevated concentration of TN at this site may be related to the effluents discharged by various industries located on the banks of this river. Another reason for the observed high content of sediment nitrogen may be the increased amount of nitrogen fixation by the freshwater bacteria. The low values during the premonsoon season can be due to desorption of nitrogenous nutrients to the overlying water column to support higher organic production characteristic of this season. However, the main contributor of total nitrogen seems to be the industrial effluents at this site. Salinity as well as temperature was found to be regulating TN distribution at this site (Table C.3).

Generally, low concentration of nitrogen was detected in the estuarine sediments (1.418 to 1.518mg/g). This can be due to the sandy nature of the substratum, which is a poor adsorber of ions. At this site, considerable dilution of the nutrient-rich estuarine sediments with nutrient-poor marine sediments was highly probable by the intense wave action. However, the monsoon period dominated in TN content at this site. This can be related to the increased precipitation of nitrogenous materials from the watershed. Terrestrial runoff, which was enriched in nitrogen-nutrients, may also have contributed to this estuary. Since nitrogenous fertilizers are increasingly used in agricultural practices, heavy influx of freshwater during the monsoon season might have introduced nitrogen-rich particles into this estuary. Among the hydrographical parameters, pH correlated inversely with TN at this site (Table C.3).

### ➤ Total Phosphorus (TP)

The physical and chemical characteristics of the sediments and their adsorption-desorption behaviour are among the most necessary set of information to have when discussing the phosphorus exchange processes between sediments and overlying waters. Phosphorus is considered to be present in the sediment as interstitial, adsorbed and phosphorus-bound to some soluble inorganic or organic compounds. Phosphorus is deposited on the sediments as allogenic apatite minerals and as oceanic associates and precipitates with inorganic complexes. The relative importance of these different fractions depends on the external supply of apatite minerals, organic matter complex forming agents and to a large extent on the productivity of the system.

Phosphorus undergoes many exchange processes once it is introduced into the water column. Golterman (1973) reported that when phosphorus was adsorbed onto the sediment materials, one fraction was adsorbed onto anionic site and another to crystalline lattice structure by substitution of $OH^-$ ions. The principal factors controlling the exchange processes were redox potential and Ca and Mg ion concentration and the pH of the water.

In shallow water systems where the mud acts as a reservoir of phosphorus in various forms and as a generator into overlying water under the suitable conditions, knowledge of the phosphorus content in the sediments is important. The distribution of total phosphorus, which includes all the forms, is governed largely by the hydrobiological features of the overlying water, the texture and mineralogical composition of the sediment.

Total phosphorus, in this study, exhibited wide variation in concentration in each of the systems analyzed. Distinctly high values were noted at station 1 and at station 3 whereas station 2 and station R displayed much lower values. Station 1 recorded TP in the range 1.05 to 13.15mg/g while, station 2, another mangrove site recorded TP in the range 1.02 to 5.20mg/g. The riverine sediments exhibited TP in the range 0.380 to 10.46 mg/g. Here, seasonal variation was only marginal. The estuarine sediments recorded distinctly low TP content. Here, the compound ranged between 0.480 to 1.49 mg/g (Table A.16). Premonsoon period dominated in TP content at stations 1, 3 and R while at staion2, postmonsoon season recorded maximum concentration levels. Monsoon season exhibited lowest concentration invariably at all stations (Figure 3.10).

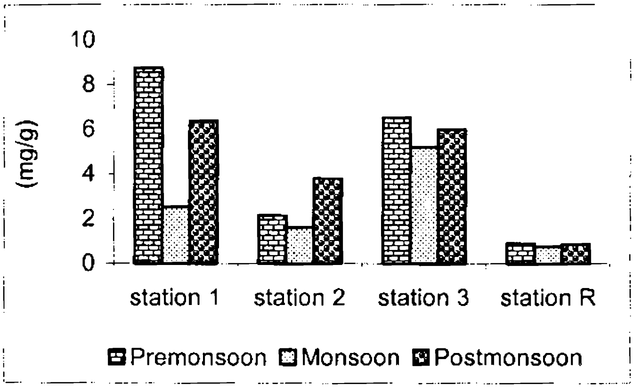

**Figure 3.10:- Seasonal mean variation of total phosphorus**

In the mangroves, redox potential in the sediments can control the phosphorus solubility through changes in the $Fe^{3+}/Fe^{2+}$ ratios. It is accepted that low redox potentials in anoxic layers promotes the formation of $Fe^{2+}$ through dissolution and reduction of Fe(III) oxyhydroxides with the release of associated phosphorus. This promotes an increase in the dissolved reactive phosphorus in the interstitial waters, with Fe being converted to insoluble Fe sulphides (Krom and Berner, 1981; Caraco *et al.*, 1989). This process is catalyzed by enzymes released by nitrate and sulphate reducing bacteria and depends on the carbon source. Since Fe concentration in these mangroves was found to be very high, association of phosphorus with Fe oxides and hydroxides may be the reason for this general elevated concentration of TP in mangrove sediments.

Clough *et* al. (1983) have shown that organic phosphorus accounted for 75-85 percentage of the total phosphorus in the mangrove sediments of Sierra Leone, Nigeria. According to Sommers *et al.* (1972), most of the organic phosphorus in mangrove sediments probably occur as complexes with humic and fulvic acids. Paludan and Morris (1999) reported that phosphorus can be preferentially bound to humic acids and are trapped in the Fe(III) pools. Since humic acid fraction was found to be very much dominating in the Cochin mangroves according to the study by Rini (2002), organic phosphorus may have complexed with humic acids and contributed to the TP content of the sediments.

Phosphorus has been reported to concentrate in the fine fraction of the sediments such as silt and clay (Nasnolkar *et al.*, 1996). The clayey nature of the mangrove sediments might have facilitated adsorption of phosphorus onto them. The highly entangled root systems of the mangrove plants acted as traps for sediments and nutrients, which would have increased the residence time of the compound in the water column subsequently increasing adsorption onto particles. In addition to this, large amount of aquaculture wastes were discharged into these mangroves. Alongi *et al.* (1992) and Boto *et al.* (1992) have shown that aquaculture effluents or sewage enriched in nutrients added to mangrove areas may be sequestrated and processed by sediment bacteria. Mangrove forests could process and immobilize long-term inputs of wastes (Paez-Osuna *et al.*, 1999).

Seasonally, non-monsoon periods exhibited very high concentration at both the mangrove sites under study. This can be ascribed to the increased microbial mineralization of organic matter in these seasons releasing huge amount of phosphorus. Considerable dilution of the compound in the monsoon season by the heavy influx of nutrient-deficient sediments associated with runoff water may be the reason for the observed low TP levels.

TP varied between 2.61 to 11.3 µg/l in the mangrove sediments of Sunderban (Hoq *et al.*, 2002). TP in the Futian mangroves was 0.15 %, in a study by Li (1997). In the Bangrong mangroves, Thailand, phosphorus was present in higher concentration in the surface sediments. However, concentration of P was very low in these sediments (0.9 to 0.2µM) (Holmer *et al.*, 2001).

In the river sediments, TP exhibited only marginal seasonal variation. However, monsoon season was noted with lowest concentration probably due to the increased rate of release of the compound to the water column, as the dissolved fraction was very low during this period. Bowers *et al.* (2003) have further shown that increasing river flow could mobilize the fine phosphorus-rich bed sediment that had accumulated during periods of low flow. Sediment disturbances also found to release P-rich porewaters into the water column. The main contributor of TP into this river may be the effluent from the fertilizer factory. The elevated concentration of TP during the non-monsoon periods could also reflect the increased mineralization of organic matter facilitated by the warmer climate.

The estuarine sediments recorded relatively low TN content in the sediments. Here, TP varied between 0.768 to 0.906mg/g. The lower TP content can be attributed to the poor capacity of the sandy sediments to adsorb nutrients onto them. Here also the minimum concentration was noted during the monsoon period. Lower values of TP during the monsoon months were believed to be due to the leaching of phosphorus (both in the interstitial and adsorbed forms) from the mud to the overlying waters. During the monsoon season, the increased freshwater inflow, the intense circulation of water and the very low salinity all might have facilitated the release of P from the sediment. Since Cochin estuary is shallow (2-5m) that one of the major factors governing the distribution and variation in phosphorus would be the difference in the regenerative property of the bottom sediment.

### ➤ Total organic carbon (TOC)

Carbon accounts for only ca. 0.08% of the combined lithosphere, hydrosphere and atmosphere but it is an important element and its compounds form the basis of all life. Carbon-rich sedimentary deposits are of great importance to all humans. Organic matter is virtually completely decomposed and recycled in soils. Carbon-rich sediments may contain both inorganic and organic carbon. Inorganic carbon may be present as both biogenic and abiogenic carbonate. Sedimentary organic carbon is mainly in the form of particulate organic carbon that has settled out from the overlying water column. Detritus, is, therefore, generally important in the formation of carbon-rich sediments. After the incorporation of detritus into the sediments, recycling of carbon can continue in the upper sediment layers.

Phytoplankton and zooplankton are obviously most important contributors to marine and freshwater sedimentary organic matter, while higher plants are important in swamps. There is one further major contributor to sedimentary organic matter, bacteria. A large proportion of energy flow in ecosystems can pass through the detrital food chain, in which heterotrophic bacteria are prominent participants. Heterotrophic bacteria are important in all sedimentary environments, and although they consume organic detritus they supplement the organic matter with their own remains. While bacterial biomass may be relatively small, bacterial productivity can be very high in aquatic environments.

Organic matter in surface sediments plays a major role in influencing community structure and metabolism of benthos. The main carbon species in suspended and bottom sediments include carbohydrates, fats, and proteins from decomposing biota, humic acids from decomposing humus, and carbonates from detritus. Of these, simple sugars, fatty acids and proteins are labile compounds and rapidly mineralize. Other compounds such as humic and fulvic acids and complex carbohydrates are refractory and break down slowly. The ecological significance of carbon as a nutrient is through its organic forms.

The preservation of mangrove forests rests on the belief that carbon and energy fixed by mangrove vegetation is the most important nutritive source for animal communities in and near mangrove wetlands (Saenger, *et al.*, 1983). The accumulation of organic carbon enhances the production and associated captive fishery. Organic carbon forms the basis of a dependent trophic chain of bacteria, fungi, cellular algae and other detritus feeding organisms.

Organic carbon, in the present study was highest in the mangrove sediments followed by the river sediment and then the estuary. At station 1, TOC ranged between 69.39 to 112.65mg/g whereas at station 2, the range was 58.75-to 102.39 mg/g. The riverine site recorded TOC in the range 7.66 to 51.96 mg/g, while the estuarine sediments exhibited TOC in the range 11.38 to 15.93 mg/g (Table A.17). Seasonally, postmonsoon was characterized by highest concentration at station 1, while monsoon recorded the maximum concentration at station 2 as well as at station 3 (Figure 3.11). Premonsoon season recorded highest concentration at the estuarine site.

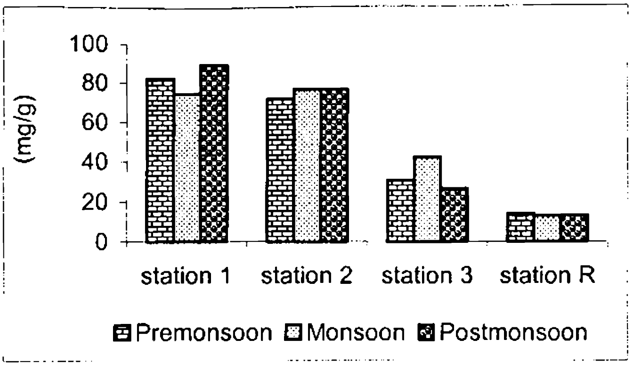

**Figure 3.11:- Seasonal mean variation of total organic carbon**

In the mangroves, major primary production is the mangrove plants themselves. Leaves, twigs, shoot, and roots — very part of the plants — contribute to the organic pool of the mangroves. Thus the mineralization process of this enormous quantity of organic matter in the mangroves often creates anoxic condition both in the sediment and water column. Organic matter produced or deposited on the sediment surface in mangroves thus supports aerobic and anaerobic detritus food chain. Aerobic microbial decomposition of organic matter is usually more rapid than the rate of oxygen diffusion to the interior of the sediments, and oxygen becomes quickly limiting. Anaerobic bacteria in the upper few millimeters of the sediment therefore carry out most of the decomposition, except where animal burrows and plant roots channel oxygen to the deeper sediment layers (Anderson and Kristensen, 1988; Aller, 1994). Anaerobic decomposition is performed by a wide variety of bacteria utilizing a number of electron acceptors to oxidize carbon.

At station 1, postmonsoon period was found to be dominating in TOC content. This can be attributed to the increased rate of leaf litter fall during this period. In the monsoon period, since the area is very near to the urban metropolis, heavy influx of terrestrial sediments would have led to low organic matter. However, at station 2, premonsoon season was characterized by low organic matter content. This season was associated with high temperature, which will help bacteria to flourish. Mineralization rates, which are, rapid therefore result in the lowering of organic carbon content of the sediments. According to Alongi, *et al.*

(1993), several factors such as warm temperature, release of nutrients by mangrove roots, rapid deposition of organic matter etc. account for the bacterial activity. At this site also postmonsoon season recorded highest concentration may be due to the increased litter fall. Correlation analysis revealed significant enrichment of organic carbon in the finer fraction of the sediment.

Unlike other nutrient elements, only organic carbon was significantly lower in the river sediments compared to the mangroves. Here, TOC ranged from 26.60 to 42.05 mg/g. Highest concentration observed during the monsoon season can be attributed to the increased amount of terrigenous organic matter associated with heavy influx of freshwater. In addition to the autochthonous organic matter, several synthetic organic compounds may be present in this river sediment, as many industrial establishments are located on the banks of this river. Rapid mineralization of organic matter facilitated by the warm temperature of the non-monsoon periods would have resulted in increased oxidation, lowering the TOC of the sediment. TOC was found to be dependent on pH of the overlying water as evidenced from correlation analysis (Table C.3). Significant enrichment of organic carbon was seen in the silt fraction of the sediment.

Relatively lower values of organic carbon were recorded in the estuarine sediments. Sandy nature of the substratum along with intense wave action may be the reasons for this observed low value. Seasonal variation was only marginal at this site. However, non-monsoon periods exhibited higher values. Influx of organic-poor terrestrial sediments during the monsoon period would have diluted the estuarine sediments. Decomposition products of phytoplankton after the maximum production period of the optimum light conditions may be the reason for the observed hike in TOC content in the non-monsoon months.

### 3.3.1 C/N ratio

The carbon to nitrogen ratio was used to identify the source of organic matter in sediment. An understanding of the nutrient regeneration is based on the C/P, C/N and N/P ratios. The amount of detritus and its further decomposition influence the carbon and nitrogen content of the sediment. Substances rich in nitrogen (low C: N) favour net mineralization, whereas those poor in nitrogen (high C: N) favour net immobilization. The generally high C: N ratio of mangroves

(Table A.18) and high rate of bacterial production indicate that the rates of immobilization may be high in mangrove sediments.

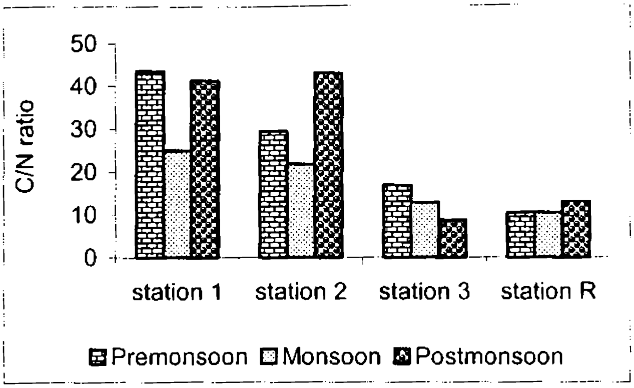

**Figure 3.12:- Seasonal mean variation of C/N ratio**

At both the mangrove sites, monsoon season recorded low C/N ratios (Figure 3.12). The monsoon associated heavy influx of terrestrial runoff might have introduced sediment in these mangroves that might have diluted the organic-rich sediments of the mangroves or it may be due to the microbial mineralization followed by rapid assimilation of nitrogenous compounds in this highly reactive environment. Thus, it can be inferred that there was a net immobilization of nutrients during the non-monsoon months. Holmer (2001) also observed a significant immobilization of nitrogen during the degradation of N-poor mangrove detritus in a study on the Bangrong mangrove sediments, Thailand. The larger loss of carbon compared to nitrogen in the mangrove leaves led to an overall decrease in the C/N ratios of mangrove detritus. A decrease in C/N ratio of detritus is usually attributed to colonisation by bacteria (Steinke *et al.*, 1993; Wafer *et al.*, 1997; Pedersen *et al.*, 1999).

The low rate of mineralization in mangrove sediments was explained by high concentration of tannins. Tannins are known to be enzymatic inhibitors and antimicrobial agents (Cundell *et al.*, 1979), and studies have confirmed a negative correlation between tannin content and bacterial population (Robertson, 1988; Alongi *et al.*, 1992; Steinke *et al.*, 1993). The low C/N ratio indicated that N was preferentially mineralised relative to carbon.

At the riverine site, premonsoon season exhibited highest C/N ratio. This was due to the exceptionally high value during the month of April. Bacterial action may be high during this period, bringing about rapid degradation of organic matter. At this site, though nitrogen nutrients were added to the system by way of effluents, there was a net immobilization of nitrogen during this season. Low C:N ratios during the postmonsoon season indicate that mineralization process was prevalent during this period. Total nitrogen estimated was highest during the postmonsoon period at this site. Thus at this riverine site there was net immobilization of nitrogen during the premonsoon and monsoon periods.

At the estuarine site, C/N ratio varied between 6.98 and 16.08. Here, the seasonal variation was less significant. The general lower values of C/N at this site can be attributed to the sand dominance of the substratum. Nitrogen was found to undergo mineralization at a faster rate at this site compared to the mangroves. The general low C/N ratio indicates that there was net mineralization of nutrients taking place in this estuary.

### 3.3.2 C/P ratio

C:P ratios are widely used as an index of pollution by domestic sewage in any aquatic environment. The sediments of mangrove systems are rarely in agreement with the theoretical Redfield ratio (Alongi, 1996). Outwelling of mangrove litter significantly influences the sediment concentrations of organic carbon and total nitrogen (Alongi, 1990). Kairesalo *et al.* (1995) found that mineralization of organic matter by bacteria may either mobilize or immobilize phosphorus. The richer the substrate is for P or N compared to bacterial biomass, the more easily P or N will be released by mineralization. Therefore, decrease in sediment bacteria increased the concentration of inorganic phosphorus in the interstitial waters, in turn, an accumulation in solid phase occurs (Touminen *et al.*, 1996). A decrease in bacterial population decreases the ultimate release of phosphorus from sediments to overlying water through decreased oxygen consumption leading to high phosphorus sorption at the oxic sediment-water interface (Kairesalo *et al.*, 1995).

In this study, C/P ratios exhibited distinct seasonal distribution in each of the systems analyzed. At station 1, C/P ratio varied between 6.46 to 106.98, whereas relatively lower variation in the ratio was observed at station 2, which is also a mangrove site. Here, the variation was from 16.47 to 77.03. At station 3, C/P ratio varied from 1.77 to 43.24, while the estuarine sediments recorded C/P ratio in the range 9.52 to 33.33 (Table A.19). Seasonal mean variation of C/P ratio is depicted in Figure 3.13. Postmonsoon season exhibited highest C/P ratio at station 1, whereas in this season, station 2 recorded lowest ratios. Here, premonsoon displayed highest C/P ratio. In the river sediments, postmonsoon and premonsoon seasons recorded the highest and lowest C/P ratios respectively. However, at the estuarine site, seasonal variation was not much significant. Here, postmonsoon recorded lowest values.

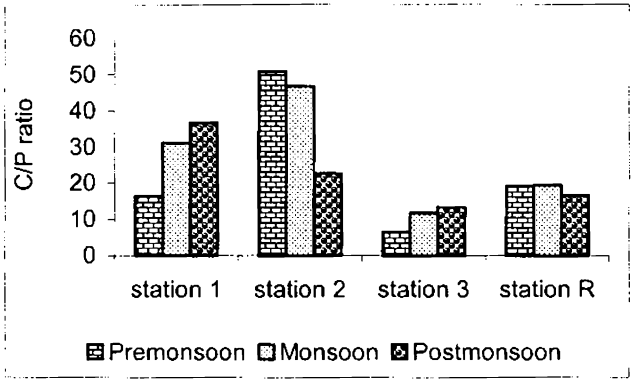

**Figure 3.13:- Seasonal mean variation of C/P ratio**

Of the two mangrove sites, station 2 exhibited higher C/P ratio. This can be related to the greater amount of phosphorus present at station 1. Since, this site was located very near to the urban area, abiogenic phosphate sources may be significant here. The lower values observed during the premonsoon season can be attributed to the increased mineralization processes characteristic of this season. At station 2, however, C/P ratio was generally high may be due to the increased mineralization of phosphorus and its rapid assimilation by the soil organisms. Thus, it could be inferred that at this station, phosphorus present may be of biogenic origin whereas at station 1, substantial amount was provided by the mineral fraction or by external inputs.

Generally low ratios were observed at station 3, the riverine station. This can be attributed to the increased amount of phosphorus brought into this river through the industrial effluents. Particularly low values during the premonsoon season confirm this external input. Difference of the ratio in the monsoon and postmonsoon was only meagre.

C/P ratio was relatively lower in the estuarine sediments compared to the mangroves. Low C/P ratios could be the result of increased load of phosphates reaching the estuary through domestic sewage. The C/P ratios observed in estuary indicated that the major portion of the phosphorus in the sediment was of abiogenic origin from domestic sewage and from other anthropogenic sources.

### 3.6 N/P ratio

The classical Redfield ratio (16: 1) was very difficult to obtain in coastal ecosystems like the estuaries and mangroves because of the human perturbations, which have considerably altered the physico-chemical status of these systems. Nitrogen limitation in coastal waters can be due to the remineralization of organic matter in the sediments, where nitrogen may be lost by denitrification (Valeila, 1984).

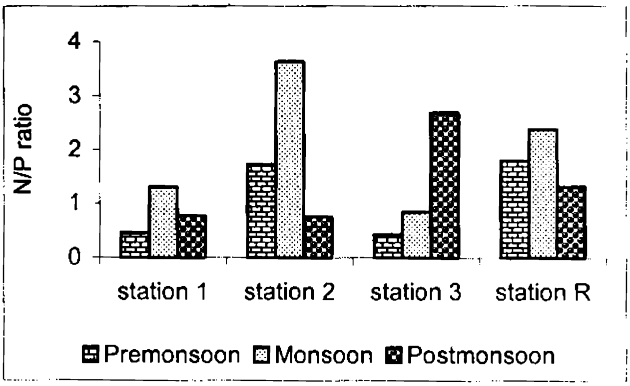

**Figure 3.14:- Seasonal mean variation of N/P ratio**

In this study, spatial variation in N/P was low compared to the seasonal variation. In the mangroves and at the estuary, monsoon season was characterized by high ratio (Figure 3.14). In the river sediments, postmonsoon season recorded maximum ratio. At station 1, N/P varied from 0.08 to 1.76 whereas at station 2, much higher values were observed. The variation was between 0.32 and 5.93. The river sediments exhibited much higher N/P ratios. Here, the ratio varied from as low as 0.19 to as high as 9.70. However at the estuarine site, the ratio was in the range, 0.75 to 5.52 (Table A.20).

Of the two mangrove sites, higher annual mean ratio was noted at station 2. Though, at station 1, concentration of nitrogen was much higher than station 2, N/P ratio was low. This can be attributed to the simultaneous increase in the phosphate concentration. At station 2, introduction of phosphate by external input was not significant. The monsoon elevation in the ratio can be attributed to the land runoff rich in nitrogenous compounds. In the non-monsoon months, bacterial activity may be very high bringing about intense mineralization of organic matter. Since the mangrove detritus is composed mainly of nitrogen-poor lignocelluloses, low N/P was expected. N/P ratio can be taken as an index of the extent of extraneous influence on a productive water body, since the nitrogen if produced is autochthonous, variation in N/P depend upon phosphorus, which is mostly external (Shanmukhappa, 1987).

In the river sediments, low N/P ratio obtained can be attributed to the increased amounts in which these compounds are brought into this river. Total phosphorus may be supplied in excess amounts to this river sediment lowering the ratio. Postmonsoon hike in the ratio can be due to the elevated concentration of nitrogen compounds. The estuarine sediments also recorded low N/P ratio. The monsoon season displayed higher values indicating the terrestrial input of nitrogenous nutrient compounds. Low N/P values of Cochin estuary may also indicate that the major portion of the phosphorus in the sediments was of abiogenic origin.

N/P ratio was high in surface sediments as compared to the ratios of creek waters in a study by Ram and Zingde (2000) in the Gorai creek, Mumbai. This suggests the removal of phosphate from interstitial water. $Fe^{3+}$ can chemically react with orthophosphate to form insoluble $FePO_4.2H_2O$ (Berner, 1980). With the development of anoxic condition in the sediments, this $Fe^{3+}$ is reduced and release the adsorbed phosphate into the overlying water. Nasnolkar *et al.* (1996) in a study on the Mandovi estuary observed N/P ratio in the range 2.92 to 37.51 indicating low ratios during postmonsoon. The high ratios indicate low phosphorus content in the sediment. Usually, P is contributed into this estuary from the organic matter as well as from the mineral matter. The texture of sediments during monsoon was very rich in sand. However, during the other periods the same stations show sediment rich in clay or silt and were clayey or silty sediments. It therefore appears that apart from the organic matter, the contribution from the mineral P probably plays an important role in defining the variation of N/P ratios of their sediments. Shengquan *et al.* (1993) related high N/P ratio to the utilization of nitrogenous fertilizers in the paddy fields and the increasing discharge of industrial and domestic wastes in the Hang Zhou Bay, China.

## 3.4 Statistical analysis

Cluster analysis was carried out in order to find the similarities of the aquatic systems in the processing of nutrient compounds. It was evident from the analysis that the two mangrove habitats showed the most similar pathways for the different nutrient elements (Figure 3.15). The unique environmental characteristics may be the prime factor determining the fate of nutrients. The estuarine system exhibited similar processing pattern to the mangroves, while the riverine system behaved in a totally different way. This can be related to the heavy anthropogenic input of nutrient compounds into this riverine system.

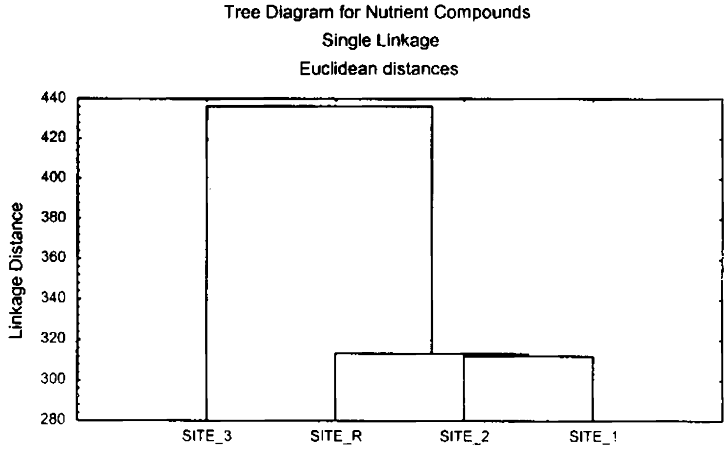

**Figure 3.15:- Dendrogram of nutrient compounds**

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# Chapter 4

## Bioorganics

### 4.1 Introduction

The chemistry of organic compounds is based on carbon, the twelfth most abundant element in the Earth's crust. Carbon accounts for only about 0.08 percentage of the combined lithosphere, hydrosphere and atmosphere but it is, nevertheless, an extremely important element and its compounds form the basis of all life. In the atmosphere, carbon exists mainly as carbon dioxide, which is taken up by plants during photosynthesis. Energy is passed from the primary producers to various heterotrophs along food chains and ultimately reaches to top carnivores.

### 4.2 Dissolved organic compounds

In aquatic system, it is traditional to divide the organic matter into two major categories — dissolved organic matter (DOM) and particulate organic matter (POM). Dissolved organic matter is an ubiquitous and abundant form of nutrients and energy potentially available to microorganisms in aquatic systems. It is the largest reservoir of reduced carbon in the ocean (Benner *et* al., 1986). In open ocean environments, the bulk of dissolved organic matter results either directly or indirectly from phytoplankton production (Sharp, 1982), whereas in nearshore and estuarine waters, the sources of dissolved organic matter are more diverse and include intertidal and subtidal vascular plants and macro-algae, as well as planktonic and benthic algae (Gallagher *et al.*, 1976; Newell *et al.*, 1980; Penhale and Smith, 1977). In subtropical and tropical coastal regions throughout the world, mangroves are important primary producers that contribute considerable quantities of organic matter, primarily as leaves, to adjacent waters and sediments (Heald, 1971; Lugo and Snedeker, 1974; Walsh, 1974). Detrital material from mangroves serves as the base for elaborate food webs in estuarine and coastal environments (Odum and Heald, 1972; Rodelli *et al.*, 1984).

Dissolved organic carbon is the most abundant form of reduced carbon in most aquatic systems, and it is one of the largest reservoirs of reduced carbon on earth. As such, the cycling of dissolved organic carbon is the major component of the global carbon cycle, and understanding factors regulating dissolved organic carbon cycling is critical for assessing potential impact of environmental change on the global carbon cycle. Heterotrophic microorganisms, primarily bacteria, are the major consumers of dissolved organic matter and the decomposition of dissolved organic matter is largely an enzymatically-mediated process. The production and consumption of dissolved organic matter are considered as predominant pathways of carbon flow in most aquatic environments. The process of microbial mineralization of dissolved organic matter is very efficient, although some components of dissolved organic matter are resistant to microbial degradation (Benner and Zeigler, 1999).

Zika (1981) and Mottis *et al.* (1995) have opined that dissolved organic matter is responsible for most of the absorption of UV radiation in seawater and lakes. The UV portion of the solar spectrum is considered responsible for most of the photochemical transformations of dissolved organic matter (Moran and Zepp, 1997). Thus, dissolved organic matter plays an important role in the protection of aquatic organisms from the harmful effects of UV radiation.

According to Benner and Zeigler (1999), most of the dissolved organic matter in freshwater and estuarine environments is derived from macrophytes through leaching of soils and plant tissues. This dissolved organic matter is relatively rich in aromatic structures and is resistant to microbial degradation. This dissolved organic matter pool represents a large potential energy source and the fate of the dissolved organic carbon will have important consequences for the carbon budget of entire ecosystem. However, the nature of dissolved organic matter is poorly understood, because it has been difficult to isolate sufficient amount of representative material for analysis. However, it has been observed that dissolved organic matter consists largely of refractory compounds such as humic substances and labile compounds from major biochemically important compound classes such as carbohydrates, sterols, alcohols, aminoacids, hydrocarbons and fatty acids. In this study, among the labile compounds, dissolved monosaccharides and from the refractory compounds, dissolved tannin and lignin were analysed.

## ➤ Dissolved Monosaccharides

Carbohydrates comprise one of the major classes of naturally occurring organic substances. They are actually the most abundant class of compounds produced in the biosphere. Carbohydrates exist in living organisms in combined forms, being associated with proteins, lipids and nucleic acids, and constitute intricate high molecular complexes, which form the basis of living matter.

Among the various groups of carbohydrates, monosaccharides (MCHO) have the highest reactivity. Most carbohydrates are unstable outside the living system and undergo degradation to end products. This causes a drop in pH, Eh of the surrounding environments and affects the metabolic processes of the aquatic organisms. The content of carbohydrates in marine organisms varies from a fraction of a percent to 60-70 percent, on a dry weight basis. A large amount of carbohydrates is liberated by algae into the water, as a result of autolytic division of normally functioning cells, extracellular excretion of metabolites of low molecular weight, and other specific activities.

Some 10-50 percentage of phytoplankton production enters the dissolved pool and passes through the bacteria-based food web (Andrews and Williams, 1971; Derenach and Williams, 1974; Larson and Hagshorm, 1979; Fuhrman and Azam, 1980). Dissolved carbohydrates originating from photosynthetic storage reserves and metabolic intermediates (Myklestad, 1974) often dominate the microbiologically labile pool of dissolved organic matter (Azam and Ammerman, 1984). Photosynthetic carbohydrate reserves accumulate in phytoplankton during the photoperiod (Morris and Skea, 1978). Possible sources of carbohydrates pulse include excretion from healthy phytoplankton (Mague *et al.*, 1980), autolysis or leakage from senescent cells (Sharp, 1977), zooplankton material release and dissolution of particulate matter. If monosaccharides were excreted, they are utilized by bacteria at an equal rate (Burney, 1986).

In this study, dissolved monosaccharides did not vary much in concentration between the various aquatic systems analysed. At station 1, MCHO varied from 0.951 to 8.370 ppm while, station 2 displayed MCHO in the range 0.919 to 4.618 ppm. Station 3, exhibited extremely high concentration in the month of July (64.77ppm). Except this value, this station recorded MCHO concentration in similar range with other sites. Here, the variation was from 0.336 to 6.420 ppm (excluding the highest value). The estuarine site recorded dissolved monosaccharides in the range 0.129 to 4.243 ppm (Table A.21). In all the systems under study, monsoon period recorded minimum concentration except at the riverine site (Figure 4.1). Here, postmonsoon displayed lowest concentration. Maximum MCHO levels were recorded during the premonsoon season at stations 1 and 3, whereas postmonsoon exhibited highest concentration at station 2 and at the reference site. ANOVA statistics revealed no significant variation either between months or between systems (Table. 4).

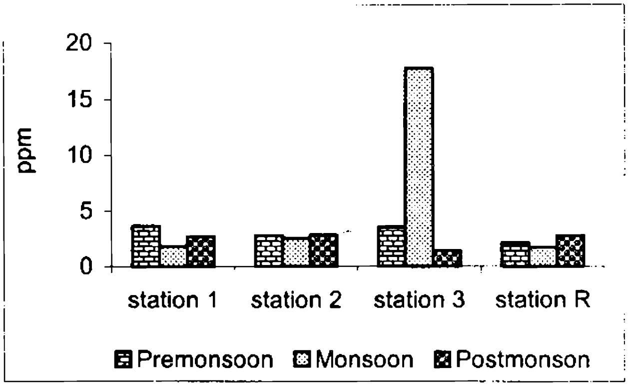

**Figure 4.1:- Seasonal mean variation of dissolved monosaccharides**

In the mangrove systems, the vegetation and its associated biota, play a major role in contributing organic matter. Organic matter produced or deposited on the sediment surface in mangrove forests support aerobic and anaerobic detritus food chains. Approximately, 30-50 percentage of organic matter in mangrove leaves is leachable (Benner and Hodson, 1985). These leachable materials of mangrove leaves were mineralized at 10-fold higher rates than structural components (Benner *et al.*, 1986). The chemical composition of the leachable components of mangrove leaves has not been thoroughly characterized; however, tannins and carbohydrates are readily leached during the first month of leaf decomposition (Cundell *et al.*, 1979; Sumithra Vijayaraghavan *et al.*, 1980). The first stage of decomposition in mangroves involves the leaching of soluble materials mainly carbohydrates. These compounds, as a result of their dissolved state, are readily available for uptake by bacteria.

According to Arnosti and Holmer (1999), dissolved carbohydrates are produced chiefly by the solubilization/ hydrolysis of particulate organic matter. Waters of the mangrove forests are generally turbid because they are shallow regions and subjected to action of tides and waves. The constant tidal action disturbs surface sediment in the mangrove substratum, resulting in high suspended matter load. The periodic resuspension of sediments probably was responsible for the high amount of suspended particulate matter (Jagtap, 1987). Thus the solubilization from the bulk quantity of suspended particulate organic matter may be a significant source for dissolved carbohydrates in the mangroves. Once hydrolyzed, most of the monosaccharides would likely be remineralized rapidly (Sawyer and King, 1993; Rich *et al.*, 1996). Not all the dissolved carbohydrates may be equally available for heterotrophic consumption. Structures that may be difficult to hydrolyze *via* commonly produced extracellular enzymes, or carbohydrates that present transport and uptake problems may persist in dissolved form. Benner *et al.* (1992) also observed that carbohydrate as abundant and persistent components of marine dissolved organic carbon.

The two mangrove stations in the present study did not vary much in their MCHO content. The lowest concentration was observed during the monsoon season at both the sites indicating that bacterial decomposition of organic matter was considerably low in this period. Elevated temperature of the non-monsoon months would have increased both the bacterial biomass as well as the decomposition reaction rate. Among the hydrographical parameters, only salinity exerted influence on MCHO (Table C.2). Nitrate also was found to co-vary with MCHO at station 2 (Table C.11). This might indicate the common origin of these compounds presumably from the decomposing indigenous flora and fauna.

The majority of carbohydrates in freshwater originates in terrestrial systems, i.e. from plants after death and dry out and may release 30 percentage of the organic matter into water. Half of this material is simple carbohydrates possibly monosaccharides and polysaccharides. The remaining half is organic acids rich in carbohydrates. Thus water leachates of plant material may be an important source of carbohydrates in water.

At the riverine station MCHO was found to exhibit highest concentration in the monsoon period indicating the increased terrestrial runoff characteristic of this season. Soil contains carbohydrate-rich organic debris not readily soluble in water (Stevenson, 1982). The enzymatic hydrolysis of particulate carbohydrates by soil microbes releases simple mono and oligosaccharides into the soil solution, which are flushed from the soil during wet season into streams and rivers. Thus the abnormally high value observed in the peak monsoon month, July, may be due to the increased land runoff during this month. The higher concentration during the premonsoon period may be the reflection of increased bacterial mineralization of both autochthonous and allochthonous organic matter. Correlation analysis revealed the influence of pH on the MCHO distribution (Table C.2).

The estuarine site exhibited random monthly distribution of monosaccharides. However, the monsoon season recorded lowest concentration. During the monsoon season, since the light penetration was low, primary production may be considerably reduced. As phytoplankton was found to be the major source of monosaccharides, decrease in production was reflected in the lower levels of MCHO. The highest concentration observed in the postmonsoon season also supports this argument. Thus, the main source of carbohydrates may be the autochthonous organic matter rather than the inputs from land in this estuary. pH as well as nitrate was found to influence the MCHO distribution at this site (Tables C.2 and C.11). The positive correlation with nitrate may indicate the common source for these two compounds.

### ➢ Dissolved tannin and lignin (T & L)

Tannins are polyphenols that occur only in vascular plant tissues such as leaves, bark, heartwood, seed and flowers (Haslam, 1989). Tannins constitute up to 20 percentage of leaf tissue (Benner *et al.*, 1989) and are a major form of terrigenous organic matter cycling in riverine and marine systems. For comparison with other organic biomarkers, lignin accounts for ~ 5% of leaf tissue (Hedges and Weliky, 1989; Benner *et al.*, 1990), carbohydrates 40-50% (Cowie and Hedges, 1984; Benner *et al.*, 1990), Cutin 5-10% (Goni and Hedges, 1990), aminoacids 5-10% (Cowie and Hedges, 1992), lipids 5-10% (Suberkropp *et al.*, 1976) and pigments ~ 1% (Tissot and Wette, 1978). Tannins are the major components of the leaf tissue and bark, therefore can have significant impact on bulk properties of organic mixtures, such as aromaticity, organic C:N ratio, phenolic OH, colour and reactivity.

Tannins are water-soluble compounds that have a high capacity to complex with proteins. The ability to complex with proteins and aminoacids leads to further geochemically important trait of tannin – inhibition of organic matter degradation. At the right concentration, tannins are literally toxic to their environment. At 15 mg/l, tannins have been known to cause fish-kills. In addition to complexing bacterial exoenzymes and directly slowing degradation, tannins may also bind up the nitrogen source used by degraders for growth.

Lignin forms a network around cellulose fibres in maturing xylem, the channelled woody core of terrestrial plants, which fulfils an important supportive function as plants grow. Cellulose is still an important component of wood (40-60%) but lignin comprises most of the remaining material. Lignin is a high molecular weight, polyphenolic compound, formed by condensation reactions between coumaryl, coniferyl and sinapyl alcohols. The seasonal changes in concentration of natural phenolic materials in aquatic systems may be driven by the climatic patterns that control hydrologic transport of detrital organic matter from the watershed. If climatic patterns shift significantly, the associated changes in concentration of natural polyphenolic material could seriously affect the functional relationships of aquatic ecosystems.

In this study, tannin and lignin showed significant variation between the aquatic systems as recealed by the ANOVA calculations (Table B.4). At station 1, which is a mangrove site, T &L varied from 0.335 to 1.407 ppm; whereas at station 2, the concentration was in the range 0.364 to 2.910 ppm. The riverine site recorded T &L in the range 0.246 to 1.831 ppm. Estuarine water was characterized by low T &L content. Here, T &L ranged between 0.010 and 0.893 ppm (Table A.22). Seasonally each aquatic system under study showed distinctive distribution pattern. Seasonal mean variation of dissolved tannin and lignin is depicted in Figure 4.2. At station 1, premonsoon recorded the maximum concentration with a postmonsoon minimum. However, station 2, which is also a mangrove habitat, exhibited peak concentration during the monsoon period and the lowest concentration was observed in the premonsoon season. Station 3, Chitrapuzha recorded T&L hike during premonsoon season while, the minimum concentration was noted during the monsoon period. Estuary exhibited generally lower concentration of T &L. However, the highest concentration was observed during premonsoon season and postmonsoon recorded the lowest. The order of abundance of the compound was station 2 > station 3> station 1 > station R.

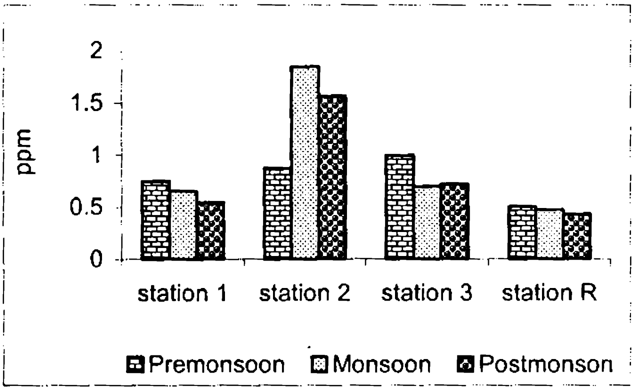

**Figure 4.2:- Seasonal mean variation of dissolved tannin and lignin**

Generally, concentration of T &L is high in mangroves as the resident plants have high concentration of these compounds. Living mangrove leaves contain about 50 percentage lignocellulose, a highly refractory structural complex consisting of aromatic heteroplymer, lignin, in close physical and covalent association with the polysaccharide, cellulose (Benner and Hodson, 1985). Sediments in mangrove swamps can be anoxic and very reducing within a few centimetres of the water-sediment interface. Moreover, anoxic condition undoubtedly exists within the dense packs of decaying leaves that often collects in undisturbed embayment. Kristensen (2000) has shown that anaerobic bacteria appear more limited than aerobic organisms in their ability to depolymerize certain large complex molecules like lignin. Tannins are known to resistant to microbial degradation. Antimicrobial effects of tannins include both the inhibition of microbial colonization of plant material (Cundell *et al.*, 1979) and the inhibition of microbial degradation of decaying plant material. Tannins inhibit microbial decomposition by binding with and inactivating microbial exoenzymes, such as cellulose.

Benner *et al.* (1990) found that lignin derived phenols are leached in considerable amount from mangrove leaves during early diagenesis. A high percentage of lignin might therefore be present in mangrove derived dissolved organic matter. Moran *et al.* (1991) traced dissolved organic matter from a mangrove swamp ecosystem at the Berry islands (Bahamas) by analysis of dissolved lignin derived humic substances and naturally fluorescing compounds.

Among the mangrove habitats, station 2 recorded higher T &L concentration than station 1. This might be due to the different geographic setting of the sites. Station 1, Mangalavanam is an open system with regular tidal flushing. Hence organic matter and nutrients are continuously exchanged with the estuarine waters diminishing the possibility for organic matter accumulation. However, station 2 is a closed system with minimal disturbances. Hence refractory compounds such as tannin and lignin might have retained within the mangrove itself lowering the nutrient quality of the creek water.

Seasonally, station 1 exhibited highest concentration during the premonsoon period. At higher salinity and temperature characteristic of this season, degradation of phenols was reported to be high with more generic diversity of phenol degrading bacteria. In an earlier study by Joseph and Chandrika (2000), in the same system observed that fungal population was dominant during this season and most of the bacterial population increased with summer temperature. Hence elevated rates of decomposition process may be the reason for this observed hike in concentration during the premonsoon period. At station 2, T & L concentration was highest during the monsoon season. At this site, water level in the creek waters was low compared to the other season as the entrance for floodwaters are closed to prevent the escape of prawn larvae to the estuary. Recalcitrant materials such as T & L was concentrated and accumulated in the system during this season.

Salinity and pH were found influence T & L concentration as revealed by the correlation analysis (Table C.2). In a study by Madhukumar and Anirudhan (2000) tannin adsorption onto sediment was found to decrease with increase of pH. Hence, increase in pH was found to favour desorption of the compound from the fine sediments was favoured. Increased salinity was reported to support elevated bacterial population, which in turn, resulted in enhanced decomposition. At station

2, temperature correlated inversely with T & L concentration (Table C.2). Water level in the creeks was low in the cool monsoon periods resulting in concentration of T & L in the overlying waters.

At the riverine site concentration of T &L was found to be very close to that of the mangroves. This may be due to two reasons. Since rivers and streams carry enormous amount of terrestrial matter, of which T & L forms a substantial proportion, concentration of these compounds may be high. Many industries were found to release polyphenols into this river resulting in elevated concentration of the compound. Seasonally, premonsoon season exhibited highest concentration probably due to the increased decomposition rates during this period. Considerable dilution might have occurred by the heavy monsoon showers reducing the compound concentration.

Both salinity and temperature were found to be positively correlated with T & L (Table C.2) indicating the enhanced rate of mineralization with the increase of these parameters. Almost all nutrient compounds were positively correlated to T&L showing their common origin presumably from the effluents from the nearby industries (Table C.11).

In general, concentration of T&L was low in the estuarine waters. The main contributor of T &L into this estuary may be the terrestrial runoff and outwelling of organic matter and nutrients from the mangroves. Dittmar and Lara (2001) have shown that in contrast to the non-conservative terrestrial dissolved organic matter, mangrove derived dissolved organic matter was transported to greater distances in an estuary indicating more refractory and conservative behaviour. Even though the seasonal variation was low, premonsoon period exhibited highest concentration indicating enhanced bacterial decomposition of organic matter. Among the environmental parameters, dissolved oxygen was found to be inversely correlated with T &L (Table C.2). This points to the origin of the compound by decomposition of organic matter, which is aided by dissolved oxygen. At the sediment-water interface, mineralization processes were reported to take place at a rapid rate and oxygen levels are often limiting resulting in anaerobic decomposition of the compound. Thus decomposition of estuarine organic matter may be the main source of this compound.

## 4.3 Sedimentary organic compounds

Organic compounds of varied origin, together with the mineral base of the sediments, form intricate heterogeneous systems. An insight into the processes governing the latter can be gleaned from the distribution pattern and existing forms of organic matter, which, in turn, are important factors controlling the microbiological activity, the trophic value of organic matter as well as degradation, redistribution and migration of organic and mineral compounds in the course of diagenesis. A large fraction of organic matter deposited on sediment surfaces is degraded and mineralized by early diagenetic processes near the sediment-water interface (Henrichs, 1992; Canuel and Martin, 1996). The degradation is mediated by an array of aerobic and anaerobic microbial processes in the dynamic interface with a concurrent release of inorganic nutrients (Mackin and Swider, 1989; Canfield *et al*; 1993). Several factors control reaction rates in surficial sediments including organic matter quality (i.e. the chemical composition), age (decomposition stage), particle association (sorption onto mineral surfaces, organic matrices, clay lattices and micropores), bioturbation (physical disturbances and macrofaunal composition) and environmental conditions (temperature and concentration of oxygen and other electron acceptors) etc. (Mayer, 1994; Kiel *et al.*, 1994; Aller, 1994; Fenchel *et al.*, 1998).

In mangrove sediments, where much organic matter remineralization is carried out under anoxic condition (Jorgensen, 1982), the concerted action of a diverse microbial community (a microbial food chain) is required to remineralize organic matter to carbon dioxide and methane. Large substrates must initially be hydrolyzed by extracellular enzymes to smaller substrates that can be transported through bacterial cell membranes. Heterotrophic bacteria utilize the hydrolyzed substrates for cellular carbon and energy, and excrete organic transformation products. These products are then utilized by other members of the microbial food chain, which, in turn, further transform the organic carbon (Arnosti and Holmer, 1999).

The level of organic carbon in sediments is reported to be a reliable index of nutrient regeneration and the productivity of a water body (Woodroffe, 1992; Robertson *et al.*, 1992). As the preservation and burial of organic matter in aquatic environments is a function of the rate of primary productivity, water depth, dissolved oxygen content in the water column, sedimentation rate, biological activity and the sediment stability, the organic carbon content of the sediments can be a sensitive indicator of the nature of source areas and the environments of deposition (Emerson and Hedges, 1988). In this study, in order to assess the nature and decomposition status of the organic matter in varied aquatic sediments, both the labile as well as refractory compounds were analysed. Seasonal variations of the compounds were also discussed and statistical analysis was conducted to determine the chief geochemical reactions undergone by them.

### ➢ Total Carbohydrates (TCHO)

Carbohydrates function as food reserves, structural materials and antidesiccants. Polysaccharides are major components in most cell walls, which provide a rigid, reinforcing layer around the cell membrane in plants, bacteria and fungi. Carbohydrates are important in the production of fats and proteins.

In this study, sedimentary carbohydrates in the mangrove sites were lower than the riverine site. At Mangalavanam, station 1, carbohydrate varied from 3.31 to 12.54 mg/g whereas at station 2, which is also a mangrove site total carbohydrate ranged between 5.600 to 14.10mg/g (Table A.23). The contribution of TCHO to the total organic carbon pool was 9.47% and 12% at station 1 and 2 respectively (Table A.27). The riverine site recorded highest annual mean concentration. Here, TCHO was found to vary between 2.34 to 22.13mg/g. TCHO contribution was highest to the organic pool at this site (33.72%). The estuarine site displayed much lower TCHO content compared to the other systems. Carbohydrates ranged from 0.16 to 2.16mg/g in the estuarine sediments. Here, only 5.21% of organic carbon was supplied by TCHO. ANOVA calculations revealed significant difference between the stations but not between months (Table B.5). Seasonally, station 1 and the estuarine site recorded highest concentration during the premonsoon period (Figure 4.3). Postmonsoon season was characterized by peak concentration at station 2, while the riverine site exhibited the highest TCHO content during monsoon.

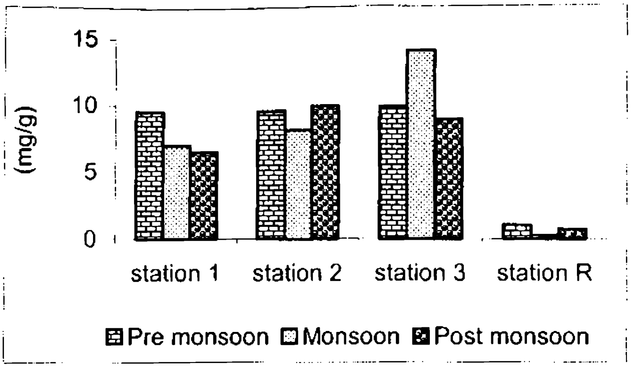

**Figure 4.3:- Seasonal mean variation of sedimentary total carbohydrates**

In the mangroves, carbohydrates are introduced primarily by the leaching of plant litter. The first stage of decomposition in mangroves involves the leaching of soluble materials mainly carbohydrates. Physical and biological decomposition are much slower processes. Physical decomposition involves the weathering of mangrove-derived material over time. Biological factors are also at work to break down and utilize all available compounds of the remaining material. Thus, the combined action of these pathways of decomposition may introduce considerable amount of carbohydrate in mangroves.

Mangrove plants also play an important role in the modification of the geochemical composition of the sediment. *Avicennia* trees are known for their extensive radial cable roots with pneumatophores, which constitute a pathway for the exchange of oxygen between the atmosphere and sediment. Earlier studies highlighted that *Avicennia* roots created oxidized rhizosphere larger than any other species (Thibodeau and Nickerson, 1986; Marchand *et al*, 2003). The introduction of oxygen by plant roots increases the redox potential of the sediment, which, in turn, favours the aerobic oxidation. However, Kristensen and Holmer (2001) have shown that the decomposition of fresh and labile organic materials in sediments is independent of redox condition, whereas partly degraded materials are degraded faster when exposed to oxygen. Carbohydrates are found to be leached in the first stage of litter decomposition itself and since the bacterial population in the mangroves of the present study were quite high, intense remineralization processes would have introduced substantial amount of carbohydrates into the sediment.

Furthermore, macrobenthic activity usually results in more rapid and complete decomposition of organic matter relative to sediments without bioturbation (Anderson and Kristensen, 1992; Aller, 1994; Banta *et al.*, 1999). The muddy substratum of mangroves would have favoured accumulation of organic matter. Many authors have reported that adsorption of organic matter on sediment particles can decrease its availability to microbial degradation (Sugai and Henrichs, 1992; Hedges and Keil, 1995). Therefore, adsorption and desorption behaviour of organic substances may partially explain the selective decomposition and long-term preservation of organic carbon in mangrove environments (Henrichs and Sugai, 1993).

Of the two mangrove systems under study, station 2 recorded higher concentration than station 1. At station 1, the sediments are flushed regularly with the tidal water whereas tidal inundation was minimal at station 2. Gong and Ong (1990) observed that highest decomposition rates occurred in sites with most frequent tidal inundation where leaves were submerged most of the time, and that in the less inundated areas, leaves decomposed more rapidly during high rainfall periods. Since station 2 is of isolated nature, higher TCHO levels can be attributed to increased rate of decomposition. Organic mater and nutrients are outwelled from mangroves by the tidal activity (Benner *et al.*, 1986). Hence at station 1, considerable amount of TCHO may be exported to the estuarine waters reducing the concentration of the compounds in the surface sediments. They have further pointed out that not all mangrove systems are exporters of organic matter. Systems that have little or no hydrologic energy may be net importers of organic carbon.

Seasonally also the two mangrove habitats behaved differently. Premonsoon season recorded the highest concentration at station 1, whereas at station 2, peak concentration was observed during postmonsoon period even though seasonal variation in the non-monsoon period was not very conspicuous at this site. The hike in TCHO content during the premonsoon period can be related to the enhanced bacterial activity facilitated by the increased temperature and salinity of this period. At station 2 also non-monsoon period recorded higher concentration and the same process can be responsible for the observed higher concentration. Dilution of the organic-rich sediments by the sediments introduced by the increased freshwater influx may have resulted in lower TCHO content during the monsoon season.

Correlation analysis showed that only temperature had significant role in determining the TCHO content (Table C.3). Temperature was found to be correlated positively with TCHO indicating the elevated remineralization processes occurring there.

The riverine sediments showed highest annual mean TCHO concentration. This can be either due to the aquatic macrophytes present at the sampling site or may be due to the increased amount of allochthonous organic matter. Seasonally, monsoon season was found to be dominant in TCHO content. This can be related to the increased terrestrial runoff characteristic of this season. In this river, both allochthonous and autochthonous organic matter may be contributing to the organic matter load. This was evident from the higher concentration in the premonsoon period as the increased light penetration facilitated elevated primary production. Correlation analysis showed highly significant correlation of TCHO with sedimentary organic carbon and the finer fraction of the sediments (Table C.3, C.12). This shows that carbohydrates may be the significant fraction of the sedimentary organic carbon. pH was also found to be influencing TCHO content in these river sediments.

The estuarine sediments exhibited generally lower levels of TCHO. This can be due to the sand dominance of the sediment, which has a poor capacity to accumulate compounds. Here, monsoon season recorded lowest TCHO concentration. This can be attributed to the dilution of both allochthonous and autochthonous organic matter by minerals and clays from upstream areas by increased rate of erosion. Reduction in autochthonous input during monsoon months may be the result of decreased primary production due to factors such as reduced light penetration, turbulence and high sediment discharge. The dominance of TCHO during the non-monsoon period may be linked to high primary productivity, transport of organic matter, anthropogenic input, high rates of decomposition and subsequent preservation due to the ambient condition prevalent in the estuary such as pH, salinity, dissolved oxygen, Eh etc.

### ➤ Sedimentary protein

Proteins account for most of the nitrogen in organisms; free aminoacids and peptides are found in lesser amounts. Proteins are present in organisms in forms of colloidal solutions, as elastogels and they are incorporated in the tough tissues. As a result of metabolism of living organisms and posthumus organic matter decay, aminoacids and peptides of various degrees of polymerisation are released into the waters. A portion of the proteinaceous compounds is incorporated in the non-living organic matter. In the bottom sediments proteins may contribute up to 0.0.6% of the organic matter. The destruction of the proteins and their incorporation into non-extractable complexes terminate mainly at the water-sediment interface and within several centimetres of the upper sediments. Proteins and their constituent aminoacids are thus the most abundant substances in phytoplankton and mangrove litter, and represent an important source of carbon and nitrogen in aquatic systems.

The mangrove sediments and the riverine sediments recorded comparable protein content in this study. At station 1, protein ranged from 0.54 to 30.61mg/g. Sediments of station 2 exhibited higher concentration than station 1. Here, protein varied between 5.51 to 32.5mg/g. Station 3, riverine site, exhibited protein content as low as 3.840 to as high as 48.69mg/g (Table A.24). Relatively much lower protein content was observed in the estuarine sediments. Protein varied from 0.24 to 1.9 mg/g in this estuary. ANOVA calculations showed significant variation in protein content between the aquatic systems studied (Table B.5). Seasonally, postmonsoon season exhibited highest concentration at all sites except at the estuary (Figure 4.4). Here, premonsoon recorded the peak concentration. At station 1, monsoon period exhibited lowest concentration whereas station 2 and 3 exhibited lowest protein content during premonsoon season.

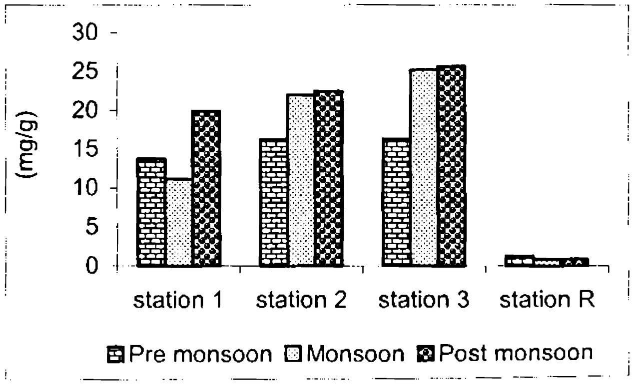

**Figure 4.4:- Seasonal mean variation of sedimentary protein**

In the mangroves, degradation of huge quantity of plant litter may release considerable amount of proteins into the surroundings. In this study, the two mangrove stations varied considerably in their protein content. Higher concentration was noted at station 2, where the tidal activity was minimum. This would have favoured the accumulation of organic matter in the sediment. By the regular inundation of tides at station1 the finer sediments are washed off frequently, and this system may have acted as a net exporter of organic carbon. Another explanation for this hike in protein concentration can be the bioturbative forces operating at station 2. Many researchers have observed that protein-rich monosaccharide secretions are produced by burrow dwelling infaunal animals like polychaetes, which are readily degradable substrates for microbial growth (Aller and Aller, 1986; Reichardt, 1988). In an earlier study by Sunilkumar and Antony (1984), polycheate fauna population was found to be very high at this site.

At both the mangrove habitats, postmonsoon season exhibited highest protein concentration probably due to the increased adsorption of proteins to the sedimentary particles. According to Ding and Henrichs (2002), proteins were strongly and rapidly adsorbed by the clay minerals and sediments, and much of the adsorbed protein was not readily desorbed. Furthermore, in the correlation analysis, significant correlation of proteins with sedimentary organic carbon was observed (Table C.12). Thus adsorption of proteins from the overlying water onto the organic matter would have favoured the build up of higher protein content in the sediments during the postmonsoon season. Among the environmental parameters, dissolved oxygen was found to co-vary with protein (Table C.3). This may indicate the origin of the compound from the decomposing organic matter. Exchangeable ammonia and protein was found to be inversely correlated in these mangrove sediments (Table C.12). Ammonium produced in these anoxic sediments need not be by way of the degradation process of proteins, in which ammonifying and nitrifying bacteria convert proteins into ammonium and nitrate respectively. As Cowie and Hedges (1992) have pointed out, bulk of organic nitrogen does not consists of proteins, even though proteins comprises 30-88% of living algal/vascular plant nitrogen. Small amounts of discrete proteins survive early diagenesis, with most proteins retained in the residual organic matter are extensively modified and cross-linked acidic species. Furthermore, mangrove plants are well known for their high tannin content. The hydroxyl groups abundant in these polyphenolic compounds forms hydrogen bonds with proteins and aminoacids and forms biorefractory complex molecules.

Highest annual mean concentration of protein was observed at the riverine site, station 3. The quantity and quality of protein delivered to sediments *via* the water column depends little on the redox condition of the water column — anoxic and oxic waters both deliver same relative proportion of protein to sediments, and its fate is to be essentially completely remineralized (Keil and Fogel, 2001). The observed high concentration of protein in this river sediment can be due to the burial of autochthonous organic matter consisting of both freshwater algae and *Eichhornia crassippes* plant remains. In addition to this, domestic and urban waste materials contain large amount of proteinaceous material. Thus, urban sewage disposals would also have contributed to the sedimentary protein content.

At this site, monsoon and postmonsoon periods recorded elevated concentration pointing to the increased amount of protein in the run-off waters. Protein concentration in the sediments can be related to the river discharge, higher concentration during the time of high stream flow. Among the hydrographical parameters, both dissolved oxygen and temperature correlated inversely with protein (Table C.3) clearly showing the decomposition of organic matter with the consumption of oxygen. Total sedimentary nitrogen exhibited remarkably significant correlation with proteins indicating that protein contributed substantially to the total nitrogen pool in these river sediments (Table C.12).

The estuarine sediments recorded much lower content of proteins due to their sandy nature, which has very poor capacity to hold organic matter. In addition to the sand dominance of the sediments, considerable dilution of the organic-rich estuarine sediments with organic-deficient marine sediments would have occurred by the action of tides and waves.

The sources of protein in this estuary include both the autochthonous and allochthonous organic matter. Accumulation of plant material into the clay minerals of the sediments where they are particularly resistant to chemical and biological degradation and the domestic wastes containing high amount of proteinaceous compound contributed to the allochthonous organic matter. Fish processing units located on the banks of this estuary discharge animal tissues, which undergo decomposition and liberate protein, which are adsorbed or settled to the bottom sediments. Low concentration observed in the monsoon and postmonsoon periods can be due to the increased utilization of the compound by the benthic organisms or to the incorporation of nitrogen compounds to humic matter by various humification pathways (Bhosle *et al.*, 1988).

Correlation statistics showed significant correlation of protein with sedimentary organic carbon, clay content and also with exchangeable ammonium (table C.3, C.12). Adsorption of protein onto surfaces was thought to be a hydrophobic reaction (Kirchman *et al.*, 1989). Many inorganic particles such as clays have zero point charge at pH < 7 (Stumm and Morgan, 1981) so they would have a net negative charge at higher pH. The high pH of the estuarine water ensures that most proteins are negatively charged except for a few basic ones. However, the thickness of the repulsive electric double layer decreases with ionic strength and the presence of cations enables the negatively charged protein to approach and bind on the negatively charged surfaces. In an adsorption study by Zsom, (1986) a positive relationship with ionic strength was observed. In the oxygenated water of the present study, degradation of protein molecules would have resulted in the ammonium production by the ammonifying bacteria as indicated by the strong positive relationship exhibited by the two compounds (Table C.12).

### ➤ Total lipids

Lipids include all substances produced by organisms that are effectively insoluble in water but are extractable by solvents that dissolve fats. The sources of lipid in the marine environment are the auto and heterotrophic organisms. A certain portion of lipid reaches the aquatic systems with allochthonous organic matter, which consists of neutral lipids and constituents of oil. All forms of lipids, dissolved or colloidal, particulate, those contained in the bottom sediments and in interstitial waters are interrelated and can be converted to one another.

The general dependence, which determines the distribution of lipids in sediments, is the direct correlation with sedimentary organic carbon. The magnitude of bio-production, the quantity of particulate carbon arriving at the sediment sites and burial rates, plus the environment arising largely under the influence of these factors and the gaseous regime of the sediment, determine the concentration of lipids and their content in the organic matter.

Total lipids, in this study exhibited similar concentration levels in the mangrove and river sediments. Estuarine sediments recorded remarkably low concentration than the other two aquatic systems. At station 1, lipids ranged from 0.88 to 4.14 mg/g, whereas at station 2, total lipids varied from 1.21 to 5.51mg/g. At station 3, total lipid varied between 0.99 and 4.04mg/g. The estuarine sediments displayed lipid concentration in the range 0.21 to 0.77mg/g (Table A.25). Seasonal mean variations of total lipid are depicted in figure 4.5. Monsoon season exhibited peak concentration at all sites except at station 2. Here, premonsoon recorded the highest concentration. Postmonsoon period was characterized by lowest lipid concentration at all sites. ANOVA statistics showed significant variation both between months and between stations (Table B.5). Percentage contribution of lipids to the sedimentary organic carbon pool was 3.15, 3.69, 8.89 and 2.53 at stations 1, 2, 3 and R respectively (Table A.29).

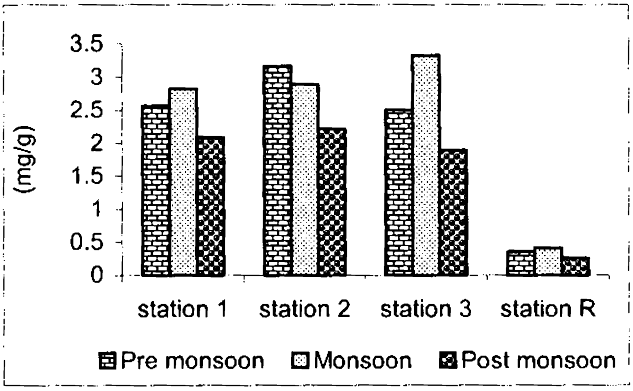

**Figure 4.5:- Seasonal mean variation of sedimentary total lipids**

Mangrove plants have fleshy leaves with thick cuticle, which is shown to be a lipid membrane (Bagchi *et al.*, 1988). The primary source of lipids in this environment is thus the plants itself, leaching of which add lipids and fatty acids to the sediments. Bagchi *et al.* (1988) further observed that mangrove leaves contain uniform high lipid content and fatty acids. Moreover, lipids in the leaves of mangroves distributed in different geographical areas are more or less similar. The observed homogeneity in lipid content in all mangrove plants investigated indicated that these fatty compounds might have some important adaptation in mangrove environment where minimisation of transpiration rate is necessary.

At both the mangrove sites, seasonal variation was only marginal. However, higher annual mean concentration was noted at station 2. The lack of significant seasonal variation can be due to the uniform lipid content of the mangrove plants at both the sites. As Bagchi *et al.* (1988) have pointed out, lipid and wax content of different mangrove species may be uniform. At station 2, slightly higher values were observed during premonsoon season, may be as a result of increased degradation rate of plant biomass by the resident microorganisms. At both the stations, postmonsoon season exhibited lowest concentration probably by the uptake of the compounds by the benthic organisms.

Many of the constituents that make up the total lipid content in mangrove sediments are labile and can be remineralized by bacteria at a faster rate. The efficiency of microorganisms for the conversion of mangrove leachates to microbial biomass is very high (64-94%) (Benner *et al.*, 1986). The large percentage of leachable materials in the mangrove leaves and high efficiencies of conversion of leachates into microbial biomass suggests that microbial production at the expense of mangrove leachates is an important source of carbon and energy to food webs in mangroves.

Correlation analysis showed both dissolved oxygen and pH were inversely correlated with lipids (Table C.3). Total lipid was also found to be enriched in the finer fraction of sediments although the correlation was less significant. Oxygen is the energetically most favourable electron acceptor for microbial respiration (Fenchel *et al.*, 1998). Hence oxygen becomes soon limiting in the sediments as the degradation process progresses. Microbial decomposition release lipids into the environment and the inverse correlation reflect that mineralization process was taking place at a faster rate in mangroves.

The river sediments showed lipid content similar to mangroves. This may indicate the increased terrestrial input of the lipid-rich sediments to this river. Brinson *et al.* (1981) suggested that productivity was highest in flowing waters than still water freshwater wetlands. Thus biological production couples with great contribution from the terrestrial runoff contributed to the lipid pool of these sediments. Compared to the other ecosystems under study, lipids contribution to the total organic matter was high in these river sediments (Table A.29).

Seasonally, premonsoon period showed significantly lower values than other seasons. Increased mineralization rates characteristic of this season would have resulted in rapid uptake of the easily assimilable high-energy substrates such as simple lipids and fatty acids. The reduction in river flow velocity might have promoted the sedimentation of suspended matter diluting the lipid-rich sediments. Monsoon as well as postmonsoon seasons showed higher lipid content. This increase in concentration can be attributed to the introduction of lipid-rich organic matter by the heavy influx of freshwater. Urban and industrial effluents may contain high amount of hydrophobic organic compounds. Among the hydrographical parameters, only pH showed any influence on lipid adsorption onto sediments (Table C.3). Grain size of particle may be playing an important role in the accumulation of lipids onto sediments as highly significant correlation was seen with lipids and the clay and silt content (Table C.3).

The estuarine site, in contrast to the river sediments, showed higher concentration of lipids during the premonsoon season. Biological activity associated with primary production by phytoplankton is the major source of lipids. Low values in the monsoon and postmonsoon season can be due to the dilution of organic matter in the estuarine sediments by sediments of poor-lipid content in the heavy runoff waters. Lower concentration during the postmonsoon period can be the result of the utilization of lipid as an energy source by heterotrophic organisms (Ittekott *et al.*, 1984). Proliferation of minerals might also influence the degradation of lipids into other compounds. The lower concentration during postmonsoon indicated availability of lipids for biological utilization as they are energy-rich substrates. Lipids in this estuarine sediment were found to be highly correlated with organic matter (Table C.12). Early diagenesis of organic matter releases compounds like fatty acids. Associated with the action of microfauna, macrofauna, and microorganisms, the formation of organics from other related compounds/substrates or the modification of pre-existing organic substrates by reduction, decarboxylation or aromatisation is induced by adsorption phenomena and a complex series of interaction between the mineral fractions of the sediment.

## ➤ Tannin and Lignin (T&L)

Unlike carbohydrates, proteins and lipids, which are ubiquitous in organic matter and have both marine and freshwater sources, tannin and lignin, are uniquely terrestrial. Thus, in addition to bulk importance, tannins have potential to provide source information that is complementary to lignin and cutin. These poly phenols are very reactive and may undergo significant changes once organic matter senesces and become part of the litter.

Lignin derived phenols have been applied in coastal environment as chemical tracers to identify sources and fate of dissolved and particulate organic matter. Lignin is a unique tracer for vascular plant materials even suitable to distinguish vegetation types. It is, therefore, widely used to trace the fate and transport of organic matter in diverse and marine environments (Hedges and Ertel, 1982; Moran *et al.*, 1991; Moran and Hodson, 1994; Kattner *et al.*, 1999).

T&L, in this study, exhibited distinct seasonal distribution pattern at each of the system analysed (Figure 4.6). The mangroves and the river sediments exhibited comparable concentrations, while the estuarine sediments recorded much low T&L content. At station 1, concentration of tannin and lignin varied from 0.72 to 9.33mg/g, whereas at station 2, the concentration was in the range 4.35 to 10.15mg/g. The river sediments exhibited T&L in the range 0.18 to 11.41mg/g. T&L varied in the range 0.15 to 1.18mg/g in the estuarine sediments (Table A.26). Relative percentage contribution of T&L to the total organic matter of the systems was 7.22, 9.20, 18.63 and 3.56 at stations 1, 2, 3 and R respectively (Table A.30).

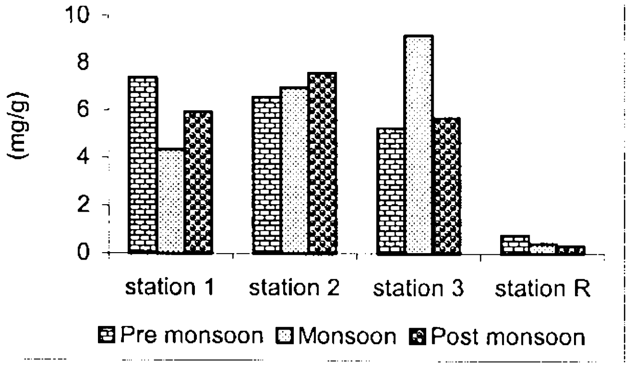

**Figure 4.6:- Seasonal mean variation of sedimentary tannin and lignin**

Living mangrove leaves contain about 50 percentage of lignocellulose, a highly refractory structural complex consisting of an aromatic heteropolymer, lignin in close physical and covalent association with the polysaccharides, cellulose and hemicellulose (Benner and Hodson, 1985). Tannins and other phenolic compounds with microbial inhibitory potential may account for a significant fraction (18%) of the dissolved organic matter in mangrove leachates (Benner *et al.*, 1986; Kristensen and Pilagaard, 2000) leaving the recalcitrant lignocellulosic detritus to be deposited and buried in the sediments.

Antimicrobial effects of tannins include both the inhibition of microbial colonization of plant material (Cundell *et al.*, 1979) and the inhibition of microbial degradation of decaying plant material. Tannins inhibit microbial decomposition by binding with and inactivating microbial exoenzymes. Moreover, rates of microbial degradation of mangrove lignocellulose were not inhibited at similar concentration of added leachates. Leachates were inhibitory to the microbial decomposition of lignocellulosic components only at very high concentration.

Of the two mangroves, station 2 recorded higher T&L concentration than station 1. Isolated nature of the site would have favoured the accumulation of organic matter in the sediments due to which recalcitrant materials like T&L are preserved in the sediments. At station 1, regular tidal activity may have washed off the organic-rich surface sediments.

In a study by Dittmar *et al.* (2001) on the Brazilian mangroves, it was observed that during ebb tide, nutrients and organic-rich porewater flows from the sediments to the creek leading to strongly enhanced concentration of the compound in the water column. After inundation, water is stored in the sediments and released again during the ebb. During storage, its composition is highly influenced by biogeochemical process in the sediments (Dittmar and Lara, 2001). Thus, by the regular tidal action, porewater infusion is promoted reducing the concentration of the compound in the sediment.

Seasonally, premonsoon season was found to dominate in sedimentary tannin and lignin content. This can be related to the increased adsorption of the compounds as the salinity increases. In an experimental study by Madhukumar and Anirudhan (2000) adsorption of tannin was found to increase with salinity. They have explained this adsorption on the basis of maximum stabilization and dispersion of colloidal particles, which in turn, increase the surface area. The increase in adsorption at high salinity may be due to the compression of the diffused double layers surrounding both sediment particles and tannin molecules, the solubility of tannin decrease with increase of ionic strength and this can also favour the transfer of tannin from the solution phase to particle surfaces as a result of the lyophobic effect.

Positive correlation observed between T&L and salinity observed in the present study (Table C.3) also supports this argument. T&L are correlated well with total organic carbon content (Table C.12). Adsorption of tannin to organic matter may be due to specific interactions such as coulombic attraction or hydrogen bonding to organic matter. T&L also showed significant inverse correlation with total nitrogen and phosphorus (Table C.12). Anions like phosphates are found to reduce adsorption of tannin (Madhukumar and Anirudhan, 2000).

The river sediments exhibited high concentration of T&L almost similar to that of mangroves. Though the concentration of tannins and lignin are expected to be present in a large amount in mangrove sediments, comparable concentration of the compounds with that in the river sediments may reflect the different decomposition pathways of the two systems. In the anoxic sediments of the mangroves, anaerobic decomposition is the favoured mechanism. Kristensen (2000) has shown that anaerobic bacteria appear more limited than aerobic organisms in their ability to depolymerize certain complex molecules like lignin. Thus, more efficient remineralization of aerobic bacteria may be one of the reasons for the observed elevated concentration of T&L in the river sediments.

Since T&L are produced exclusively by the vascular plants, terrestrial runoff would have introduced large amount of the compound into the river. In accordance with this, highest concentration of the compounds was observed in the monsoon season. The various industries located on the riverbanks may discharge polyphenolic compounds in their effluents, which would have adsorbed on to the sediment matter. Monsoon-associated hike in concentration pointed to this increased anthropogenic input, as the high-energy runoff water would have introduced polyphenol rich-sediments to the river. In a study by Bagchi *et al.*

(2002) highest input of terrestrially derived organic mater occurred during high river discharge periods. Reduced concentration of the compound during non-monsoon periods could be due to the increased sedimentation of particulate organic matter in the low-flow period.

Correlation statistics revealed negative correlation with phosphate and, though less significant, positive correlation with organic matter (Table C.12). T&L adsorption onto sediments was found to be hindered by the presence of anions like phosphates (Madhukumar and Anirudhan, 2000). Thus, with increased concentration of phosphates, tannin molecules would have preferred to remain in the dissolved state. A significant proportion of the organic matter pool was comprised of T&L in this river sediment (Table A.30). Adsorption of tannin onto organic matter may be due to specific interactions such as coulombic attraction or hydrogen bonding to organic matter.

The estuarine sediments recorded relatively lower T&L content than the other systems. Here, premonsoon season was associated with the highest concentration. Increased adsorption of tannin with increasing salinity was well recognized (Madhukumar and Anirudhan, 2000). Compression of the diffused double layer surrounding the sediment particles may have facilitated the transfer of tannin molecules from solution phase to particle surfaces as a result of lyophobic effect. T&L was found to be enriched in the finer estuarine sediments (Table C.3). The adsorption of tannin by lake sediments may result from specific interactions such as coulombic attraction or hydrogen bonding to organic matter, clays and hydrated metal oxide surfaces in sediments. Exchangeable ammonium was found to co-vary with T&L (Table C.12) indicating their common origin, probably by the natural breakdown of humic acids.

Increased bacterial activity may yet be another reason for the premonsoon hike in concentration. Macrophyte detritus are often deposited in a relatively fresh and labile form at the oxic sediment-water interface (Suess, 1980). Almost all aerobic microorganisms have the enzymatic capacity to perform a total mineralization of complex substrates. Organic matter may therefore be completely metabolised by a single organism to $H_2O$, $CO_2$, and inorganic nutrients using oxygen as the electron acceptor. A unique feature of aerobic decomposition is the formation and consumption of reactive oxygen containing radicals such as superoxide ions ($O_2^-$), $H_2O_2$, and $OH^-$. These radicals are capable of breaking bonds and depolymerize relatively refractory organic compounds like lignin (Canfield, 1994).

The higher T&L concentration observed in monsoon can be attributed to the terrestrial runoff. Dittmar *et al.* (2001) have shown that strong terrestrial runoff is characterized by a higher proportion of lignin-derived phenols. According to Prahl *et al.* (1994) hydrodynamic sorting of river-derived particulates resulted in the deposition of a greater proportion of lignin as large vascular plant detritus in estuarine sediments. Highly significant correlation between protein and T&L was observed in this estuarine sediment. Tannins have high capacity to bind with protein (Zucker, 1983). A tannin polymer has a plethora of hydroxyl groups to hydrogen bond with proteins and aminoacids. The ability for this complexation capacity leads to inhibition of organic matter degradation. Thus association of protein and T&L reflect their probable co-existence in the estuarine sediments (Table C.7).

### 4.4 Quality of organic matter

The quality and composition of sedimentary organic matter are of prime importance to benthic deposit-feeders as these organisms achieve their food requirements by ingesting organic matter (Graf, 1989). The amount of labile, energy-rich molecules can influence the detrital organism population. At elevated bacterial biomass, remineralization processes occurs at a faster rate and the release of nutrients and organic matter is enhanced. This subsequently will lead to increased primary production of the system.

The quality of organic matter may depend primarily on the concentration of labile compounds such as carbohydrates, protein, lipid etc. Biological mineralization processes are at a stake in the presence of antimicrobial compounds such as tannin. These compounds make the organic matter less assimilable for detrital feeders. Hence assessment of the relative proportion in which these compound contribute to the total sedimentary organic carbon pool can provide an insight to the nature of the organic matter. Carbon, in the form of detritus was outwelled from mangroves to adjacent aquatic systems by way of tidal action. Odum (1980) explained that there is a tight coupling between bacterial/microfaunal communities and plant detritus. This close association was believed to result in more efficient cycling of nutrients and was used as an explanation for high estuarine production. The main source of sediments into an estuary is the rivers draining into this. Thus assessment of relative contribution of each of the compound classes to the sedimentary organic carbon of these three aquatic systems is pivotal as all these are interrelated systems.

For all the compounds analysed, station 3 dominated in relative contribution of all the analyzed compounds to the total organic carbon pool. Station 2 was observed with next highest contribution followed by station 1. The estuarine site showed relatively lower proportion of the compounds. Considering the CHO:SOC ratio (Table A.27), in the mangroves and in the estuary, the ratio was < 20 indicating that most of the organic matter present in these systems are mainly autochthonous in nature. In the river sediments, the ratio was > 20 clearly showing the allochthonous nature of sedimentary organic matter.

At all sites, proteins contributed highest to the SOC pool than any other compound followed by carbohydrates (Table A.28). Lipids contributed least to the SOC at all sites (Table A.29). At station 3, relative proportion of all labile compounds was high in the total organic matter and hence sediments at this site can be of greater nutritional value. Among the two mangrove environments, station 2 was found to have higher ratios than station 1. Moreover, it must be noted that individual concentration of these compounds too was higher at this site. Hydrodynamic features such as tidal activity may be the main factor determining the fate of organic matter at this site. Organic matter may be accumulated and preserved at this site due to the low tidal action. Thus it can be concluded that station 1 acted as a net exporter of organic matter, whereas station 2 as a sink for organic matter. The estuarine sediments showed low relative proportion of all the compounds to TOC pool. This may be attributed to the huge amount of humic substances present in the estuary. Dissolved humic substances, which are abundant in the river water flocculate as they meet the saline estuarine waters. Since many rivers drain into this estuary, the major component of the TOC may be the humic substances. However, in this study, concentration of humic substances was not assessed and hence contribution of these compounds can only be presumed. Thus, the river sediments appear to be of high quality followed by the mangroves and then the estuary.

## 4.5 Statistical analysis

Cluster analysis was conducted in order to determine the similarity of the various aquatic systems in the processing of organic matter.

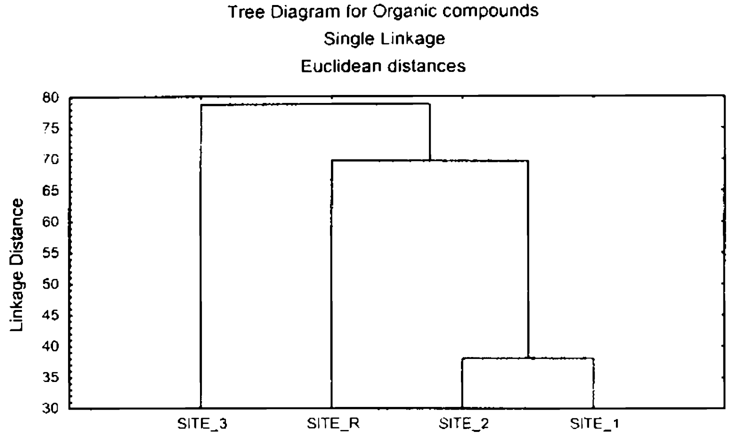

**Figure 4.7:- Dendrogram of bioorganic compounds**

The two mangrove sites exhibited similar behaviour, as they are the most closely related ones in the dendrogram. The river sediments displayed similarity to the mangroves, while the estuarine sediments behaved in an entirely different way (Figure 4.7). The physicochemical characteristics of each aquatic system together with the anthropogenic perturbations are thus the primary factors determining the transport and fate of organic compounds.

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# Chapter 5

# Trace metals

## 5.1 Introduction

Of the chemical elements, metals make up the largest group; their characteristics, however, differ greatly within the biosphere. Heavy metals are common pollutants in urban aquatic environments, and in contrast to most other pollutants, are not biodegradable and are thus persistent in the environment. Many metals, a number of which are non-essential to plant and animal metabolism, are often toxic in low concentrations (Baker, 1981). But some other metals, in trace quantities, regulate the physiological processes and decide the health of the system. Thus, metals form an integral part of the aquatic systems and no scientific investigation on such systems would be complete without an assessment of metal interactions.

Both essential and non-essential metals were selected for the study in the three major phases of occurrence; dissolved, particulate and sedimentary. The essential metals comprise of iron, manganese, zinc, copper and cobalt and non-essential metals form another group comprising of chromium, nickel, cadmium and lead.

The respiratory pigment-haemoglobin, found in vertebrates and many invertebrates contain iron, while the respiratory pigment of many molluscs and higher crustaceans, haemocyanin, contains copper. Zinc is the element present in many proteinaceous enzymes. One of the important Vitamins, Vit.$B_{12}$ contains cobalt. The second category, the non-essential metals are generally not required for metabolic activities and are toxic to the cell at quite low concentrations.

## 5.2 Dissolved trace metals

The most obvious medium of pollution assessment is the surface water of any aquatic system. The tendency and rate by which a metal participate in geochemical or biological process depends on the physicochemical forms in which that metal occurs in dissolved state in an aquatic environment. Information emerging from recent studies strongly suggests that the chemical parameters controlling metal-organism interactions are the activities of free metal ions. If a metal exceeds the critical solubility limit in seawater, it may precipitate as a solid phase or adsorb on particulates and settle to the sediments. The residing biota can bioaccumulate metals from water and release it to the water on degradation of detrital biogenic matter. Generally, the concentration of total dissolved metal in aquatic systems are very low, yet they can be considered as the most important form for the aquatic organisms.

### ➢ Iron

Iron is the most important biological and geochemical trace metal in the marine environment. It is an essential micronutrient for phytoplankton growth as an important component of such biochemical processes as photosynthetic and respiratory electron transport, nitrate and nitrite reduction, chlorophyll synthesis and a number of other biosynthetic reactions (Weinberg, 1989).

Iron in the present study recorded a maximum value of 260.30 µg/l at station 3 and a minimum of 25.60 µg/l at the reference station. From the monthly data (Table A.31), it can be seen that station 3 dominated in Fe content in almost all months. The annual average also was highest at this station, while, the estuarine station showed the lowest concentration. Iron varied from 34.05 to 217.69µg/l in the mangrove habitats, from 26.60 to 260.30µg/l at station 3, and from 25.60 to 115.33 µg/l at the reference site (station R).

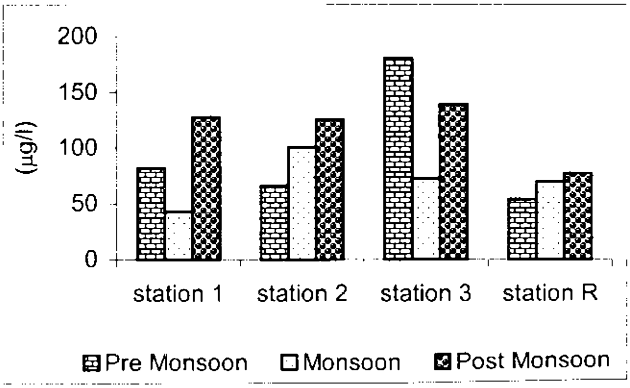


Figure 5.1:- Seasonal mean variation of dissolved iron

Seasonal variation in Fe was quite unique for each sampling site (Figure 5.1). Station 1, Mangalavanam, which, is a mangrove station showed lower values in the monsoon period whereas the 'Fisheries' station (station 2), which is a mangrove nursery showed lowest concentration in the premonsoon season. The riverine site recorded minimum value during monsoon period while the estuarine site exhibited a premonsoon minimum similar to the Fisheries station.

Chemical behaviour of iron and its solubility in water strongly depend on the oxidation intensity of the system in which it occurs, pH has a strong influence as well. The availability of iron in aqueous solution is greatly affected by environmental conditions, especially changes in degree of oxidation and reduction. Fe is present in plant debris and organic wastes in soils and the activities in the biosphere may also have a decisive role on the occurrence of Fe in water. Microorganisms are commonly involved in processes of oxidation and reduction of Fe, since some species may use these reactions as their energy source. Higher concentration of dissolved ferrous iron can occur at the site of either reduction of ferric oxyhydroxides or oxidation of ferrous sulphate. In the latter process, if sulphur is attacked first and altered to sulphate, ferrous iron is released. Kremling (1983) has pointed out that considerable change in the abundance of Fe and Mn will occur across the redoxcline i.e., $H_2S$ - $O_2$ interface.

In the mangrove ecosystem, trace metals can enter with incoming tide associated with suspended particles and Fe and Mn oxyhydroxides (Lacerda *et al.*, 1998). When reaching the reducing condition dominant in most mangroves, these oxyhydroxides are reduced and dissolved and can release their trace metal load into the water column (Lacerda *et al.*, 1999). In the anoxic waters, the Fe (III) oxide/hydroxide is transformed to Fe (II) sulphides. Some iron is dissolved as ferrous iron and iron sulphide complexes (Kremling, 1983). In this peculiar environment, enormous load of organic matter is the reason for the permanent anoxic condition. Most of the contaminants tend to be adsorbed onto suspended particles and removed from water column to the sediments (Bourg, 1988; Millward and Turner, 1995) although redox sensitive elements like Fe with great affinity for organic matter can be intensively remobilised during the early degradation of settling organic matter (Froelich *et al.*, 1979; Berner, 1980). These mechanisms may be the reason for the elevated levels of dissolved Fe in the mangroves.

Moreover, many authors have opined that benthic flux is enhanced by the high content of fine-grained fraction with high levels of organic matter in the sediments (Aller and Beninger, 1981; Irion and Muller, 1990). Apart from this remineralization of organic rich particles, enrichment of dissolved Fe may have resulted in the present study from reductive dissolution of solid Fe from within the sediment and transported to the water column.

Seasonally, postmonsoon recorded the highest value. Desorption of Fe from particulate matter facilitated by the long residence time of the particles in the water column during this period may be the reason for the elevated concentration. Lower values observed at station 1 during monsoon may be due to the dilution of the metal by the heavy monsoon rainfall coupled with land run-off. However, such a monsoon minimum was not exhibited by station 2. Here, the lowest concentration was observed in the premonsoon period. At this particular site, water level was low in the creek waters during monsoon because the entrance for floodwaters was closed in order to prevent the escape of prawn larvae. Hence, in this stagnant condition, diffusion of trace metals from the sediments is highly favoured resulting in a monsoon-associated concentration hike. Of the two mangroves, the Fisheries station (station 2) exhibited higher annual mean concentration. Reduction of oxygen in sediments through biologically catalyzed processes is piloted by high load of organic materials and water stagnation due to low tidal activity may be the reasons for the observed behaviour. Thus, the higher dissolved Fe concentration in these two mangrove stations compared with the estuary suggests that there is an important release of dissolved Fe from the sediment-water interface which is possibly due to reduction of iron oxides by bacteria during the mineralization of organic carbon.

The dynamics of heavy metals are often more complicated in rivers and streams than in lakes and oceans. In most rivers, the dissolved fraction contains the most active form, colloids. All the colloids in aquatic systems are coated with natural organic matter and this organic coating is the main reason why these natural colloids are negatively charged and very reactive to heavy metals (Beckett, R., 1990; Murray and Gill, 1978; Hong and Kester, 1985; Tripping, 1986; Tripping and Cooke, 1982). Fe has an extensive ability to form complexes with naturally occurring organic compounds. Besides, Fe occurs in high concentration in river water than in seawater.

The relatively high concentration of dissolved Fe in the riverine station can be related to the prevailing pH of that system. In the low pH, Fe present will be mostly in the soluble $Fe^{2+}$ oxidation state. Influence of pH on Fe distribution was also reported by Aston and Chester (1973). The effluents from the nearby industries are the major contributors of heavy metals into this system. The elevated levels of Fe observed in the premonsoon period can be attributed to the reductive dissolution of solid Fe from within the sediment and transported to the water column facilitated by the reduced flow regime characteristic of this season. Considerable dilution may have occurred causing a reduction in the dissolved Fe in the monsoon season. Colloidal Fe, which, can pass through 0.45μm filter can be another source for Fe at this site. Lack of correlation with any of the hydrographical parameters (Table C.2) emphasizes the role of anthropogenic input in the distribution of Fe at this station.

In the present study, a significant negative correlation of Fe with salinity was observed in the estuary (Table C.2). This non-conservative behaviour of Fe is reported in other estuaries also (Wu and Luther, 1995, 1996; Luther and Wu, 1997; Johnson *et al.*, 1999). The inverse relationship with salinity shows that processes determining Fe distribution may include fresh water source of Fe, Fe removal by particle scavenging and phytoplankton uptake, sedimentary Fe input and atmospheric deposition. In estuaries, Sholkovitz (1976) and Boyle *et al.* (1977) suggested a physical association of colloidal humic acids and colloidal Fe-O-OH. Simple co-removal of humic acids and Fe may be all that is seen with an increase in salinity as the colloids become destabilized and flocculate (Eastman and Church, 1983). In the estuary, due to high tidal activity, intrusion of seawater impoverished in metal content may dilute the estuarine water causing a reduced soluble Fe levels at this site compared to other systems. Furthermore, the increased amount of sea salts can remove the soluble Fe from the water column. Ouseph (1992) has pointed out that the chief source of Fe in the Cochin estuary is the land drainage, harbour activity and sewage. The concentration levels observed in the present study fall within the range observed in the same and neighbouring aquatic systems (Joseph, 2002; Unnikrishnan, 2001; Shibu, 1992; Ouseph, 1992).

## ➤ Manganese

The chemistry of manganese resembles that of iron in that both metals are redox sensitive and are relatively mobile in the aquatic environment. The thermodynamically stable form of manganese in oxic seawater is Mn (IV). The nitrate, chloride and sulphate salts of Mn are soluble in water, whereas, the corresponding hydroxide, sulphide, carbonate, oxide and phosphate salts are sparingly soluble and are removed in the particulate fraction from the water column (Luther *et al.*, 1986).

Dissolved Mn concentration in the study area varied between 3.060 and 244.7μg/l in the mangrove stations, from 3.20 to 20.710μg/l in the polluted river site and from 4.620 to 21.16μg/l in the estuary (Table A.32). Mangrove stations showed highest annual mean concentrations while the estuarine and riverine sites recorded comparable concentrations. Seasonally, premonsoon season was characterized by the dissolved Mn hike in both mangrove sites with monsoon season exhibiting the minimum (Figure 5.2). However, monsoon period recorded the maximum concentration in the riverine and estuarine sites.

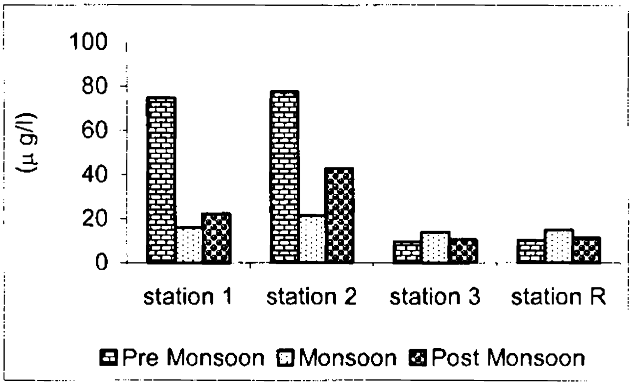


**Figure 5.2:- Seasonal mean variation of dissolved manganese**

Manganese Sulphides are very unstable ($K_{sp}$ (MnS) = 9.6 and 12.6) (Forstner and Wittman, 1979) and are only formed when total dissolved S exceeds total carbonates by a factor of at least 100 (Krauskopf, 1979). Therefore, manganese sulphides have never been detected in mangroves (Lacerda *et al.*, 1998). Under the prevailing anoxic conditions, many bacteria that can oxidize organic matter, with the reduction of Fe (II) can also reduce Mn (IV) in a dissimilatory fashion using it as an electron acceptor. Also, under the anoxic condition, Mn (IV) is easily reduced through non-enzymatic mechanisms to soluble Mn (II) (Graton *et al.*, 1990; Lovely, 1993; Sprat *et al.*, 1994; Luther (III) *et al.*, 1998). Thus, Mn would not behave like most other trace metals and a significant fraction of this element is available for plants. However, these mechanisms would also make Mn available for exportation to adjacent coastal waters. Another significant source of Mn is the freshly formed manganese coated particles entering the mangroves from nearby estuarine waters. On entering the reduced condition during the ebb tide inside the mangroves, these Mn coatings dissolve releasing soluble manganese.

The intense low redox potential of the mangrove sediments facilitates the remobilization of this element in the mangroves. The diffusive input from the sediment–water interface and pore waters are yet another source for this metal in this environment. Many authors have emphasized the importance of benthic input of this metal resulting in elevated dissolved fraction in many water bodies (Santchi *et al.*, 1990; Morris *et al.*, 1982; Davison, 1993).

The seasonal trend showed a hike in concentration during premonsoon period at the mangrove sites. Warmer temperature, characteristic of this season would have resulted in enhanced bacterial activity, which, in turn, facilitates the release of soluble Mn to the water column. Furthermore, a significant positive correlation between dissolved Mn and temperature (Table C.2) was observed supporting the argument. This covariance of temperature and dissolved Mn confirms the temperature driven effect on distribution of this metal. Most likely, the balance between oxidation and reduction rates determines Mn concentration. Monsoon dilution by the heavy influx of fresh water may explain the lower values observed in this season. Dissolved Mn concentration in the South East Brazilian mangroves were in the range 2.8μg/l – 26.10μg/l (Lacerda *et al.*, 1999). In this study, the summer concentration values of soluble Mn were much higher than the winter concentration levels. Except the peak value in April, the concentrations reported in the present study are in the range of that in the Brazilian mangroves.

Very high levels of soluble Mn in rivers are reported elsewhere (Morris *et al.*, 1982, Davison, 1993). Seasonal variation in Mn, Fe, Zn and Pb may be controlled by the redox condition of the river basin (Shiller, 1997). In the present study, monsoon season showed slightly higher values with the non-monsoon months with similar values at station 3. The monsoon maximum can be related to the land run-off coupled with the effluents from the nearby industries. According to Iwashita and Shimamura (2003), reducing conditions can occur in bottom waters of stratified lakes or reservoirs, riverbed sediments and stagnant streams. In the non-monsoon period, inflow is greatly reduced and the residence time of particulate and finely suspended sediments in the water column is increased. This facilitates the desorption process to occur and reduced conditions, which may be developed in the surface sediments greatly favours the migration of soluble form into the overlying water. Such an enhancement in concentration in the post and premonsoon may explain the low seasonal variability at this station.

None of the hydrographical parameters exerted any influence on metal distribution at this site (Table C.2). Lack of correlation with salinity and pH may be due to the narrow salinity range observed in this area. Fe and Mn are commonly associated with particles (Figueres *et al.*, 1978; Rue and Bruland, 1995) and, therefore, the independence of concentration of Fe and Mn with salinity in Chitrapuzha is probably due to inputs from sediments. In addition to this the non-correlation points to the anthropogenic perturbations taking place in this area.

Dissolved oxygen values were found to be higher in this riverine station. In the oxygenated waters Mn would remain preferably in the +4 oxidation state, which is insoluble in water. This oxidized form of Mn is found to be associated with particulate matter in the form of oxyhydroxides. This may explain the lower concentration of dissolved Mn in the river station compared to the mangroves. Sokolowski *et al.* (2001) reported annual dissolved Mn concentration of 15.3μg/l in the Vistula River whereas in the Terminos fresh water lagoon the levels were much higher (0.002-0.118mg/l) (Vazquez *et al.*, 1999). In a study by Joseph (2002) in the same river, the concentrations were in the range of that in the present study.

Factors affecting the hydrogeochemistry of Mn in estuarine waters are different from the rest of the water bodies selected for the study. Here, the prime hydrographical parameters such as salinity and temperature exhibited an inverse relationship with dissolved Mn (Table C.2). Mn is a highly reactive element and dissolved Mn concentrations are low in oxic waters as a result of oxidative scavenging onto suspended particles. Reduced Mn species oxidize to insoluble manganese oxyhydroxides as amorphous coatings, frequently associated with iron (Giblin *et al.*, 1986; Saager *et al.*, 1997). The freshly formed Mn coatings are very efficient in scavenging additional manganese and iron, as well as other trace metals from the water column. This partly explains the inverse relationship with salinity. Studies done by Laslett and Balls (1995), Owens et al (1997), Morris and Bale (1979) also reported a non-conservative nature of Mn, with positive deviation from the theoretical mixing curve at low salinities and removal at higher salinities.

Monsoon peak in concentration exhibited at this station can be due to increased run-off from land, which is rich in Mn containing particles, desorption from suspended particles (Bewers and Yeates, 1978), reductive solubilization (Duinker *et al.*, 1979; Laslett, 1995) and advective and diffusive fluxes of sediment pore waters (Morris and Bale, 1979; Kox *et al.*, 1981; Laslett, 1995). A similar distribution pattern was reported in the Cochin Estuary also (Joseph, 2002; Ouseph, 1992; Sankaranarayan and Rosamma, 1978; Babukutty and Chacko, 1995; Shibu, 1992). Kayamkulam estuary, which is also a part of the Vembanad estuary, showed similar behaviour though concentration was much higher (Unnikrishnan, 2000). Studies done elsewhere showed higher concentration than the present study (Mzimela *et al.*, 2003; Bucciarelli *et al.*, 2001; Hatje *et al.*, 2003; Gavis and Grant, 1986). However, in a study on Lake Tanganyika, Chale (2002) reported similar concentration values. The lower values recorded at the estuarine site in the present study can be attributed to its geographic disposition. The regular tidal activity brings in seawater impoverished in trace metal during each flood period. Considerable dilution together with increased sorption aided by the high saline waters favours the depletion of soluble Mn from the water column.

### ➤ Zinc

Zinc is a heavy metal, which is able to exert acute and chronic toxic effects in a range of fauna and flora. It is also able to bioaccumulate and thereby poses a potential threat to the food chain.

Dissolved zinc showed peak values at station 1, the mangrove site. The order of annual mean concentration of the sites are, station 1 > station 2 > station 3 >

station R. The two mangrove stations recorded high concentrations during postmonsoon period, while, station 3 and station R showed peak values in monsoon season (Figure 5.3). Significantly high concentration of Zn was observed in the months October and November at station 1. Concentration of Zn in the mangroves ranged from 32.90-111µg/l at station 1 and from 24–88.25µg/l at station 2. Station 3, showed wide variation in concentration (8.575–86 µg/l); while station R, the estuarine site, recorded Zn in the range, 7.75–28.75µg/l (Table A.33). ANOVA calculation showed highly significant variation between stations (Table B.6).

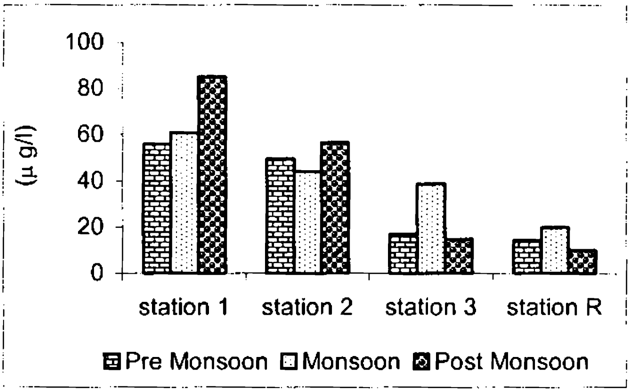


**Figure 5.3:- Seasonal mean variation of zinc**

The wide variation in the concentration of dissolved zinc at the mangrove stations can be partly due to the anthropogenic activities. Petroleum hydrocarbons were reported from station 1 in earlier studies. In addition to this, the peculiar reducing environment dominant in the mangroves regulates the dissolved zinc distribution. Pore water diffusion is particularly favoured due to the anoxic condition of the mangrove sediments. Zn, like Cu, is found to have a high complexing capacity with dissolved organic carbon (Mattheisson *et al.*, 1999). The dissolved organic matter abundant in the creek waters might have favoured the presence of Zn in the dissolved state. Zn showed a highly significant negative correlation with pH at station 1 (Table C.2). This type of correlation was noticed by Grande *et al.* (2003) in the Tinto Odiel estuary in Spain. They attributed this to the tidal flushing, which in turn, cause an increase in pH. This results in the precipitation of metals that are no longer soluble and eventually concentrate in the sediments. The elevated levels of Zn and Cu in the non-monsoon period in the mangroves can be attributed to the concentration by evaporation and increased dissolution from sediments due to high temperature and large contact time in summer (Paul and Pillai, 1983). The warmer temperature can lead to intense bacterial activity releasing high trace metal load into the water column by diagenetic processes. In fact, Zn concentration was found to co-vary with nitrate at station 1 (Table C.11). Since nutrient releases are due to remineralization of organic detritus by microbial activity, it would appear that Zn might have been released by the same process. Church (1986) and Windom *et al.* (1988) observed similar relationships between cadmium and phosphate in the Delaware estuary and between zinc and nitrate in the Bang Pakong estuary and reached similar conclusions.

Zn can have a large riverine source. The fine suspended sediments of the rivers are associated with large quantity of Zn (Stevenson and Betty, 1999; Sokolowski *et al.*, 2001). The process of removal (desorption) from particles might be an important factor responsible for the presence of soluble Zn at the riverine site in the present study. Seasonally, Zinc showed remarkably high monsoon concentration. This can be related to the land run off and influx of metal-rich freshwater. The increased particulate matter load along with suspended sediments brought in by the streams would also be a possible reason for the abnormally high values in monsoon season. The runoff water may contain discharges from the agricultural area containing fertilizer, pesticides and rhodenticides. The effluents from the nearby industries may be the most probable source of this metal. A significant quantity of Zn may have been present in the effluents and the monsoon showers augment its release from the sediments. Senthilnathan and Balasubramanian (1999) observed a similar distribution pattern in the Pondicherry Harbour waters and attributed the summer minima to the utilization and uptake of Zn along with nutrients by residing biota. A similar distribution pattern and concentration range was reported in a previous study by Joseph (2001). Subarnarekha River, one of the polluted rivers of India, recorded higher values for dissolved zinc both in the monsoon and premonsoon seasons (Senapati and Sahu, 1996). Ouseph (1992) observed the zinc concentration in Periyar, one of the major rivers draining into Cochin estuary, to be in the range 24-65 μg/l. This value is higher than that observed in the present study.

There is much published information on the presence, speciation and partitioning of Zn in estuarine waters (Elbaz-Poulichet *et al.*, 1996; Comber *et al.*, 1995; Ouseph, 1992; Lazlett and Balls, 1995; Flagel and Sanudo-Wilhelmy, 1993; Boughriet *et al.*, 1993; Harper, 1991). Dissolved Zn varied between 7.750µg/l and 28.750µg/l in the estuarine station in this study. The concentration was much less than those of the mangroves. Seasonally, monsoon recorded the maximum and postmonsoon the minimum concentration. This site behaved similar to the riverine site. The monsoon hike can be the result of land runoff and influx of metal-rich freshwater. The suspended sediments and particulate load of the rivers draining to this estuary are considerably increased during this season causing a subsequent increase in the dissolved metal content. Warnken (2001) has pointed out that other than inputs from rivers, inputs from sediments by diffusive, bioturbative and bio-irrigative processes contribute to the estuarine Zn load. Pore water intrusion may account for part of the observed high levels of dissolved zinc during premonsoon period compared to the postmonsoon season, especially in the anoxic sediments. Since, mobile bed sediment is enriched in trace metals compared with suspended particulate matter, the principal source of dissolved metal may be the desorption from fine, re-suspended bed particles, possibly augmented by metal bearing sedimentary organic matter (Martino *et al.*, 2002). Besides, Windom *et al.* (1988) have shown that the dissolved concentration of Zn increased due to degradation of sediments or suspended particulate organic matter. Other sources of Zn in the estuary may be intense boat traffic. The sacrificial anodes used in boats are a significant source of Zn to the water (Mattheisson, 1999).

The concentration levels in the premonsoon season were higher than in the postmonsoon season at the estuarine site. This may be due to desorption of Zn from particles at higher salinities. The tendency of dissolved Zn to resist removal during estuarine mixing has been noticed by Nair *et al.* (1990) and Shibu *et al.* (1990) in the northern part of the Cochin estuarine system and in other estuaries (Duinker, 1980; Eaton, 1979; Danielsson *et al.*, 1983; Windom *et al.*, 1988). But this observation is in contrast to the previous work done by Ouseph (1992) in the Cochin estuary itself. However, in a recent study, Joseph (2001) observed a similar monsoon maximum. The concentration levels recorded in the present study is within the range reported for other Indian estuaries (Govindsamy and Azariah, 1999; Senthilnathan and Balasubramanian, 1997; Subramanyan and Ananthalakshmi Kumari, 1991; Satyanarayana *et al.*, 1990; Joseph, 2001; Shibu, 1992; Babukutty, 1991) but are lower than the estuaries in other parts of the world (Mzimela *et al.*, 2003; Mattheissen *et al.*, 1991; Carrasco *et al.*, 2003; Stevenson and Betty, 1999; Velasquez *et al.*, 2002; Baeyens *et al.*, 1998).

### ➢ Copper

Copper is an essential metal for all biological life, but is toxic at higher concentration, especially in the early developmental stage of many organisms (Spear and Pierce, 1979). Copper is found to preferentially adsorb to organic matter (Davis, 1984). Particle bound and organic complex bound copper reduces the reactivity and hence its toxicity (Engal *et al.*, 1981; Apte *et al.*, 1990; Gardner and Ravenscroft, 1991). The reactivity will depend on both the chemical and physical environment to which Cu is introduced.

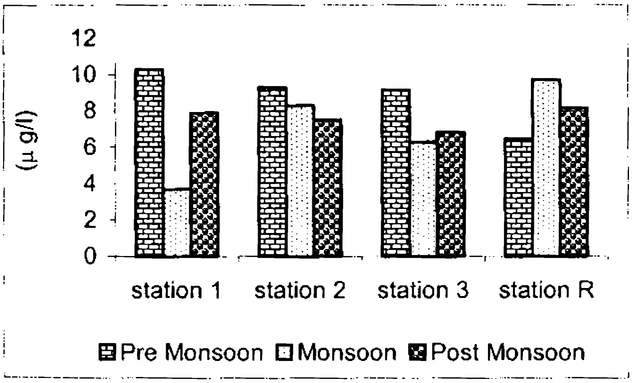


**Figure 5.4:- Seasonal mean variation of dissolved copper**

Dissolved copper varied from 1-16.9µg/l in the mangroves, from 4.1 to 14.5µg/l in the river Chitrapuzha and from 2.3 to 17.6µg/l at the estuarine station (Table A.34). Seasonal mean variation of dissolved copper is depicted in Figure 5.4. In the mangroves as well as in the river, premonsoon period was characterized by the highest dissolved copper concentration. At stations 1 and 3, monsoon recorded the minimum, whereas, at station 2, postmonsoon season exhibited the minimum. The estuary showed a completely different picture with a monsoon hike and premonsoon minimum. ANOVA calculations showed a significant variation within months but not within season or stations (Table B.6). Highest annual mean concentration was observed at station 2, while the lowest concentration was recorded at station 3.

In the mangrove stations Cu was found to co-vary with salinity (Table C.2)). This positive correlation with salinity indicates that variables other than salinity is controlling the metal levels in this system (Vazquez *et al.*, 1999). Processes such as mobilization and removal can control total metal concentration in these mangroves. Shallow depth of the mangrove promotes the resuspension of sediment by tidal action. This activity encourages the release of soluble Cu from the sediments to the water column. The reducing condition of the mangroves remarkably favours pore water diffusion of Cu into the overlying water. In a pore water metal content study, it was shown that interstitial water of the top few centimeters of the core are enriched in Cu content than the rest of the core (Joseph, 2001). This finding again confirms the reductive dissolution of copper from the sediments. Redox sensitive elements such as Fe and Mn were found to present in great concentration in this study. Scavenging action of these metals also control distribution of other elements like Cu, Zn etc. Some organisms are known to concentrate significant amounts of Cu. Relatively high concentration of the element in the mangroves may be due to its release from organisms during their decomposition.

Only a small amount of Cu is associated with particulate matter. Bulk of the metal stays complexed, probably with humic substances as Cu has a strong binding strength to humic substances. According to Irwing- Williams series, only Hg exceeds Cu in affinity to humic substances (Chester, 1990). In these mangroves, humic substances were detected in great amounts (Rini, 2002). The inverse relationship with pH (Table C.2) can be related to the tidal activity. The tides chlorinate and increase the pH of the system. This sudden increase of pH results in the precipitation of metals that are no longer soluble and concentrate in the sediment (Borrego, 1992; Borrego *et al.*, 2001; Braungardt, *et al.*, 1998; Grande *et al.*, 2000; Sainz *et al.*, 2002). According to Shiller and Boyle (1985), pH gradient could influence the solubility through acid-base reactions or through the influence of pH on the adsorption-desorption of trace metals and redox reactions.

General distribution of dissolved Cu in the river very much resembled the mangroves. Copper is used as a catalyst in many industrial processes, which might have led to large inputs of anthropogenic copper into the river. Moreover, the two main components in river water discharge are minerals and organic matter and both of them are identified as the main carriers of copper to the watershed (Bergkvist *et al.*, 1989).

The premonsoon maximum at this station points to the strong association of copper with organic complexing agents such as humic and fulvic acids, which resist desorption even if sea salts concentration is increased (van den Berg *et al.*, 1987; Muller, 1996, 1998). Mattheissen (1999) has shown that a proportion of dissolved Cu will probably have been adsorbed on colloidal particles, which would pass through 0.45μm filter. It is doubtful that materials adsorbed on to such particles are fully bioavailable, although, some fine particles are indeed able to bioaccumulate across cell membranes by pinocytosis, and copper can easily desorb from such particles under such conditions (Benoit *et al.*, 1994; Windom *et al.*, 1983). Since river water is rich in colloids, this desorption mechanism may be another source for dissolved copper in the summer season. Monsoon minima can be due to the dilution of the metal by the heavy influx of freshwater. A significant positive correlation with salinity and temperature further confirms this observation (Table C.2). In the Sagami river and tributaries temperature is found to be the factor determining the seasonal distribution (Iwashita and Shimamura, 2003). In the Subarnarekha River, Cu concentration was high in the premonsoon than in postmonsoon (Senapati and Sahu, 1996). Govindsamy and Azariah (1999) linked premonsoon maximum of Cu to the major source of metal pollution, intensive human activity, discharge of domestic as well as industrial effluents and municipal wastes. Further, higher concentrations of Cu, nitrate and phosphate were recorded at station 3 in the same season perhaps, as a result of organic matter decomposition. Significant positive correlations with nitrite and phosphate also point to this source (Table C.11).

Thus, the enhanced level of Cu in the non-monsoon period observed at the riverine and mangrove stations in this study can be related to the concentration of the metal by evaporation and increased dissolution from the sediments, due to the higher summer temperature and larger contact time of the particles.

The distribution of Cu in the estuary was different from the remaining aquatic systems analyzed. Here, a monsoon maximum and a premonsoon minimum were seen. Significant negative correlations with salinity and temperature were also obtained (Table C.2). Interestingly, Cu showed strong correlations with dissolved Fe and Mn (Table C.8). This inverse relationship was noted by many authors (Martino *et al.*, 2003; Riso *et al.*, 1993; Sokolowski *et al.*, 1999; Windom *et al.*, 1983; Windom and Smith, 1985; Ouseph, 1992; Paul and Pillai, 1983; Senthilnathan and Balasubramaniam, 1997; Sholkovotz, 1976; Byrd *et al.*, 1990; Flagel *et al.*, 1991; Aller, 1994; Sanudo-Wilhelmy *et al.*, 1996; Elbaz- Poulichet *et al.*, 1987; Bayens *et al.*, 1998; Garnham *et al.*, 1991; Paalman *et al.*, 1994; Schlekat *et al.*, 1998). This relationship reveals that large quantity of Cu is removed from the water column and precipitated as suspended matter, which may contaminate the bottom sediment. This behaviour again showed contribution from fresh water sources and indicated that physical mixing is a significant factor in contributing the soluble Cu. In a study on estuaries of South East Coast of India, Senthilnathan and Balasubramaniam (1997) observed a decreasing nature of dissolved copper with increasing salinity and related this to the dilution of metal-rich river water by metal-impoverished seawater and to the rapid sedimentation occurring in estuaries. In addition, a sudden increase in salinity associated with sudden change in freshwater conditions in the summer months would result in the coagulation and precipitation of colloidal clay particles and co-precipitation of metal with/or adsorption onto the particles and remove considerable amount of metal from solution. Thus the non-conservative behaviour can be attributed to the internal sources such as metal desorption from suspended particles, diagenetic remobilization from bottom sediments or anthropogenic inputs.

The monsoon maximum found at this estuarine site can be due to land run-off and influx of metal-rich freshwater. Monsoon-associated hike in dissolved copper has been observed in other Indian estuaries like Zuari, Uppanar, Vellar and Kaduviar. Uptake of Cu by biota is more pronounced during periods of low river flow when the flushing time is increased (Uncles *et al.*, 1983), when increased river flow reduces the flushing time and adsorption onto particles is hindered by slow kinetics (Millward *et al.*, 1992). In the latter case, metals are more likely to be flushed from the estuary in the dissolved form.

Other possible source of Cu in this estuary would be the intense boat traffic. Cu is an efficient biocide and has been used in anti-fouling paints on boats. In a laboratory study by Valkirs *et al.* (2003), it was found that the Cu emission from anti-fouling agents could be a substantial portion of the total dissolved copper loading into a harbour or estuary. Approximately 70% of the estimated total annual Cu loading in the San Diego Bay originates from either leaching process or mechanical cleaning of anti fouling coatings. Cu was found to have a strong association with Fe and Mn in this study. This indicates that Cu occur in association with oxyhydroxides of Fe and Mn and desorption of these amorphous particles could increase the concentration of metals bound to them. A benthic flux of soluble Cu driven by aerobic degradation of sedimented materials at the bottom enhanced by high content of fine-grained fraction with relatively high levels of organic matter in the sediments is also possible. A similar conclusion was reached by other researchers also (Tappin *et al.*, 1995; Aller and Beninger, 1981; Irion and Muller, 1990).

### ➤ Cobalt

Cobalt, one of the biologically essential metal, showed a diverse distribution pattern in this study. ANOVA statistics revealed insignificant variation between stations and season (Table B.6). The annual mean concentration was highest at station 3. Of particular interest, one of the mangrove stations exhibited lowest annual mean concentration. At all stations except station 2, monsoon recorded the minimum value (Figure 5.5). Postmonsoon period was shown to have elevated concentrations at station 2 and 3, whereas station 1 and R were characterized by a premonsoon maximum. Cobalt varied from 0.050 to 1.330μg/l at the mangrove sites, while the riverine and estuarine sites recorded the element in the range 0.130 to 2.330μg/l and 0.170 to 3.900μg/l respectively (Table A.35).

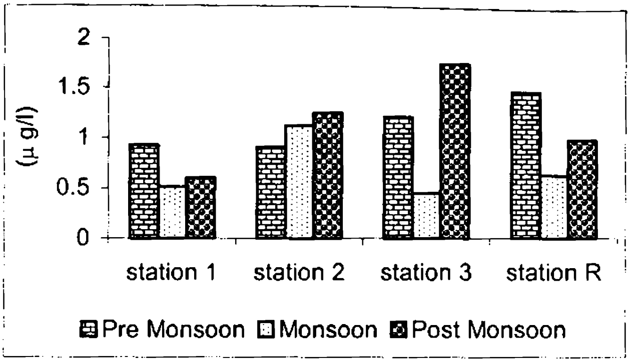


**Figure 5.5:- Seasonal mean variation of dissolved cobalt**

Among the mangroves, the Fisheries station exhibited higher concentration. This can be due to the intense reducing condition existing there. As the tidal activity is low limiting the possibility of influx of oxygenated estuarine water, anoxic condition was prominent in this area for longer periods of time throughout the year. Thus, pore water infusion is highly favoured in this environment. Brooks *et al.* (1968) and Presley *et al.* (1972) have shown that Co in the interstitial water is 2-5 fold higher than the overlying water. This higher concentration, in turn, showed that precipitation as sulphide does not control the dissolved metal concentration. Instead, mobilization takes place by the formation of metal complexes. Such a source of dissolved Co has been suggested by Martino *et al.* (2003), under reducing condition. The bacterial and chemical degradation of particulate organic matter and resuspended sediment formed by the intense bioturbation can further contribute to the soluble Co pool in this system.

At the 'Fisheries' station, Co showed highly significant positive correlations with Mn and Ni, whereas, only Fe exhibited a significant correlation with Co at station 1 (Table C.8). All these clearly show a common source for these metals, probably by the reductive dissolution of Fe and Mn oxides. Forstner and Wittman (1981) have observed desorption of Co from clay minerals and freshly precipitated $Fe(OH)_3$, when the minerals are brought into contact with seawater. The monsoon minimum indicates that considerable dilution took place during this period. Only station 2 showed minimum values in the premonsoon season. This may be due to the removal of substantial portion of the soluble metal from water by the biota and binding onto suspended particles. Since inflow of fresh water is considerably reduced in this period, residence time of particles in the water column is increased causing an efficient readsorption of Co onto suspended particles. This re-adsorption mechanism was kinetically proven by Ciffroy (2003) in a laboratory study.

At the estuarine site as well as at station 1, dissolved Co showed a significant positive correlation with salinity (Table C.2). This confirms the desorption mechanism of Co with salinity changes. Several workers have noted this behaviour (Forstner, 1979; Ciffroy *et al.*, 2003; Martino *et al.*, 2002; Senapati and Sahu, 1999; Govindsamy and Azariah, 1999; Breuer *et al.*, 1999). In a kinetic study on the sorption behaviour of metals, Dyressen and Kremling (1990) have shown that Co and Ni have the intermediate values of solubility values with Mn being most soluble and Cd the least. Thus, desorption mechanism is operative in the case of Co if the ionic strength of the solution vary accordingly. But, mere increase in the ionic concentration may not be the only reason for this non-conservative behaviour. For Co, inorganic complexing ligands such as chlorides are weak ligands. Hence other than ionic exchange, changes in biological conditions between fresh and estuarine waters could be invoked. This process could also explain the readsorption effect observed for Co in the postmonsoon season. Pore water infusion of soluble Co may be one of the predominant sources of Co at station 1. Bearing in mind how regularly the surface sediment is disturbed in the estuary and the rate of physical and chemical processes taking place in pore water, it seems unlikely that pore water infusion contribute significantly to dissolved Co in the overlying water column. Since concentration of particulate and sedimentary trace metals were considerably greater than the dissolved concentration observed in this study, desorption from these two phases are highly probable. Furthermore, inverse correlations with nutrient elements (Table C.11) indicate that dissolved Co is not resulted from the remineralization of organic matter even though it is an essential metal.

Thus, the discrepancy in seasonal distribution shown by Co can be attributed to variations in different environmental parameters such as salinity, sediment load, nutrient chemistry, discharge of domestic and industrial effluents and land run-off reaching this area.

## ➤ Chromium

Chromium is a wide spread element in the aquatic systems, though in most freshwaters it is present at only around 1μg/l (Ehrlich, 1996). Cr is found in small quantities in RNA of a few organisms. Cr is one of the less toxic of trace metals, considering its oversupply and essentiality. There are two important oxidation states of chromium in the environment, +3 (as the chromic cation) and +6 (as in chromate and dichromate anions). In well-oxygenated waters, +6 is the thermodynamically stable species. However, +3 being kinetically stable could persist bound to naturally occurring solids. Interconversion of $Cr^{+3}$ and $Cr^{+6}$ occurs in conditions similar to natural waters. While oxidation of Cr (III) to Cr (VI) appears to be exclusively abiotic (catalyzed by Mn(IV) oxides), chromate-reducing bacteria appear to be wide spread in the environment and Cr(VI) reduction can take place under both aerobic and anaerobic conditions (Wang and Shen, 1995).

In this study, the monsoon period dominated over the other two seasons in chromium content at station 1 and 3. At station 2, premonsoon season showed a peak concentration, whereas, slightly high postmonsoon peak was observed in the estuary. Interestingly, highest annual mean concentration was observed at the estuarine site only for chromium. The order of abundance of the metal was station R > station 2 >station 1 > station 3. Chromium varied fro 1.260 to 6.500μg/l at the mangrove stations, from 1.600 to 4.470μg/l at the riverine site and from 1.650 to 14.530μg/l at the estuarine site (table A.36). Seasonal mean variation of dissolved chromium is depicted in Figure 5.6.

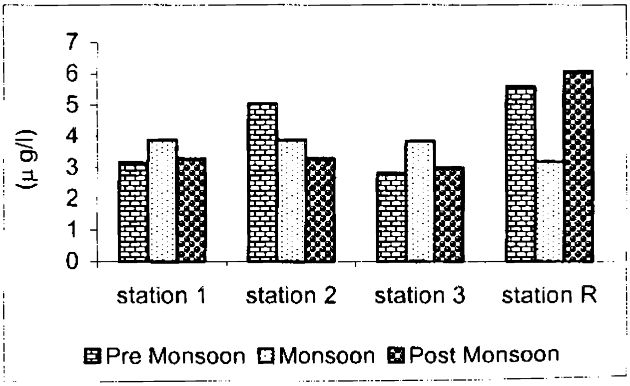


**Figure 5.6:- Seasonal mean variation of dissolved chromium**

In the mangrove habitats, processes determining the distribution of chromium are very complex since it is a redox sensitive element. Cr(VI) is easily reduced by Fe(+2) dissolved sulphides and certain organic compounds with sulfhydril groups. The reduced species of chromium has high affinity for particulates and is removed from the system. The reduction of oxygen and increase of hydrogen sulphide favours this reaction. In this study, Cr showed an inverse relation with Fe. This might be due to the increased solubility of Fe under reducing conditions while Cr is adsorbed onto particulates and sediments under this condition. Again, Cr was found to have an inverse relationship with salinity (Table C.2). This may be due to the input of freshwater containing Cr into this site as land run off increases to a considerable extent during the monsoon season. Moore and Ramamoorthy (1992), have shown that municipal waste waters release considerable amounts of Cr into the environment. pH was found to be a factor controlling Cr concentration at station 2 (Table C.2). This could be expected, as Cr is a redox sensitive element. Remineralization of organic matter is found to contribute significantly to the Cr pool of a system (Sirinawin *et al.*, 2000). In this study also, positive correlation between both phosphate and nitrogenous nutrients with Cr was observed (Table C.11) confirming this source.

In the riverine station also land run-off contribute significant amount of soluble Cr. Highest Cr concentration in water was recorded at the time of high freshwater inflow in a study by Mzimela *et al.* (2003). The heavy influx of freshwater would have promoted desorption of Cr from sediments of the industrialised area to the water column significantly changing its Cr content. Here, Cr was found to co-vary with Zn (Table C.8). This indicates a common source for these two metals. Furthermore, Cr did not show any relation with nutrients (Table C.11) emphasizing an anthropogenic origin.

At the estuarine site, monsoon season recorded a minimum in concentration. This might be due to the dilution of the metal by the heavy freshwater flow. Cr did not exhibit any correlation with the hydrographical parameters and with nutrients (Table C.2, C.11). This non-correlation of Cr with nutrients was observed earlier by Sirinawin *et al.* (2000). In oxygenated waters, Cr would be present in the thermodynamically stable +6 state. Cr(VI) being more soluble than Cr(III), which has great affinity for particulates, may explain the elevated Cr concentration observed in the estuary than the river or mangroves.

### ➢ Nickel

Nickel is an important co-factor in urease, an enzyme responsible for uptake of nitrogen by phytoplankton. It is considered as the weakest reactive element and has least affinity for the particulate phase. Therefore, Ni exists preferentially in the dissolved form (Sokolowski, 2000). Dissolved Ni in unpolluted freshwater usually ranges from 1-3µg/l. Inputs from mixed urban and industrial sources may increase this level considerably.

Dissolved Ni, in this study, was characterized by a premonsoon peak in concentration at all stations. Lowest concentration was observed in the monsoon season at all stations except the estuarine site, where postmonsoon season recorded the minimum (Figure 5.7). At the mangrove sites, Ni varied from 1.857 to 28.85 µg/l, whereas at the riverine site the variation was from 7.194 to 23.46µg/l. the estuarine site recorded Ni in the range 3.486 to 15.79µg/l (Table A.37). ANOVA calculations showed significant variation between seasons, but much less variation in Ni concentration among the aquatic systems (Table B.6). This might be due to the fact that Ni forms inert unknown chelates or macro cyclic complexes that react slowly against scavenging reactions in both oxic and anoxic waters (Magnusson and Westerlund, 1980).

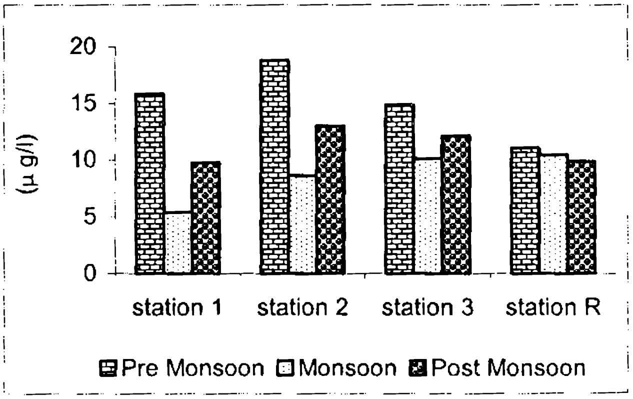


**Figure 5.7:- Seasonal mean variation of dissolved nickel**

Among the mangrove habitats, station 2 showed greater concentration than station 1. Ni pollution results from various sources such as chemical industries, shipyard and cement. The concentration levels were random most probably due to irregular discharge of emanations from the sources and also due to complex water movement in the creeks coupled with diurnal tidal mixing. Bennon *et al.* (1978) also reported a similar situation in Gulf of Fos, France. Mangrove tannins are found to bind metals rendering them inactive and thereby delaying their bioavailability (Saifulla *et al.*, 2002). The low concentration in water compared to the other two phases is due to precipitation as sulphides in the sediments and complexation with organic matter (Lacerda *et al.*, 1999). According to Moore and Ramamoorthy (1992), Ni forms moderately strong complexes with humic and fulvic acids. If ratios of fulvic acid and Ni are greater than 2, the formation of Ni-fulvic acid complexes is favoured. It is well established that humic substances are found in plenty in mangroves. In a study by Turner *et al.* (1998), it was revealed that for Ni, scavenging by particles was suppressed by the formation of strong organic complexes.

Highly significant positive correlation with salinity was seen at station 1, while at station 2, the correlation was less significant (Table C.2). The conservative nature of Ni was observed by a number of researchers (Laslett and Balls, 1995; Sanudo-Wilhelmy and Gill, 1999; Hatje *et al.*, 2003; Shiller and Boyle, 1991; Dai *et al.*, 1995). This indicates that variables other than salinity are controlling the levels of metals at station 2. Continuous decomposition of organic matter can also release incorporated metal into the water. Moreover, anthropogenic inputs from the petroleum activities contribute to Ni contamination. Temperature was found to be highly correlated with Ni at station 2 indicating a temperature driven distribution of the metal at this site (Table C.2).

According to Drever (1997), hydrous Fe and Mn oxyhydroxides have high adsorption capacity for Ni, as is evident from their strong correlation between them (Table C.8). Sokolowski (2000) has shown that dissolution of solid Fe could also contribute to the elevated levels of dissolved Ni by release of the metal from Fe oxyhydroxides under anoxic conditions. In this study also, remarkably high correlation between these metals were seen.

Seasonal distribution of dissolved Ni showed a premonsoon maximum and a monsoon minimum at station 3. Desorption from particulate materials and resuspended sediments are possible, as this system experiences a sudden change in ionic strength in the premonsoon period. This change could be expected by the saline water intrusion occurring in this period due to the reduced stream flow. Besides, Ni showed good positive correlation with dissolved Fe (Table C.8) indicating that this metal is associated with the amorphous Fe and Mn oxides, the dissociation of which releases the trace metal adsorbed onto them. Jenne (1968) concluded that fixation of Ni, Co and Zn on soils and sediments is caused by the Fe and Mn oxides present in them.

Herzl *et al.* (2003) suggested that Ni forms organic Ni complexes with high conditional stability constants and this reaction would limit their dissociation during competition for Ni with suspended particulate matter, and hence their removal. As station 3 is situated near â range of industries, numerous kinds of organic compounds may have leached into the water column. Complexation of Ni with these compounds may account for the elevated levels of soluble Ni. The significant role played by colloids in the transport and transformation of organic matter and associated trace metals such as Cd, Cu and Ni is well established (Dai *et al.*, 1995). Since colloidal particles are abundant in rivers, association with them is yet another important mode of transport. In the Subarnarekha River also, premonsoon season showed maximum concentration (Senapati and Sahu, 1996). Ni could be taken up by or adsorbed onto cyanobacteria (Corder and Reeves, 1994; Asthana *et al.*, 1995; Parker *et al.*, 1998). Diatoms also are capable of taking up nickel hence a mass removal of the metal by these organisms is also possible.

At the estuarine site, dissolved nickel did not vary much between seasons. However, a higher value was observed in the premonsoon, followed by monsoon and postmonsoon seasons. Desorption of Ni from suspended particulates and fine-grained sediments are well recognized (Vazquez *et al.*, 1999; Martino *et al.*, 2002; Elbaz-Poulichet *et al.*, 1999; Ouseph, 1992; Shiller and Boyle, 1991; Dai *et al.*, 1995). Ouseph (1992) has shown that the steady increase of Ni from monsoon to non-monsoon periods indicates that the longer residence time of finer fraction of suspended solids in the river water facilitating further build up by ion exchange processes. Ni has shown to have good positive correlation with phosphate at station 3andR (Table C.11) pointing to the organic regeneration of the metal.

However, none of the hydrographical parameters exhibited any correlation with dissolved Ni at this site (Table C.2). This clearly favours an anthropogenic input of Ni into this estuary. The automotive combustion of Ni-containing diesel oil represents 57% of anthropogenic emissions. About 25% originates from extraction and industrial applications, followed by waste incineration, wood combustion, coal combustion and fertilizer production (Moore and Ramamoorthy, 1992). The Cochin Shipyard located on the banks of this estuary is yet another major source of Ni in this estuary. In the Peconic River estuary, Breuer *et al.* (1999) observed that 50% of Ni present in the estuary was from anthropogenic source.

### ➤ Cadmium

Cadmium, even in trace quantities, is fatal to biological life. Chemically, it is an oxyphilic and sulfophilic element. Cd is present totally as a divalent species up to pH 8, in the absence of any precipitating anions such as phosphate or sulphide. In this form, $Cd^{2+}$ will be available for sorption onto suspended solids and complexation with organic matter and will be transported in those forms.

Seasonal distribution of dissolved cadmium showed some interesting features (Figure 5.8). Abnormally high values were noted at station 2 and 3 in the postmonsoon period. If these two values are excluded as outliers, station 2 along with station R have premonsoon maximum, with monsoon being the minimum. At station 1, postmonsoon season recorded higher values but monsoon and premonsoon values were more or less same. A monsoon hike in soluble Cd levels was seen at station 3. Cadmium varied from below detectable limit to 6.740µg/l (excluding the outlier), from below detectable limit to 2.670 (excluding the abnormally higher value), and from below detectable limit to 7.740µg/l (Table A.38).

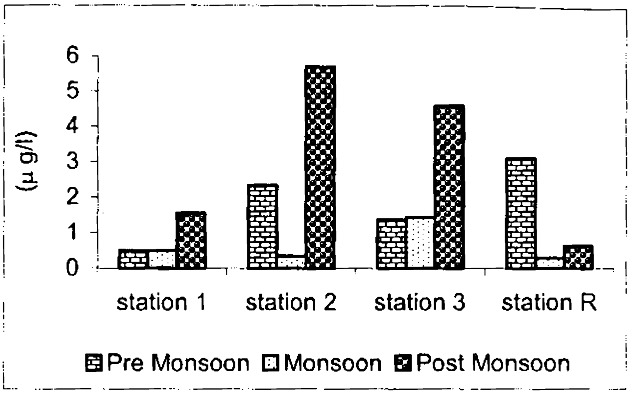


**Figure 5.8:- Seasonal mean variation of dissolved cadmium**

The annual mean concentration recorded the highest at station 2 among the mangroves. The highest concentration in the premonsoon season showed clearly that salinity is an important factor in Cd distribution. Since the chlorocomplexes of Cd is more soluble than the sulphides, Cd has been preferentially desorbed from the particulates and resuspended sediment particles. Furthermore due to the intense anoxic condition existing the mangrove environment, pore water infusion favoured by the degradation of fresh organic matter is likely to occur at this site. According to Gabiel *et al.* (1987), this pore water diffusion process was very efficient in the Laurentian trough where about 80% of the Cd released was returned to the water column through upward diffusion. At station 1, the lower concentration can be attributed to the intense tidal activity, which wash out the sediments frequently. The oxygenated water at high tide might have a dilution effect. Postmonsoon maximum at this station can be attributed to the greater desorption from particulates. The comparatively quieter conditions during this period would have favoured the longer residence time of particulates in the water column. Again, in the mangroves, pH is found to regulate soluble Cd (Table C.2). Dissolved Cd was found to have well correlated with Zn in the mangroves. This indicates a common source for these metals. Desorption and dissolution from resuspended sediment has been proposed to be responsible for the addition Zn by early researchers (Elbaz-Poulichet et al, 1987; Bayens *et al.*, 1998). As for Zn, in addition to competitive sorption by seawater cations, dissolved Cd is increasingly complexed by chloride ions as salinity increases.

Monsoon season dominated in Cd levels at the riverine site. Moreover, seasonal values were higher at this station than the mangroves. This could be expected from its proximity to industrial effluent discharge points. According to Elbaz-Poulichet (1987), phosphate fertilizers are found to contain large amount of Cd. Since a storage place for fertilizers and insecticides are located on this riverbank, leakages are highly possible. Heavy monsoon rainfall facilitates leaching from soils containing this contaminant and substantial portion of this reaches the river. According to Sholkowitz (1978), a fraction of dissolved Cd in freshwater is present in colloidal state, associated with hydrous Fe oxides and humic acids. This fraction is removed from solution with the colloids at low salinity when flocculation occurs due to the augmentation of the divalent cation activity.

In a speciation study of Cu, Cd and Pb on coastal waters of Kandla-Porbander shelf region, Gorai (1997) found the effects of anthropogenic inputs that mostly occur as complexed forms with inorganic ions and also adsorbed forms. Many other authors have confirmed the anthropogenic source of this metal (Elbaz-Poulichet and Martin 1987; Velasquez *et al.*, 2002). In addition to this, Cd did not show correlation with any hydrographical parameters reflecting its point sources (Table C.2).

In estuaries, cadmium was highly correlated with salinity. Several studies indicated this behaviour for Cd (Boyle *et al.*, 1982; Duinker *et al.*, 1982; Edmond *et al.*, 1985; Salomons and Kerdijk, 1986; Elbaz-Poulichet *et al.*, 1987; Comans and Van Dijk, 1988; Donat *et al.*, 1994; Elbaz-Poulichet *et al.*, 1996; Zwolsman *et al.*, 1997; Kraepiel *et al.*, 1997; Turner *et al.*, 2002; Hatje *et al.*, 2003). High Cd concentration in high salinity season found is attributed to desorption from sedimentary particles. Furthermore, speciation of Cd is dominated by inorganic forms because of competitive adsorption and complexation with seawater ions. The stability and solubility of the chlorocomplexes formed enhance the mobilization of Cd in estuaries and usually prevent the competing readsorption process from occurring (Elbaz-Poulichet, 1987). In addition, the competitive complexation between particulate surface sites and inorganic dissolved ligands depends on the concentration of dissolved ligands and on the complexation constants of these ligands in each environment. It has long been established (Garnier et al, 1996;

Kraepied *et al.*, 1997) that the impact of dissolved inorganic ligands on the dissolved complex formation is ordered as Ag >> Cd >> Zn > Mn, Co > Cs. Competitive complexation with inorganic ligands (mainly Chlorine) may explain why Cd showed the highest desorption rates and why desorption greatly increased with increasing salinity (Comans and van Dijk, 1988).

Hatje *et al.* (2003) has pointed out that, in low turbidity micro tidal estuary, the contribution of resuspended particles to dissolved Cd maximum is expected to be very limited due to the low concentration of these particles on the mixing zone. Even though Cochin estuary is a micro tidal estuary, the shallow depth of the sampling site promotes resuspension of the sediment to occur by constant wind driven waves and tidal mixing. This activity encourages the release of metals from sediment into the water column. Paul and Pillai (1983) and Ouseph (1992) concluded that solubilization of Cd from resuspended sediments was occurring in this estuary. Moreover, anthropogenic inputs from various industries located near the rivers draining to this estuary are the major contributor of soluble cadmium.

### ➢ Lead

Lead is present in and transported through aquatic systems in both dissolved and particulate forms. The behaviour of lead in natural waters is thus a combination of precipitation equilibrium and complexing with organic or inorganic ligands. The degree of mobility of lead depends upon the physico-chemical state of the complexes formed.

Concentration of lead in uncontaminated freshwaters is generally ≤ 3 µg/l. However, much high level often occur near the high ways and urban regions due to the combustion of gasoline. At the major industrial zones, rivers may contain up to 20-89 µg/l lead (Pande and Das, 1980).

In the present study, lead displayed a distinct monsoon maximum at all stations (Figure 5.9). Except for station R, premonsoon period recorded the minimum. At station R, postmonsoon concentration levels were slightly lower than the premonsoon period. ANOVA calculations showed a significant variation in concentration between months (Table B.6). Highest annual mean concentration was recorded at station 3, the riverine station, while the minimum concentration was observed at station 2. The mangrove sites recorded Pb in the range 1.460 to 25.96µg/l, while at the riverine and estuarine site Pb varied from 4.62 to 42.76µg/l and 2.42 to 25.01µg/l respectively (Table A.39).

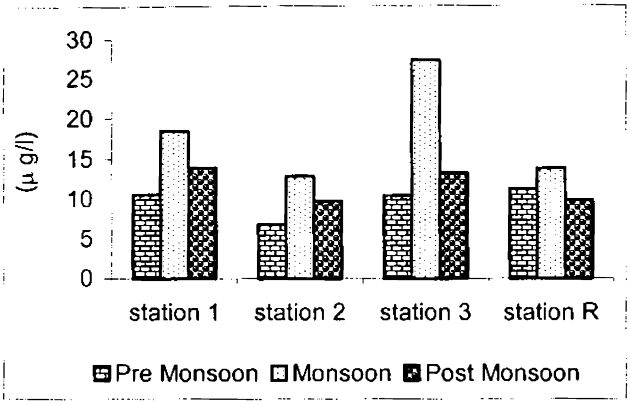


**Figure 5.9:- Seasonal mean variation of dissolved lead**

Among the mangroves, station 1 was characterized by high annual mean concentration. This can be expected from its location near the city. Automobile fuels are recognized as the single largest source of lead. Dissolution of lead from the Aeolian fallouts may be the reason for the observed concentration peak. A significant inverse relationship with salinity was observed at this station confirming the atmospheric source of this metal (Table C.2). Many authors have related the absence of dissolved Pb concentration with salinity to the atmospheric input of the metal (Yeats and Campbell, 1983; Balls, 1985; Buat-Menard, 1986). At station 2, lead did not correlate with any of the nutrient elements (Table C.11) suggesting that Pb distribution is mainly controlled by external cycling, such as scavenging, here (Bruland, 1983, Chester, 1990).

The monsoon maximum in Pb concentration can be attributed to the precipitation source of this metal. As Pb is found in large quantity in the atmosphere, monsoon showers would have washed down the atmospheric particulate matter into the aquatic systems subsequently leading to monsoon hike in concentration. The decrease in dissolved lead concentration in the premonsoon season can be attributed to the transfer of dissolved Pb to particulate phase, either by biological uptake or scavenging. Moreover, this tendency is accompanied by a significant correlation with nitrite (Table C.11). Thus the lower values in the summer months suggest removal of dissolved Pb to organic particulate matter (by either active uptake or passive sorption) and a partial release of Pb to solution by organic matter remineralization (Schaule and Patterson, 1981, 1983; Brugmann *et al.*, 1985; Lambert *et al.*, 1991; Boyle *et al.*, 1986).

In addition to the atmospheric source, input of Pb from interstitial waters of metal-contaminated sediment is also significant. Martino *et al.* (2002), has pointed out that this source can function persistently and effectively if there is enough time for benthic anoxia and early diagenesis to be established in the sediments. This is highly possible in the mangroves as the system itself is highly anoxic due to the enormous organic load added to it. Thus, pore water infusion could be another source for this metal.

The riverine station exhibited the highest annual mean concentration in accordance with its location near the industries. The surface water layer is considered as the first reservoir for the discharged materials. The aerosol fallout in the highly industrialized area may lead to high Pb concentration. Due to the high temperature involved in the production processes, the fumes from these factories may contain greater amounts of Pb (Saad *et al.*, 2003). Rainfall acts as an external source by bringing down the particulate matter to the water column. Furthermore, Pb did not exhibit any correlation with the hydrographical parameters confirming its anthropogenic origin (Table C.2). Increased land run-off may be yet another cause for the elevated concentration levels. Due to this abundance of Pb at the polluted site, any natural geochemical behaviour would be entirely masked. A benthic flux of Pb is also possible at this site. According to Tappin *et al.* (1995), this benthic flux is driven by aerobic decomposition of organic matter at the bottom surface enhanced by the high content of fine-grained fraction with relatively high levels of organic matter (Aller and Beninger, 1981; Irion and Muller, 1990). The lower values in the pre and postmonsoon months may be due to the reduced river flow and the lesser contribution from precipitation (rain).

At the estuarine site also, lead showed a monsoon maximum. This can be related to the heavy rainfall characteristic of this season, which favours in the addition of lead-rich particulates to the water column. This monsoon peak in Pb levels was observed earlier in other studies (Ouseph, 1992, Joseph, 2001) as well.

The comparatively higher concentration observed at this site might have resulted from the polluted rivers draining into this estuary. The observed positive relationship of Pb with the nutrient elements and lower values in the premonsoon period leads to the assumption that a removal mechanism is operating for this metal by the organic particulate matter. Coagulation of the riverine colloids rich in Pb may be taking place at this mixing zone further reducing the dissolved concentration. This precipitation reaction is observed by other researchers also (Cotte-Krief *et al.*, 2002; Riso *et al.*, 1993; Saad et al, 2003; Ouseph, 1992; Windom *et al.*, 1985; Danielsson *et al.*, 1983; Windom *et al.*, 1988; Boyle *et al.*, 1974; Sholkovitz, 1976). Thus the phase of variation observed depending on the sampling stations indicates the complex factors controlling seasonal variations of this metal.

## 5.3 Particulate Trace Metals

The knowledge of particulate trace metals in less dynamic estuaries can be used to examine and quantify chemical reactivity and pollution sources. The reactivity and dynamics of particulate trace metal in the estuarine region are instrumental to the short-term and long-term fate of metals in shelf seas and the distribution and fluxes of these suspended particles appear to be regulated by the mixing and differentiated settling of a complex assortment of source materials. Particle composition is probably modified, additionally, by biogeochemical reactivity occurring both within the sediment and in the water column during suspended particle transport (Turner *et al.*, 1992: Dauby *et al.*, 1994; Millward *et al.*, 1997). Thus the dominant mechanism that control the concentration of most trace metals in aquatic systems appears to be physical and chemical adsorption on biologically produced particulate matter. Furthermore, Louma (1983 and 1989) had shown that metals present in particulate form are more bioavailable to the aquatic organisms than those in the dissolved phase. In mangroves, trace metals are found mainly associated with particulate matter Lacerda (1998). Thus, for a realistic and complete assessment of river fluxes and potential pollution, the composition of particulate matter is an obligatory parameter in addition to the concentration of the dissolved elements.

## ➢ Iron

Iron, a redox sensitive element, shows contrasting behaviour in aquatic systems depending on the physico- chemical conditions. Fe has an extensive ability to form soluble complexes with naturally occurring organic compounds. But dissolved Fe has a strong tendency to form insoluble hydroxide polymers and due to changes in pH, Eh and ionic strength encountered by river borne dissolved iron in estuaries it may lead to its removal from solution. These amorphous oxyhydroxides of iron act as efficient scavengers for other trace metals. Hence the biogeochemistry of particulate Fe is central to the understanding of trace metal chemistry in aquatic systems.

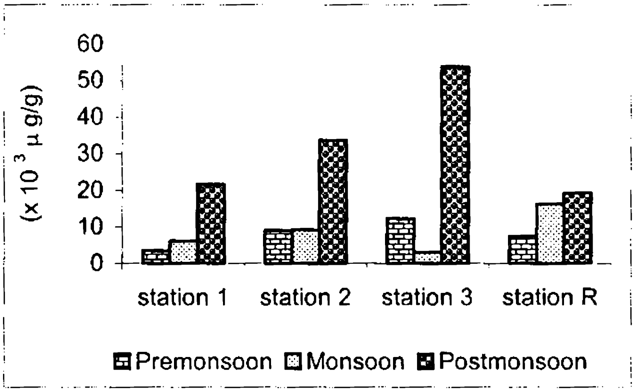


**Figure 5.10:- Seasonal mean variation of particulate iron**

In the present study, iron showed highest concentration in all the three phases of occurrence. At all stations, particulate iron showed a characteristic postmonsoon peak (Figure 5.10). ANOVA calculation revealed highly significant variation between months and seasons (Table B.7). The highest annual mean concentration was noted at station 3, as is the case with dissolved phase. Mangrove sites and the estuary exhibited similar concentration levels. Station 2 recorded slightly higher values than station 1. Fe ranged from 0.012 x $10^3$ to 78.29 x $10^3$μg/g in the mangrove habitats and from 0.893 x $10^3$ to 65.91 x $10^3$μg/g at station 3 and from 0.719 x $10^3$ to 48.76 x $10^3$μg/g at the estuarine station (Table A.40).

Iron has an extensive ability to form soluble complexes with naturally occurring organic compounds. In mangrove environments, wide variety of organic compounds is produced as a result of the remineralization process. A major part of suspended particles, in fact, consists of organic particles (Tanoue *et al.*, 1982). Thus the role of organic materials in suspended particulates is more important than that of the inorganic suspended matter. Further more, Mc Cave (1984) has shown that the suspended particles, which mainly consist of organic material, have a continuous size spectrum. Usually, particles present in aquatic systems are coated with oxide or by various organic entities. It has frequently been suggested that particle coatings may control the metal binding and other surface characteristics of natural sediments (Day *et al.*, 1994). Such coatings may be more homogenous than bulk particles, giving rise to surface characteristics that are relatively independent of particle type (Luther *et al.*, 1998). Thus the presence of organic colloids of humic and fulvic substances in the mangroves might have significantly altered the adsorbing surfaces irrespective of the particle size facilitating increased adsorption of metal on to them.

Benthic animals and rooted plants disturb the simple structure of sediments by burrowing into them or by growing roots. This affect the rate of transport of gases, solute and particulate matter within the sediment and between the sediment and overlying water (Vale and Sundby, 1998). Roots of the plants are efficient conduits of atmospheric oxygen to the sediment and the well-developed aerenchyma system of the roots allows oxygen to diffuse from leaves to the roots. The diffusion takes place in the gas phase and the oxygen not consumed by root respiration is available for diffusion into the sediment. Burrows created by animals have the same function of exchange between the bottom water and burrow water. The diffusion geometry of burrows becomes similar to those of root systems.

The presence of oxygen at the root-sediment and burrow-sediment interface creates local oxidising conditions in otherwise reducing sediments. This affects the chemistry of Fe and Mn, the soluble reduced forms of which diffuse towards these interfaces, where they get precipitated as insoluble Fe and Mn oxides. Thus bioturbation may be the reason for excess particulate iron observed in the mangrove habitats.

Furthermore, many others have opined that the organic matter produced in marshes is seasonally regenerated, producing acidic zone near the surface that acts to weather Fe mineral phases (Boulegue *et al.*, 1982; Lord and Church 1983; Ferdelnan *et al.*, 1991; Luther *et al.*, 1992; Velde *et al.*, 2003). Iron–rich particle type may be another reason for the enhanced iron levels in particular matter. Removal of Fe (II) by precipitation in anoxic waters was suggested by Gavis and Grant (1986). The relatively large particulate Fe concentration observed in the mangrove waters further strengthens this explanation.

Though 'colloidal pumping mechanism' is highly recommended for the settling of Fe in waters, particle coagulation can be operative also. Jannasch *et al.* (1988) have shown that particle coagulation is more effective in Fe removal from water than colloidal sedimentation. The high concentration of Fe and organic matter in the suspended materials are characteristics of fulvic and humic acid colloids, which are abundant in the mangrove systems. Another important source for particulate Fe in the mangrove habitats is the diagenetic remobilization from the sediments. The role of pore water outflows as a source of Fe and Mn enrichment in suspended matter is also widely recognized (Feely *et al.*, 1986; Sundby *et al.*, 1986; Paulson *et al.*, 1988; Dehairs *et al.*, 1989).

In the present study, particulate Fe showed no correlation with any of the hydrographical parameters except with pH at station 1 (Table C.4). This may be due to the abundance of Fe in the particulate phase and changes in particle composition due to the low chemical reactivity of this metal. Another reason for this non-correlation may be that the distribution of particulate Fe was controlled almost entirely by physical processes (i.e. resuspension and sedimentation). Since particulate concentration is generally high relative to dissolved trace metals, transformations from one to another would not significantly affect the particulate metal levels. Seasonally, postmonsoon was characterized by peak concentration at all the sites. In this period, the relatively calm and quieter conditions in the creek waters might have favoured the longer residence time of particles in the water column and the time available for adsorption of the metal. Ciceri *et al.* (1992) have shown experimentally that particulate Fe concentration increased over long time scales. In the postmonsoon season, particle concentration was much lower than the monsoon season and consequently a concentrating effect comes into play. Other researchers have related this increase in particulate metal concentration with the reduction of particle concentration to the accompanied reduction in the buffering capacity of the suspended particle loading (Owens *et al.*, 1997; Turner, 1999).

Particulate Fe showed highest annual mean concentration at station 3, the polluted river site. Fe exists primarily as colloids in freshwater and there is a fair chance for it to form amorphous oxyhydroxides in estuaries. In an experimental study, Wen *et al.* (1997) found that metals such as Fe and Zn are sequestrated from the dissolved phase into particulate phase *via* colloidal pumping. The rate of colloidal aggregations thus controls the transfer of metal into the particulate phase before its removal from the water column by sedimentation. Though, the colloidal fraction is believed to be pass through 0.45 m filter, Benoit and Rozan (1998) have pointed out that overloading of filters cause a marked decline in the effective pore size of the Fe colloids, eventually leading to complete blockage of Fe from the filtrate fraction. This is a strong possibility in the present study as the fine re-suspended material was in plenty often causing the filter clogging.

However, the most probable source of particulate Fe at this site seemed to be the effluent discharges from the industries and sewage out fall from the urban areas. Ouseph (1992) has opined that rivers draining into the Cochin estuary such as Chitrapuzha, carry with them increased particulate matter load rich in trace metals from the effluent discharge points. Non-correlation with the hydrographical parameters at this site lends further credence to this explanation (Table C.4).

Monsoon season was characterised by the minimum concentration of particulate iron at this site. This may be due to the dilution effect as a large amount of particles find their way to the river through intense land run-off. Such a decrease in particulate metal levels with increasing particle load was noted elsewhere (Owens *et al.*, 1997; Turner, 1999; Forstner *et al.*, 1989; Zhang and Liu, 2002). The dilution probably occurred as a consequence of the presence of particles having fewer complexation sites. There could also be large mega particles with small specific surface area or they could be composed of materials with intrinsically low abundance of adsorption sites. The postmonsoon hike in particulate Fe concentration may be the result of increased residence time of the particles in the water column facilitating adsorption on to them. The heavy influx of freshwater in the monsoon season might have increased the sediment resuspension rates. This phenomenon, in turn, promotes injection of pore water species into the water column (Tramontano and Bohlen, 1984). After release into the water column, dissolved Fe gets immediately oxidized and precipitated (Zwolsman, 1994). The oxidative precipitation mechanism may be higher in the postmonsoon period. Moreover, Jarvie *et al.* (2000) have shown that for the particulate fraction of elements with a strong micro particulate (colloidal) component, such as Fe, the effects of river flow are minor relative to within-river processes.

Hydrous Fe and Mn oxyhydroxides are ubiquitous in the estuarine environment and they have high adsorption capacity for other trace metals. In this study, particulate Fe showed a unique distribution at the estuarine site. Postmonsoon period was recorded with highest concentration similar to the other sites whereas the monsoon season was reported the second highest in concentrations. The annual mean concentration was similar to that of the mangrove sites. In fact, an intermediate value between the two mangroves. At this estuarine site also, hydrographical parameters did not exert any influence on the particulate metal distribution (Table C.4).

The elevated concentration of particulate Fe at this site may be due to the much observed particle concentration effect of salinity. Physical association appears to be important in estuaries in which hydrous oxides are trapped within aggregates of organic matter (Boyle *et al.*, 1977). Chemical association could also be important, in that metal oxides can adsorb some dissolved species (Morris *et al.*, 1981). In addition, metal oxides, organics and metal-organics may form coatings on suspended matter. Fe existing as colloids in the freshwater get precipitated as amorphous oxyhydroxides in estuaries. The removal of Fe by flocculation processes is observed to be up to 70% (Eastman and Church, 1983).

Anthropogenic activities can be a major contributor of particulate Fe in the Cochin estuarine system. Ouseph (1992) has shown that Periyar River, one of the major rivers draining into this estuary brings heavy metals in the form of fine-grained suspended matter from the effluent discharge points. Sankaranarayanan and Rosamma (1979) attributed the high particulate Fe in the Cochin estuary to the land drainage, harbour activity and sewage.

The postmonsoon hike in concentration may be due to the longer residence time of the finer fraction of suspended solids in river water facilitating further build up by ion exchange processes. The higher concentration during monsoon season than the premonsoon period can be attributed to the increased fresh water run-off, which brings in fine materials to the estuary and the turbulent condition prevailing in the estuary causing sediment resuspension.

Experimental research on metal behaviour up on mixing of river and seawater (Sholkovitz, 1978) has clearly indicated the removal of metals like Fe, from solution to solids. However, experimental studies of the opposite process, release of metal to solution, have given contradictory result (Hoff *et al.*, 1982; Comans and van Dijk, 1988; Gerringa, 1990; Paulson *et al.*, 1991). Thus the influence of salinity on metal adsorption process is not consistent. The low concentration of Fe in the premonsoon season shows that salinity is not the primary factor determining particulate Fe distribution in this estuary. Instead, resuspension of bottom sediments and/or huge amounts of riverine materials may be the deciding factors. Sediment resuspension also promotes injection of pore water species into the water column (Tramontano and Bohlen, 1984). After release into the water column, dissolved Fe is immediately oxidized and precipitated (Zwolsman, 1994). It is clear that diagenetic remobilization can be a major source of Fe and Mn to the suspended matter. Lack of correlation between the hydrographical parameters and particulate Fe (Table C.4) at this site supports the anthropogenic sources and sedimentary inputs of this metal.

Correlation study of particulate Fe with other particulate trace metals showed only a few significant relationships between them (Table C.9). The dissimilarity of Fe and Mn and other trace metals causes difference in their behaviour in aquatic systems. In particular, Fe and Mn are present in suspended particles largely in forms that cannot readily exchange with solution, unlike other metals, which mainly exist as relatively labile surface complexes.

## ➢ Manganese

The behaviour of manganese in aquatic systems is strongly influenced by its redox chemistry. Although, the oxidation of $Mn^{2+}$ into precipitatable $MnO_x$ in aquatic environments theoretically is a slow process, the reaction is catalyzed by pre-existing or freshly generated Mn oxide phases and microbial activity. In fresh waters oxidation exhibits zero-order kinetics with respect to dissolved Mn concentration, the rate is reduced with an increase in ionic strength through occupation of catalytic sites by major seawater cations (Morris *et al.*, 1979; Duinker *et al.*, 1982; Diem *et al.*, 1984; Yeats and Strain, 1990). According to Martin and Maybeck (1979), the average world river suspended matter contains 1050ppm Mn. Particulate matter appears to be the major mode of transport for Mn as observed in the Amazon, where 90% of Mn was in the particulate fraction (Moore and Ramamoorthy, 1992).

In this study, particulate Mn ranged from 24.13 μg/g to 7023.4 μg/g in the mangrove systems, from 10.69μg/g to 2966.3μg/g at the riverine site and from 43.37μg/g to 2218μg/g at the estuarine site (Table A.41). Seasonally, postmonsoon was recognized with maximum concentration at all sites (Figure 5.11). Monsoon season recorded the minimum Fe concentration at all sites except the estuarine station. In the estuary, premonsoon and monsoon showed similar concentrations. Mangrove habitats recorded higher concentration than the other systems in almost all seasons. Among the mangroves, station 1 showed higher annual mean concentration while, the riverine as well as the estuarine sites were similar in annual mean particulate Mn content.

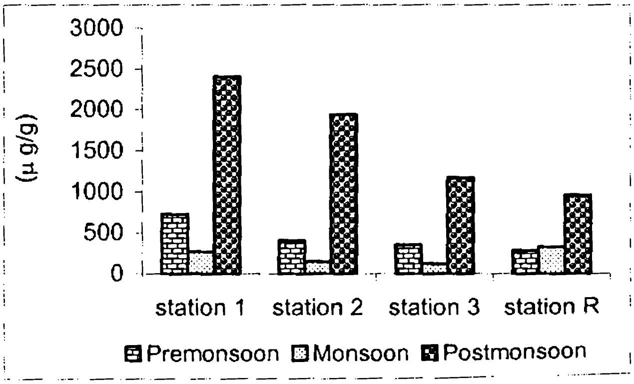


**Figure 5.11:- Seasonal mean variation of particulate manganese**

The main pathway of trace metals in the mangrove ecosystems is with the incoming tides associated with suspended particles and Fe and Mn oxyhydroxides (Lacerda, 1998). The intense anoxic conditions inside the mangrove habitats greatly modify the chemistry of the trace elements entering them. The differential solubility of the oxidized and reduced species of Mn greatly influences their distribution in the different phases. The reduced form of this metal is more soluble and in the mangroves, concentration of dissolved Mn detected in this study was very high. However, certain peculiarities of these ecosystems have an upper hand in determining the distribution pattern of different species of Mn. These are the bioturbative and bio- irrigative processes operating in these habitats.

The interactions of plants and animals on intertidal and subtidal sediments greatly improve the exchange of materials between the interiors of the sediments and the overlying water. The roots of the mangrove plants are efficient conduits of atmospheric oxygen to the sediment because of their well-developed aerenchyma systems, which allow oxygen to diffuse from leaves to the roots, the oxygen not consumed by root respiration is available for diffusion into the surrounding sediments. Similarly, many benthic animals construct burrows that are connected to the overlying water. The exchange of burrow water with bottom water allows the transport of oxygen to the interior of the burrows, where it can diffuse into the anoxic sediments. The diffusion geometry of the burrows become similar to those of root systems where large number of burrows permeate the sediment and that in some respects burrows play a functional role similar to that of roots.

The presence of oxygen at the root-sediment and burrow-sediment interfaces creates local oxidizing conditions in otherwise reducing sediments. This affects, in particular, the chemistry of Fe and Mn, whose soluble reduced forms diffuse towards these interfaces, where they are precipitated as insoluble Fe and Mn oxides. This mechanism may account partly for the increased particulate Mn concentration observed in the mangrove environments (Vale and Sundby, 1998).

In the mangroves, influx of Mn enriched pore waters, followed by adsorption onto suspended solids are found to occur (Lacerda, 1999). When dissolved Mn reaches oxidized surface waters enriched in suspended solids, the dominant oxidizing conditions of the flood waters result in the oxidation of Mn(II) to Mn(IV) and adsorption onto suspended particles. Particulate Mn resulting from the oxidation of the reduced species are also noted by Graton *et al.* (1990) and Luther *et al.* (1998). The positive correlation observed between particulate Mn and dissolved oxygen at station 1 (Table C.4) may due to this oxidative precipitation. Regnier and Wollast (1993) have further shown that oxidizing conditions corresponds to higher particulate Mn concentrations. The intense bioturbation in the mangroves might have enhanced the amount of suspended sediments of fine grain size, which facilitated the adsorption of the amorphous oxyhydroxides onto them due to their large surface area. Furthermore, the role of pore water outflow as a source of Fe and Mn enrichment in the suspended matter is widely reported in literature (Feely *et al.*, 1980; Sundby *et al.*, 1986; Paulson *et al.*, 1988; Dehairs *et al.*, 1989).

Elevated concentration of Mn was observed in both the mangrove stations in the postmonsoon period and a minimum in the monsoon. Intense rainfall in the monsoon season may have caused sediment resuspension and increased amount of suspended matter might have had a dilution effect resulting in a concentration levels drop during this season. The relatively calmer conditions of the postmonsoon period would have favoured longer residence time of the particles in the water column. Oxidation of $Mn^{2+}$ to $Mn^{4+}$ is reported to be kinetically a slow process (Moffett, 1994). Furthermore, sorption of Mn has long been recognized as a result of bacterially mediated oxidation (Diem and Stumm, 1984; Moffett and Ho, 1996; Johnson *et al.*, 1995). Since bacterial activity is very high in the mangrove ecosystems, chances for re-adsorption processes can be invoked for Mn during this period. Dissolved Mn concentration was highest in the premonsoon season at both the mangrove sites, while, the particulate fraction was lower. The intense summer conditions would have resulted in greater evapo-transpiration, causing the reduced species to dominate.

At the riverine site, particulate Mn was lower than in the mangrove, just as the dissolved fraction. This can be ascribed to the reduced input of this metal to the river compared to the mangroves. Seasonally, postmonsoon period showed greatest concentration with monsoon season showing the minimum. None of the hydrographical parameters was found to have any influence on the particulate metal distribution (Table C.4) thereby indicating a common source for all these metals. In rivers, Mn is transported mainly in the particulate form (Trefry and

Presley, 1982). The overwhelming particulate to dissolved ratio for Mn was found to be controlled by the abundant suspended material found in the river. Recent studies have shown that metals like Fe, Mn, and Al occur in the form of colloids (Horowitz *et al.*, 1996; Shiller and Taylor, 1996). Since colloidal fraction of trace metals are found to be in very high proportion in river water, a major portion of Mn may remain associated with them. Furthermore, these colloids are removed with increasing efficiency during the separation process of particulate component as filters get progressively overloaded.

The thermodynamically stable state of Mn in oxygenated waters is +4, which is insoluble. $Mn^{2+}$ is soluble and gets oxidized to $Mn^{4+}$ in an oxidizing environment. The resuspension of fine-grained particles, which may be rich in Mn, from bottom sediments in the comparatively shallow water, may be another source of this metal. In a sorption kinetic study by Ciffroy *et al.* (2001), it was revealed that re-adsorption on particles was high in the winter season in freshwater. This is possible for metals for which sorption over a long time was found to be predominant. In the case of Mn, oxidative precipitation was found to be kinetically a slow process (Moffett, 1994). Thus, readsorption of dissolved Mn species may be another reason for the elevated levels in the postmonsoon season.

Tankere *et al.* (2000) observed low particulate Mn levels in the surface water in the summer season. He has related this to the inhibition of particulate Mn formation by sunlight. Sunda and Huntsman (1987) demonstrated that sunlight could cause photo inhibition of Mn oxidizing microorganisms. Sunda *et al.* (1983) also reported on experiments that demonstrated photo reduction of manganese oxides by dissolved organic substances. Such reactions appeared to be important in maintaining Mn in a dissolved reduced form in photic waters. Thus, the increased light intensity in the premonsoon season may be the reason for the observed reduced particulate manganese levels.

Heavy influx of run-off and intense monsoon falls may have acted as diluents in the case of particulate Mn. Turner (1999) and Muller (1994) have shown that both dissolved and particulate metal concentrations are equally sensitive to external metal sources. At this site, the dissolved fraction was highest in the monsoon period while the particulate component was minimum. The postmonsoon hike thus clearly shows the oxidative precipitation of dissolved Mn onto suspended particles brought in by the heavy land run-off. Besides, Kerala region is well known as a zone of intense weathering. It is quite possible that Fe and Mn leached by the weathering processes were transported through the rivers as finely divided suspended particles. All other trace metals analyzed were found to have strong positive significant relationships with Mn reflecting their common origin (Table C.9). Non-correlation of hydrographical parameters with particulate metal clearly shows an anthropogenic origin of this metal at this site (Table C.4).

The estuarine site also exhibited a postmonsoon hike while the premonsoon and monsoon periods recorded comparable concentration levels. The tremendous volume of suspended material carried by the rivers get flocculated and deposited very quickly upon mixing with seawater. Manganese is a very reactive element and dissolved manganese concentration is low in oxic waters as a result of oxidative scavenging onto suspended particles. Reduced Mn species get oxidized to insoluble Mn oxyhydroxides and amorphous coatings (Giblin *et al.*, 1986; Saager *et al.*, 1997). The freshly formed Mn coatings are very efficient in scavenging additional Mn and Fe as well as other trace metals from the water column. The oxidative precipitation may be one of the sources of particulate Mn in this estuary.

Since rivers draining to Cochin estuary are considered to be polluted, the main contributor of this metal into this estuary may be industrial effluents. According to Ouseph (1992), river Periyar supplies enormous load of suspended matter into this estuary from the various point discharge sources. Particulate Mn, in this study, exhibited no correlation with any of the hydrographical parameters confirming its anthropogenic origin (Table C.4).

In the Scheldt estuary, Netherlands, it was shown that sediment resuspension promotes pore water injection to the overlying water column (Tramontano and Bohlen, 1984). Dredging operations are taking place in the Cochin estuary to maintain the Cochin Harbour. These dredging operations promote sediment resuspension, which further facilitate the release of metals to the water. After release into the water column, dissolved Mn gets oxidized slowly and gets precipitated as particulate oxyhydroxides. Duinker *et al.* (1980) also observed such a precipitation of particulate Mn by remobilization of the element from the sediments.

Although, desorption of Mn was noted with increasing salinity, re-adsorption, the amplitude of which depends on salinity, was identified for Mn (Ciffroy, 2001). In addition to ionic exchange, changes in biological conditions between fresh and estuarine water could be invoked for Mn since sorption of Mn has long been recognized as a result of bacterially mediated oxidation (Diem and Stumm, 1984; Moffett and Ho, 1996; Johnson *et al.*, 1995). After the heavy monsoon showers, the disturbed sediments start to settle in the quieter postmonsoon period. The larger, fast settling particles, which mainly include the weakly enriched aggregates quickly redeposit. The finer, slower settling particles stay in suspension much longer. These particles serve as nuclei for the autocatalytic oxidation-precipitation of dissolved Mn, which reaches the water column (Sundby, *et al.*, 1981). Turner (1999) has pointed out that with increasing salinity there is an increasing competition for autocatalytic sites by seawater cations and increasing precipitation of oxidized Mn. This may be the reason for elevated particulate Mn concentration in the postmonsoon season. The concentration levels reported in this study were higher than those reported by Joseph (2001) and lower than those for the neighbouring Kayamkulam estuary (Unnikrishnan, 2000).

### ➤ Zinc

Zinc shows variable behaviour in binding to particulates depending on the physico-chemical characteristics of the aquatic systems. Zn, as $Zn^{2+}$ is available for sorption onto suspended mineral colloids and complexation with organic matter. Under natural environmental conditions, the hydroxide formed may even promote mobilization of Zn due to reduction of the cation and increase the solubility of sparingly soluble salts.

In the present study, particulate Zn showed very high concentration in one of the mangroves sites. Rest of the stations exhibited more or less similar values. At station 1, concentration of Zn ranged from 28.19μg/g to 2352.6μg/g, from 16.7μg/g to 1271.47μg/g at station 2, from 16.32μg/g to 1535.95μg/g at station 3 and from 36.12μg/g to 790.6μg/g at station R (Table A.42). Except for the estuarine site, all other stations showed a postmonsoon hike (Figure 5.12). At this station premonsoon exhibited the highest concentration. Minimum concentration was detected in the monsoon period at all stations. Of the metals studied, premonsoon-associated hike in concentration was observed only for Zn. ANOVA showed a significant variation of particulate Zn both between season and between stations (Table B.7).

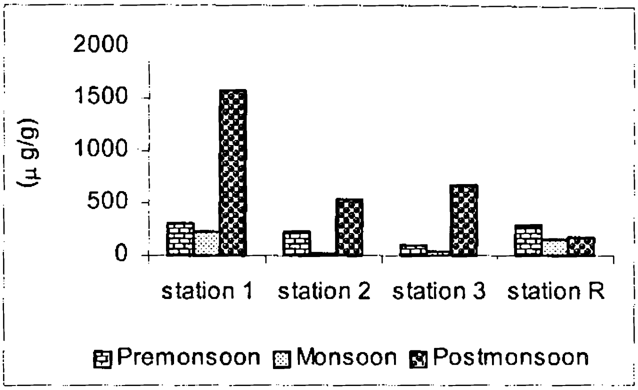


**Figure 5.12:- Seasonal mean variation of particulate zinc**

Of the two mangrove habitats analyzed, station 1 recorded much higher annual mean concentration than station 2. Station 1 is located near the estuary and is flushed well during the flood period. The concentration levels showed much variation only in the postmonsoon season. This may be due to the point discharge sources present at this site. Mangalavanam (station 1) is located near the urban metropolis where there is high probability for anthropogenic inputs. Storage facility for cement is also located at this site and leaching from this source is another possibility. Petroleum contamination from the huge containers is yet another source of Zn at this site. For the dissolved phase also, this station recorded higher concentration and among the seasons, the postmonsoon period exhibited the peak concentration. Since dissolved as well as particulate concentration were abnormally high at this site, presence of a potential polluting source of Zn presumably from cement and petroleum can be safely inferred.

The intense reducing environment of the mangroves is the primary factor controlling trace metal cycling in these systems. The reducing condition is triggered by degradation of organic matter and consequently, reduced Fe and Mn, and presumably trace metals associated with hydroxide phases are injected into the water column, where they get precipitated or adsorbed on to the suspended matter (Turner and Millward, 2000). Previous studies have emphasized the association of Zn with Fe and Mn oxides (Zwolsman *et al.*, 1997; Windom *et al.*, 1991; Warnken *et al.*, 2001). However, these resuspended sediments enriched by Zn by the rapid adsorption of metals released from the reducing pore waters is in a dynamic state of exchange between the water column and bed sediments. In this study also, both the mangrove sites exhibited highly significant correlation between Zn and particulate Fe and Mn reflecting a common source for these metals (Table C.9). At both the stations, particulate Zn did not exhibit any correlation with the hydrographical parameters (Table C.4). This may be due to the anthropogenic sources of this metal. Zwolsman (1997) has further stated that Zn coprecipitated with Mn, and once released from bed sediment re-adsorbs or precipitates as ZnS in the overlying oxygen depleted water column.

Zn is reported to be strongly complexed with organic ligands. The metal may interact in solution with dissolved organic matter by chelation/complexation processes that are, in turn, concentrated by adsorption onto fine particulate such as clay minerals (Piatina and Hering, 2000). Since the finer sediment was found to be a major fraction in the study, the readsorption of Zn is a high probability. Moreover, benthic animals, unlike plants, actually manipulate particles. In addition to simply pushing them aside as they move through the sediments, animals transport particulate matter when they excavate burrows and when they feed (Vale and Sundby, 1994). ZnS formed in the mangroves as a result of sulphate reduction, was found to have get adsorbed or precipitated onto these particles. Van der Sloot *et al.* (1990) have observed very high particulate Zn in the anoxic zone of Fram Varren Fjord, Norway. He related this to the preferential association of Zn with colloidal mineral phases or with organic fractions.

The possible components of suspended particulate matter in mangroves i.e., Fe and Mn oxides, humic substances and microbial cells are known to have substantially different binding affinities for metals (Ferreira *et al.*, 1997; Green Pedersen *et al.*, 1997). Particle coating may control the metal binding and other characteristics of natural sediments (Day *et al.*, 1994). Such coatings may be more homogenous than bulk particles giving rise to surface characteristics that are relatively independent of particle type. Thus, the great variety of organic coatings present in the mangrove environment would have resulted in a greater adsorption rate.

Seasonally, the monsoon period showed significantly low values due to the heavy influx of fresh water together with land run off, which might have a dilution effect on the particulate metal present. Introduction of particles depleted in trace metals is highly favoured in this season and results in a reduction in particulate metal concentration. Zn was found to be highest in the postmonsoon period. This hike in concentration may be the outcome of longer residence time of particles in the water column. However, this was also possible in the premonsoon, but Zn is found to desorb to a greater extend as salinity increases (Wells *et al.*, 2000; Hegeman *et al.*, 1992). Thus a hike in postmonsoon may be due to the longer residence time of particle and intermediate salinity both favouring increased adsorption.

Similar to the dissolved fraction, particulate Zn at the riverine site recorded concentration values nearer to that of the estuary. At this site also postmonsoon season was associated with maximum concentration and with a monsoon minimum. Zn showed strong relationship with Fe (Table C.9) indicating an important micro particulate (colloidal) component (Horowitz *et al.*, 1996) for this metal. In rivers, the amount of material transported in the particulate form is much greater than that transported in solution. In heavily contaminated waters, adsorption of Zn onto suspended matter was observed (Martin *et al.*, 1993). As Zn was found to be highly correlated with Fe and Mn, adsorption on to these metal oxyhydroxides is indeed feasible. Fe and Mn oxyhydroxides are found to be amorphous colloids by nature. Laboratory studies conducted on colloids have revealed that trace metals such as Fe and Zn were sequestrated from the dissolved phase into particulate phase via colloidal pumping (Wen *et al.*, 1997).

Postmonsoon hike in concentration observed at this site may due to the increased residence time of slow settling particles facilitating adsorption of metals on to them. In addition to this, mobilization from sediment was enhanced at low river flow conditions (Jarvie *et al.*, 2000). Particulate fraction of Zn showed least values in the monsoon season probably due to the heavy land run off. In this season the dissolved fraction showed the highest concentration showing that major portion of Zn was in the soluble form in the run off water. None of the hydrographical parameters exhibited correlation with particulate Zn (Table C.4) pointing to the contamination occurring at this site through the effluent discharges from the industries having greater levels of Zn.

In contrast to the rest of the systems studied, the estuary exhibited a premonsoon maximum and a monsoon minimum. In most estuaries studied, Zn was found to be dissolved from particulate matter as salinity increases (Wells *et al.*, 2000; Ciffroy, 2003; Hegeman *et al.*, 1992). However, in this study, Zn showed a positive relationship with salinity (Table C.4). Such behaviour for Zn was reported earlier by Ouseph (1992) in the same estuary and was attributed this increase from monsoon to non-monsoon periods to the longer residence time of riverine particles facilitating further build up of the metals onto them by ion exchange processes. The effluent discharges also affect the usual behavioural pattern of an element. Non- correlation with hydrographical parameters augments this argument.

The elevated levels of Zn may be due to the flocculation processes of Fe and Mn oxyhydroxides as the ionic strength increases. Sediment resuspension may be another possible source for this metal. Fernex (1992) has shown that for Zn, the diffusive benthic flux is of the same order of magnitude as the sorption exchange estimates. Zn, unlike other metals studied, showed negative relationships with other metals (Table C.9). This reflected the anthropogenic source of this metal. The rivers draining into Cochin estuary are considered to be polluted and in addition to this, a zinc smelter factory is situated on the banks of the Periyar River draining to the estuary. Zn is extensively used as a rodenticide and the nearby agricultural areas used for prawn farming might have contributed Zn in this form to the estuary.

## ➢ Copper

In aquatic systems, copper can exist in three broad categories— particulate, colloidal and soluble. Particulates contain varying fractions (12-97%) of the total copper transported by the rivers. Cu interacts strongly with sulphur forming relatively stable insoluble sulphides. Humic materials in natural water bind >90% of total Cu, while those in seawater binds only 10%. In the seawater, Ca and Mg because of their large concentration, displaces Cu from humic acids (Moore and Ramamoorthy, 1992).

In this study, mangrove sites showed much higher particulate copper concentrations than the rest. At all stations postmonsoon season dominated in concentration, while, monsoon recorded the minimum. The order of abundance of particulate Cu at the study sites were station 2 > station 1 > station 3 > station R. The two mangrove habitats did not differ much in copper content. However, in both the monsoon and premonsoon seasons station 1 exhibited comparatively higher values whereas station 2 recorded a distinctly large concentration peak only in the postmonsoon period (Figure 5.13). At the mangrove sites, copper ranged from 7.570 to 653.98μg/g, while at station 3, it varied from 5.03 to 257.84μg/g. the estuarine site recorded Cu in the range 8.220 to 104.07μg/g (Table A. 43).

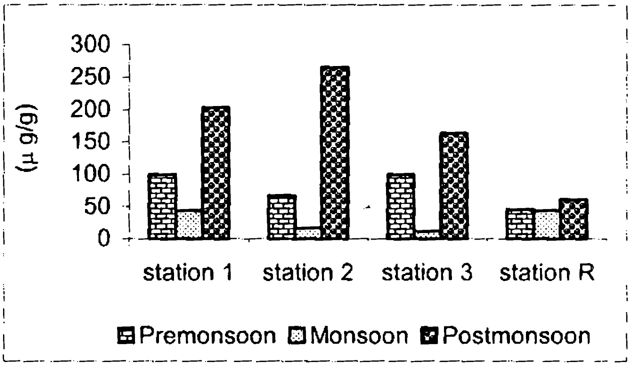


**Figure 5.13:- Seasonal mean variation of particulate copper**

The high concentration of copper in the mangrove systems can be attributed to the well-known ability of Cu to form complexes with organic matter (Kramer and Duinker, 1984; Valenta *et al.*, 1986; van der Berg *et al.*, 1987; Zwolsman *et al.*, 1993). Hirose (1990) has shown that copper was not bound on the suspended particles as inorganic salts but were directly associated with the binding sites of the particulate organic matter. Since organic compounds are abundant in the mangroves, the observed elevated levels may be the result of these stable Cu-organic complexes in particulate matter. Copper in the anoxic Baltic waters showed highest percentage in suspended form (Dyressen and Kremling, 1990). Furthermore, metals like Cu, which are strongly complexed with organic ligands may interact (chelation/complexation) in solution with dissolved organic matter that are in turn, concentrated by adsorption onto fine particulates such as clay minerals (Hirose, 1990). This type of re-adsorption was also observed in an experimental study by Gee and Bruland (2002). They found that Cu is rapidly removed from the dissolved phase and more than one process was found to control the dissolved and particulate Cu concentration.

Fe and Mn oxides are well known for their ability to act as scavengers of trace metals. Due to the degradation of huge organic matter load in the mangrove environments, Fe and Mn oxides get solubilized under the reducing condition and presumably trace metals associated with hydroxides thereof are injected into the overlying water column, where they get precipitated and/or adsorb onto suspended particles and surficial sediments (Turner and Millward, 2000).

Lead *et al.* (1999) have shown that Cu binding to particles was relatively insensitive to grain size and compositional variations in suspended particulate matter. Pore water diffusion may be another source of this metal. Furthermore, for Cu, Gee and Bruland (2002) have noted that dynamic exchange of metals between dissolved and particulate phases was of the same order of magnitude or even larger than the benthic fluxes and external sources.

Particulate Cu showed positive relationship with dissolved oxygen at station 1 (Table C.4). This indicates the association of Cu with Fe and Mn oxides, which might have formed in the aerobic environment and the dissolution of which release copper into the overlying water. In addition, Cu showed high correlation with particulate Mn and not with Fe at this site (Table C.9). Fernex *et al.* (1992) stated that Cu co-precipitated with Mn oxides and not with Fe. Mn also showed positive correlation with dissolved oxygen at this site. Thus, Cu may be present associated with Mn oxides here. At station 2, though, both particulate Fe and Mn correlated with particulate Cu, correlation coefficient with Mn was higher than that with Fe (Table C.9). Hence at this station Cu was associated with both Fe and Mn oxides. The very high concentration of Fe observed at this station also favoured such an association.

The postmonsoon peak in concentration at both the mangrove environments can be attributed to the longer residence time of the particles facilitating further adsorption. Cu is found to desorb from particulates as the salinity increases. This may be the reason for the lower levels in the premonsoon season even though longer residence time of particles in the water column was expected in this season also. Another possibility was the enhanced evapo-transpiration occurring in this season leading to intense anoxic conditions. Under these conditions, sulphate reduction is enhanced and Cu may form insoluble CuS, which might have incorporated to the sediments. The heavy influx of monsoon waters may bring with it large 'mega' particles impoverished in metal content. The dilution of metal rich particles inside the mangroves with the incoming diluent particles may be the reason for the observed low metal levels in the monsoon period.

The riverine station also exhibited a concentration range similar to that of mangroves. Here also postmonsoon was observed with maximum concentration while, monsoon showed the minimum. In rivers, trace metals are transported in a large proportion as colloids (Hart and Hines, 1994). Of these colloids, the amorphous Fe and Mn oxides and hydroxides are the major fraction and they are found to be good scavengers for other trace metals. In this study, Cu was found to have excellent correlations with both Fe and Mn (Table C.9). This clearly reflects the association of Cu with these polymeric oxyhydroxides.

Cu is used in many industries as catalysts and promoters. The effluents coming from these industries may contain large amount of Cu. The single largest source for Cu in this river may be the anthropogenic inputs. Previous studies have shown that in contaminated rivers re-adsorption of dissolved copper onto particles prevailed (Wangersky, *et al.*, 1989; Gerringa, 1990; Gerringa *et al.*, 1991). In the Vistula River, Sokolowski (2001) observed that Cu existed equally in the dissolved and particulate phases and the influence of suspended particulate matter on its distribution is obvious. Cu showed a negative correlation with pH at this site. Lead et al (1999) have pointed out that removal of Cu from solution in the presence of natural suspended matter is probably the result of rapid uptake of metal onto binding sites at the particle surfaces. This process was found to be pH dependent and can be attributed to competition between the metals and protons for the binding sites (Ferreira *et al.*, 1997; Hamilton-Taylor *et al.*, 1997).

Since Cu exhibited high correlation with Fe, relatively high micro particulate component for this metal is expected. Besides, Benoit *et al.* (1994) have observed particle concentration effect for Cu. This effect is attributed to the increased colloid concentration in the filtered fraction in proportion to the quantity of suspended matter retained on the filter. Due to the frequent clogging of the filters the colloidal dimensions of the particles were modified and retained on the filter. This process may partly explain the observed elevated concentrations. Moreover, the dissolved fraction of Cu was found to be lowest at this site clearly showing that majority of the soluble form was colloidal in nature, which might have get retained in the filter due to the particle concentration effect.

Here, Cu exhibited positive relationship only with Ni other than Fe and Mn (Table C.9). This leads to the conclusion that these two metals had a common origin. Seasonally, a monsoon minimum was observed probably due to the dilution by the resuspended particle. Adsorption of Cu on particles would have been favoured in the postmonsoon season due to the longer residence time of the particles in the water column as river flow is reduced. Experimental studies have shown that Cu was found to be increasingly coagulated as the concentration of electrolytes is increased in river water (Sholkovitz and Copland, 1981). This may explain the higher values of Cu in the premonsoon season than the monsoon period.

The estuarine site recorded distinctly low copper content than the other sampling sites under study. Here also, postmonsoon period showed the maximum concentration. Monsoon and premonsoon season showed only a slight variation in concentration. Cu exhibited highly significant correlation with dissolved oxygen and Mn but not with Fe at this site (Table C.4, C.9).

Lower levels of Cu in estuaries were noted elsewhere (Regnier and Wollast, 1993). This can be attributed to desorption and solubilization of riverine particulate matter as the salinity increases. Dissolved Cu in the estuarine waters was found to be largely complexed with organics (Kramer and Duinker, 1984; Valenta *et al.*, 1986; van der Berg *et al.*, 1978; Zwolsman *et al.*, 1993), and desorption from the particulate matter can be expected with increasing pH in accordance with the well known characteristics of humic substances (Bourg, 1983).

Fernex (1992) in a study on the Camargue Delta in France reached the conclusion that Cu co-precipitated with Mn oxides and not with Fe oxides. In the present study also Cu exhibited correlation only with Mn showing that the scavenging particles for Cu in this system were Mn oxides. In addition, Mn showed a positive correlation with dissolved oxygen. The oxidized form of Mn is insoluble and is formed at a faster rate as dissolved oxygen levels increases. During the precipitation of this oxidized species, it might have sorbed Cu onto it.

The main source of copper to the Cochin estuary may be the effluent discharges from various chemical industries situated on the banks of the rivers draining to this estuary and the intense boat traffic. Cu emissions from the antifouling paint surfaces can be a substantial portion of the copper loading into this estuary. Fishing as well as passenger boats release significant amount of Cu into this estuary. Copper boards and copper nails used in the boats are found to undergo rapid degradation thereby contributing significantly to the copper pool in this estuary. Another possible mechanism is the re-adsorption of dissolved Cu onto particles. The resuspended particles are enriched with the metal by the rapid adsorption of Cu from the reducing pore waters and were in a dynamic state of exchange with the overlying water column (Turner and Millward, 1999). Lead *et al.* (1999) have shown that Cu binding to particles is relatively insensitive to grain size and compositional variation in suspended particulate matter.

Seasonally, postmonsoon period recorded slightly higher concentration values than the other two seasons. Ouseph (1992) has related this increase from monsoon to non-monsoon months to the increased residence time of riverine particles in this period facilitating further build up of the metal by ion exchange processes. $Cu^{2+}$ was found to have high affinity for humic acids and Sholkovitz and Copland (1981) have shown that metals with strong association with humic acids will also be the ones with greatest extent of cation induced coagulation. Thus the sudden change from the near freshwater conditions of the monsoon season to the increasing ionic concentration of the postmonsoon would have led to an increased particulate metal content.

### ➤ Cobalt

Cobalt shows varied behaviour with particulate matter in the aquatic environment (Moore and Ramamoorthy, 1992). About 40-70% of the adsorbed Co was found to desorb from clay minerals. However, desorption from Fe and Mn hydroxides are limited.

In this study, particulate cobalt showed a distinct seasonal distribution pattern in each of the aquatic systems analyzed (Figure 5.14). The highest as well as lowest concentrations were detected in the mangrove systems itself. The order of abundance of Co was, station 1 > station R > station 3 > station 2. The concentration ranged from 0.08µg/g to 26.03µg/g in the mangroves, from 0.04µg/g to15.5µg/g at the riverine site and from 0.45µg/g to 14.03µg/g at the estuarine site (Table A.44). ANOVA calculations also showed significant variation both between season and stations (Table B.7).

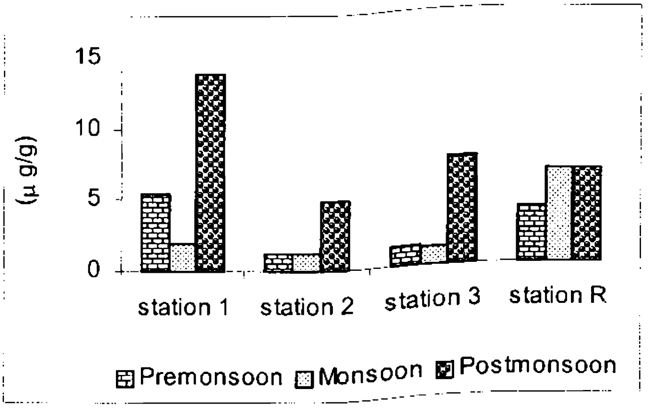


**Figure 5.14:- Seasonal mean variation of particulate cobalt**

Of the two mangrove systems analyzed, station 1 recorded distinctly high particulate Co content. This station also displayed the highest annual mean concentration while, station 2 showed the minimum. Thus contrasting behaviour was observed in the mangroves. At station1, Co showed high positive correlation with dissolved oxygen, while at station 2, pH had a positive though much less significant correlation (Table C.4). At both the stations Co showed high correlation with all other trace metals under study (Table C.9). At station 1, monsoon recorded minimum concentration whereas at station 2 premonsoon and monsoon exhibited similar particulate Co levels. At both these sites postmonsoon period was characterised by the maximum metal content.

Co is found to have slightly larger affinity for sorption under anoxic conditions, even though it forms stable compounds under reducing conditions and so will tend to be released to water (Liss, 1976). The observed higher concentration of Co may be due to increased adsorption on to re-suspended particles. Ciffroy *et al.* (2003) have shown that with cobalt, inorganic dissolved ligands are weak in complexation reactions and hence re-adsorption mechanism was found to be occurring for Co. The high correlation with Fe and Mn shows that Co is associated with amorphous Fe and Mn oxyhydroxides and removal from these entities was found to be much less. Besides, in mangroves, humic substances were present in enormous quantity and $Co^{2+}$ has least affinity for humic substances (Stumm and Brauner, 1976; Sholkowitz, 1978). Hence Co present in this system will be associated with particles or with amorphous hydrous Fe and Mn oxides.

Sorption behaviour of Co is very sensitive to pH in both fresh and seawater (Liss, 1976.). Thus the observed correlation with pH indicates that the change in pH may result in large variation in the concentration levels of Co in the particulates. Furthermore, Benes and Steinnes, (1994), have shown that adsorption of cations to particles increases from almost nil to maximum with increasing pH. The association with Fe and Mn shows why Co co-varies with dissolved oxygen. The oxidized species of Fe and Mn are precipitated while their reduced forms are soluble. Thus with the increase of dissolved oxygen, precipitation of Fe and Mn is enhanced together with Co as these two metal hydroxides are efficient scavengers.

Station 1 was located near the estuary and during high tides the entire forest is covered with floodwaters. The estuary was found to receive huge amounts of effluents from industries. As the metal-rich estuarine water enter the comparatively calm environments of the mangroves, adsorption as well as precipitation occurs leading to high particulate metal content. But, station 2 was of isolated nature. Thus the large amount of particulate Co at station 1 may be anthropogenic in nature. The postmonsoon hike in concentration may be due to the elevated adsorption rate of the metal on suspended particles. Dilution by heavy influx of freshwater containing metal-poor particles may be the reason for the low metal concentration in monsoon.

Station 3, the riverine station showed lower Co concentration than the estuarine site. Here also postmonsoon season was characterized by peak concentration. However, in the monsoon and premonsoon, Co concentration did not vary much, though monsoon showed lower values. None of the hydrographical parameters was found to have any correlation with Co, while all other particulate metals selected for study showed significant correlation with particulate Co (Table C.4, C.9).

The main contributors of particulate Co to this system are the industrial effluents. Fine-grained particles in the suspended matter may act as nuclei for adsorption to the colloidal Fe and Mn oxyhydroxides, which in turn, adsorb other trace metals onto them. The co-variation of Co with Fe and Mn confirms the association of Co with them. Co may have a strong microparticulate component presumably of anthropogenic nature. Jarvie (2000) has further shown that for metals, which have a high microparticulate component, the effect of river flow, are minor compared to the within-river processes related to tidal conditions, which control mobilization of particulate and microparticulate materials generating huge variations in concentration.

The high colloidal fractions in rivers may have led to the increased particle concentration. Large amount of suspended matter often caused clogging of the 0.45μm filters and there is a fair chance for alteration in the colloidal dimensions of particles. Aggregation of colloidal particles may thus result in elevated Co levels in the filter-retained material. Hydrographical parameters were not correlated with Co. The metal may have been introduced to the river in the form of fine particulates or may have got rapidly precipitated on discharge into the river in the soluble form.

In the estuary, Co presented a different distribution pattern. Here, postmonsoon and monsoon seasons had similar concentrations with a premonsoon minimum. The annual mean concentration was higher at this site than that of the river. Particulate Co showed significant correlation only with Fe and Cr. A significant inverse relationship with salinity was noted at this site.

Zwolsman and Van Eck (1999) noted non-correlation of particulate Co with Mn in the Scheldt estuary. They have related this to the special precipitation dynamics of Mn oxides. Co is preferably present along with sulphides. These metal sulphides are gradually oxidized resulting in release of the metal in the dissolved state whereas Mn gets precipitated upon being oxidized. In this study, salinity was found to be a major factor influencing the distribution of Co. Salinity and Co concentration were inversely related (Table C.4). This type of behaviour was observed in other estuaries also (Zhang and Liu, 2002). The decrease of metal levels with increasing ionic strength points to the desorption reactions of the metal. The high values shown by the dissolved fraction of the metal in the premonsoon season justifies this assumption. The ion exchange processes as the river water mixes with seawater is the reason for the desorption reactions.

The high annual mean concentration noted at this site points to the anthropogenic inputs to this system. Since Cochin estuary is considered to be contaminated by the effluents from various industries, harbour activities, sewage disposal etc., particulate material was likely to be present at high concentration ranges. In addition, dredging operations are carried out every year to maintain the shipping channel. This resulted in large amount of re-suspended sediments in the water column. Dredging may disturb the otherwise stable sediments, causing them to release metals, which might have got deposited in them. The monsoon run-off might have brought in particles rich in metal content from the industrial discharge points. This may be the reason for the high monsoon value. Adsorption of pore water released metal onto the re-suspended particles was highly favoured in the postmonsoon season resulting in a concentration hike.

### ➢ Chromium

Chromium is a redox sensitive element with an anthropogenic input in many of the aquatic systems. Industrial as well as domestic waste disposals increase the chromium content in natural waters. Cr is one of the less toxic of the trace metals, considering its oversupply and essentiality. The two main oxidation states of Cr in natural water are +3 and +6. In well-oxygenated water, +6 is the thermodynamically stable species while +3 is the kinetically stable species. Interconversion of $Cr^{+3}$ and $Cr^{+6}$ occur in conditions similar to natural waters (Moore and Ramamoorthy, 1992).

Cr, in this study, showed distinct distributional characteristics. The highest as well as the lowest annual mean concentrations were detected in the mangroves. At all stations, postmonsoon recorded the highest concentration (Figure 5.15). In the mangroves, abnormally high values were noted in November. The concentration ranged from 1.35μg/g to 563.5μg/g at the mangrove sites, from 0.300 to 501.47µg/g at station 3 and from 6.550 to 129.52µg/l at the estuarine site (Table A.45).

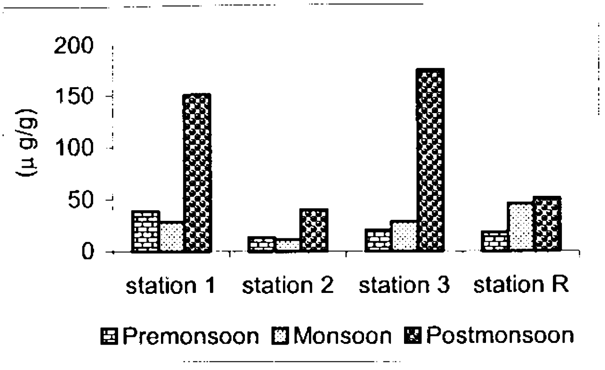


**Figure 5.15:- Seasonal mean variation of particulate chromium**

Of the two mangroves, station 1 recorded higher concentration. The elevated levels of the metal in the mangrove environments can be related to the redox nature of the element. Cr exists as +6 ions in oxygenated waters. But, on entering the reducing condition prevailing in the mangroves, it gets reduced to +3 state rapidly. Moore and Ramamoorthy (1992) have shown that $Cr^{+6}$ is easily reduced by dissolved ferrous sulphides and certain organic compounds with sulfhydril groups. These compounds, are present in plenty in mangroves and hence reduction to $Cr^{3+}$ is highly possible. Aston (1976) has reported that $Cr^{3+}$ is highly sorbed to particulates and suspended sediments. Thus, the high concentration of the metal in mangroves can be due to the reduction of $Cr^{+6}$ ions and subsequent adsorption onto particulate material.

Station 1 was situated near the estuary and was flushed with tidal water regularly. The nearness of the site to the estuary and the domestic sewage discharges into it might have increased the metal content. Municipal wastewaters are found to release considerable amounts of Cr into the environment (Moore and Ramamoorthy, 1992). At station 2 the entry of tidal water is regulated. The isolated nature together with low metal input through anthropogenic sources at this site may be the reasons for the low metal content. Dissolved chromium, on the other hand, was higher at station 2 than at station 1. This points to the fact that at station 2, Cr remained preferentially in the dissolved phase.

At both the mangrove sites, particulate Cr showed very high correlation with the rest of the metals analyzed (Table C.9). This indicates a common source of these metals, presumably the Fe and Mn oxyhydroxides. None of the hydrographical parameters exhibited any correlation with Cr emphasizing its anthropogenic origin (Table C.4). Besides, Cr is likely to be incorporated to sulphidic minerals because $Cr^{3+}$ ($d^3$, $t_{2g}{}^3$) has high ligand field stabilisation energy (12 Dq) due to its electronic configuration and is kinetically inert to substitution reactions (Burgess, 1988). Thus sulphide will not react easily with $Cr^{3+}$ that is dissolved or supported on solid oxide phases. At both the stations, postmonsoon recorded maximum concentration due to the increased adsorption onto particulates. Lower concentration in the monsoon period may be the result of dilution of the metal-rich particles with incoming metal-impoverished particles of the run-off waters.

Station 3, the riverine station, recorded high particulate Cr content. The main source of this metal in the river may be the run-off from the effluent discharges in the form of fine-grained particles. Various other natural processes such as resuspension, weathering and *in situ* reduction may have contributed substantially to the Cr pool of this river. In a study by Jarvie (2000) on the River Trent, high particulate component was observed and was attributed to the relatively low tendency of Cr to become associated with particles by scavenging reactions.

Jarvie (2000) has further shown that elements like Cr, with low solubility have greater particulate and microparticulate components. Aston (1976) has stated that Cr has the same concentration both in the oxic and anoxic conditions. Hence, the observed low seasonal variation may be due to the conservative nature of Cr in the oxic and anoxic environment. Since Cr has a strong microparticulate component, colloidal aggregation might have occurred during the separation process of the particulate fraction. Cr exhibited positive relationships with many of the trace metals analyzed indicating a common source of them. Anthropogenic sources of the metal were augmented by its non-correlation with hydrographical parameters. Turner (1999) has reported that sorption reactions are at least partially reversible and there is, therefore, a thermodynamic tendency for particle-water interactions. Adsorption onto re-suspended or previously existing natural particles may be very high during the postmonsoon period subsequently resulting in elevated concentration.

In the estuary, particulate Cr concentration was lower than that in the river and an abnormally high value was observed in December. If this value was excluded as an outlier, monsoon period would have the maximum concentration and premonsoon, the minimum. Estuarine chemistry of Cr is well understood and many studies point to the desorption reaction occurring with increasing salinity (Turner, 1999; Zwolsman and Van Eck, 1993; Salomons and Eysink, 1981). Thus desorption at higher salinity may be the reason for the low metal content in the premonsoon season.

Sedimentary dynamics may be the primary factor determining the particulate metal distribution in the Cochin estuary. As Jarvie (2000) has pointed out, strong linear relationships between Cr and Fe reflected sediment transport processes. Anthropogenic perturbations were highly likely to contribute to a significant fraction of the metal to the estuary. The rivers draining to this estuary were heavily contaminated with effluent discharges from numerous industries. As Ouseph (1992) observed, effluent discharge materials were brought into the estuary in the form of fine-grained particles. Another source of Cr to the estuary is boat traffic. The paints used on the boats contain large quantities of Cr in the form of zinc chromate causing the leaching of which add a substantial amount of the metal to the water. Hydrographical parameters were found to have no significant relationships with particulate Cr, again supporting the anthropogenic source (Table C.4).

Generally, elevated concentration of particulate Cr in the monsoon period indicated that riverine input and run-off from land were the main source of Cr. Since Cr has a large microparticulate component, flocculation is highly favoured as the river water enters the estuary. In a study of suspended Cr from San Francisco Bay, Abu-Sabu and Flegal (1995) noted that processes, which contribute to the enrichment of Cr in suspended matter were weathering and municipal and industrial discharges. Taylor and McClennan (1985) have stated that the weathering process tend to enrich first row of transition elements in suspended particulate matter and sediments.

### ➢ Nickel

The fate of nickel in the aquatic environment is strongly influenced by its aqueous reactions with soluble species and with particulates. The mechanism by which Ni can be associated with solid phases is controlled by several important parameters such as pH, pE, ionic strength, types and concentration of numerous organic/inorganic ligands and the presence of solid surfaces for adsorption. Ni binding to particulates in river water exhibits variable behaviour. 97-98% of Ni in the Amazon and Yukon rivers was found to be in the particulate form whereas in some other systems only 5-30% of Ni was associated with particulates (Wilson, 1976).

Nickel, in this study, exhibited a uniform distribution pattern. In the mangrove environment it ranged from 7.63g/g to 135.7µg/g whereas the riverine site recorded Ni in the range 4.1µg/g to 186.4µg/g while at the estuarine site Ni varied from 6.41µg/g to 76.55µg/g (Table A.46). ANOVA calculations showed significant variation between both seasons and stations (Table B.7). Postmonsoon period was characterized by peak concentration at all sites (Figure 5.16). The monsoon season recorded the minimum at the mangrove and riverine sites while similar values were recorded during monsoon and premonsoon seasons in the estuary.

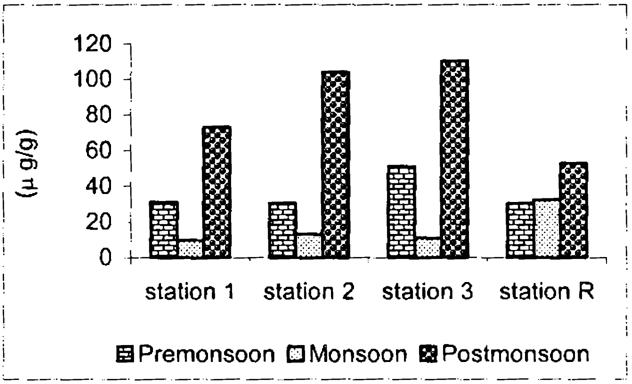


**Figure 5.16:- Seasonal mean variation of particulate nickel**

The 'Fisheries' station (station 2) showed higher annual mean concentration than station 1 (Mangalavanam), which is located near the estuary. The estuarine station (station R) as well as station 1 both exhibited similar annual mean concentration values. Both the mangrove sites exhibited a postmonsoon maximum and a monsoon minimum. Significant variation in concentration between the two mangrove environments was observed only during the postmonsoon period.

Unlike sediments, which can integrate changes in the quality of water column over long periods of time, suspended matter profiles are very sensitive to variations in physico-chemical parameters. In anoxic waters, Ni showed an intermediate affinity for particulate matter (Dyressen and Kremling, 1990). Estimated adsorption rate for Ni is nearly two times higher than for desorption. Increasing particle concentration causes an increase in metal-sorption forward rate constants (Honeyman and Santschi, 1988). In the shallow mangrove waters intense bioturbation may have caused sediment resuspension subsequently resulting in elevated suspended matter concentration. Exchange rate studies between dissolved and particulate forms indicated that sorption processes could result in dynamic internal cycling of Ni, causing concentration fluctuations that can be significant even on daily time scales.

Though Ni complexes strongly with organic ligands (Piatina and Hering, 2000), the metal may interact in solution with dissolved organic matter (chelation/complexation processes) that are in turn concentrated by adsorption onto fine particulates such as clay minerals. Gee and Bruland (2002) have further shown that the exchange of metal between the dissolved and particulate forms are found to be the same order of magnitude or larger than the benthic fluxes and internal sources. Achterberg et al (1997) have shown that Ni-organic complexes are mostly derived from the humic substances and the ligands are mostly aromatic in nature. Since humic acids were found to be present in great concentration in the mangroves, this type of association may be predominant there. In a geochemical study of Ni, Sholkovitz and Copland (1981) have shown that metals like Ni, which most strongly associated with humic acids will also be the ones with greatest extent of cation-initiated coagulation. Thus the higher values at station 2 may be due the presence of huge amount of Ni-humic acid complexes.

Variations found in the mean concentration at the two mangrove stations may be due to the irregular discharges from the polluting sources and also due to the complex water movement in the creek mixed with the semi diurnal tidal mixing. At station 2, particulate Ni displayed significant correlations with other metals suggesting a common origin for these metals (Table C.9). Drever (1997) has shown that Fe and Mn oxyhydroxides have adsorption capacity for trace metals and the adsorption of Ni by such oxyhydroxides was supported by the significant relationship between Ni and Fe. But at station 1, Ni showed correlation with all metals studied except Fe. This indicates that Ni may be associated with Mn oxides here. Particulate Mn may present, as $MnCO_3$. while Ni, on the other hand may be partially associated with sulphides. These metal sulphides were gradually oxidized during the restoration of dissolved oxygen with increasing salinity, resulting in release of metal in the dissolved phase. At the same time manganese hydroxides were formed, which are very effective scavengers of trace metals. The close relationship between Ni and Mn indicated that Ni was mobilized from suspended matter but then scavenged back by Mn oxides. The strong positive relationship of Ni with dissolved oxygen also supported this explanation.

Geochemical studies of Ni in rivers showed contradictory results. In the Amazon and Yukon rivers, 97-98% Ni was transported in the particulate form (Moore and Ramaswamy, 1992) while in the Vistula River Sokolowski (1999) found that the dominant transportation mode for Ni was through solution. The strong association of Ni with other trace metals at this study site reflected a common source of these metals presumably the scavenging Fe and Mn oxides. The strong association with particulate Fe pointed to a strong microparticulate (colloidal) component for this metal. Jarvie *et al.* (2000) have shown that colloids were involved in transferring dissolved Ni to particulate phase. Colloidal pumping hypothesis for transfer of trace metals to particulates is widely recognized (Farely and Morel, 1980; Honeyman and Santschi, 1989; McCave, 1984). It is very important that colloid dynamics were not driven by any change in ionic strength, unlike colloid destabilization in estuaries. Wells *et al.* (2000) have shown that microbial degradation of colloidal particles released associated metals to solution, whereby metals were transported back to particulate phases via cellular uptake or sorption to particle surfaces.

Investigating the coagulating nature of Ni in river water with various electrolytes, Sholkovitz and Copland (1981) found out that Ni was increasingly coagulated with increasing electrolyte concentration. In pristine river systems, lower reactivity of Ni towards particulate matter was noted. This was attributed to the propensity of the metal to form a range of stable soluble inorganic and organic complexes, which reduces adsorption onto particulate matter (Gerringa, 1990; Bilinski *et al.*, 1991; van der Berg, 1992; Benoit *et al.*, 1994). However, Martin *et* *al.* (1993) in the study on Lena River, Russia, found that the adsorption tendency of the metal increased with the contamination of the river water. Since station 3 was found to receive effluents from a large number of industries, pollution of river water may be very high. Among the major polluting sources of Ni, refineries, shipyard wastes and chemical industries are identified to have an upper hand (Khan, 1995). The highest annual mean concentration was again observed at this site clearly showing the anthropogenic inputs of the metal. The observed increase of particulate Ni from monsoon to non-monsoon periods reflected the enhanced adsorption onto suspended matter in the reduced flow conditions.

Particulate Ni showed some interesting distribution pattern in estuaries. Snodgrass (1980) concluded that Ni concentration in the polluted estuaries were of the same order as in unpolluted estuaries. The concentration and speciation of Ni in estuaries were found to depend on competing processes such as coagulation, precipitation, sorption and complexation/chelation with dissolved organic and inorganic ligands.

At the estuarine site Ni varied linearly with Mn and not with Fe (Table C.9). This can be explained by considering the precipitation dynamics of Mn oxides. The close relationship of Ni with Mn in suspended matter shows that Ni may have mobilized from particulate matter but then scavenged back by Mn oxides. This type of behaviour was observed by Zwolsman and Van Eck (1999) in the Scheldt estuary, the Netherlands. Covariation of Ni with dissolved oxygen can be related to the formation of Mn hydroxides with increasing dissolved oxygen. Mn oxidized to $Mn^{4+}$ and mightt have carried with it other trace metals by scavenging action.

Adsorption of the metal onto resuspended particles was suggested in previous studies (Honeyman and Santschi, 1998. Gee and Bruland, 2002). Since resuspension was highly possible in the Cochin estuary, readsorption onto fine-grained particles may be an important pathway for the removal of the metal from the water column. However, the coagulative removal of Ni on estuarine mixing was found to be low (Sholkivitz and Copland, 1981). The main contributors of particulate Ni to this estuary were the rivers that carry enormous load of effluents with them. River Periyar, one of the largest rivers draining to this estuary has many chemical industries situated on its banks. The Cochin Shipyard is also located near the sampling site. Hence emanations from these sources may be the main contributors for Ni in this estuary. Ni can have an atmospheric input as well since automobile fuels contain large amount of this metal.

## ➢ Cadmium

A major portion of cadmium is transported to the sea in the solid phase through river suspended matter, rainfall and plain drainage and aerial dust (Martin and Meybeck, 1979; Martin and Whitefield, 1983). A high percentage of total particulate Cd was found in the exchangeable and carbonate fractions of suspended sediments in freshwaters (Moore and Ramamoorthy, 1992). Cadmium sorbed on suspended solids in fresh water may well desorb when river water mixes with saline water.

In this study, Cd showed distinctly high values in the postmonsoon period at all stations. The values were so high in this season that other seasons were almost masked in the graphical representation. The annual mean concentration levels showed a maximum at station 3 and a minimum at the estuarine site. The two mangrove stations showed comparable results. Particulate Cd ranged from 0.95μg/g to 1923.3μg/g at station 1, from 0.68μg/g to 2089.4μg/g, from 1.6μg/g to 3369.7μg/g at station 3 and from 1.6μg/g to 1560.8μg/g at station R (Table A.47). Monthly data showed abnormally high values in January at all stations. Dominant system perturbations occurred in this month might have led to a sudden increase in the Cd content. Seasonal mean variations of dissolved cadmium are depicted in Figure 5.17.

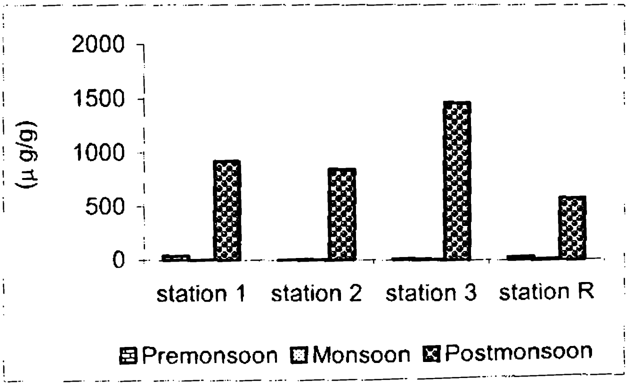


**Figure 5.17:- Seasonal mean variation of particulate cadmium**

Of the two mangrove sites selected for study, station 1 showed high annual mean concentration levels. Seasonally, only during the monsoon season station 2 showed higher values. Due to the intense sulphate reduction in the mangroves, Cd would have got incorporated into the sediments as CdS. The particulate matter concentration in the anoxic waters may be higher than in oxic waters since CdS formed would remain attached to the fine-grained clay particles, which are abundant in these systems. In a study (Dyressen and Kremling, 1990) on anoxic waters, Cd showed a high affinity for the particulate component. Since bioturbation is the major factor modifying sediment nature in mangroves, Cd released in the soluble form by these forces, re-adsorbs rapidly onto the suspended particles. Besides, Cd was found to form stable compounds with organic ligands such as humic substances. Thus the metal could be present in the dissolved fraction also to a considerable extent. However, the sudden increase in concentration in the postmonsoon period may be the result of sedimentation of coarse metal–deficient particles brought in by the monsoon showers leading to the enhanced adsorption onto fine particulates.

At both the mangrove sites, particulate Cd exhibited high correlations with other particulate metals indicating a common source. Anthropogenic inputs are of considerable importance. Hydrographical parameters were found to have no influence on the particulate Cd distribution (Table C.4). This suggested that physical rather than chemical pathways were controlling the cycling of Cd in these systems. Pore water infusion and resuspension can be the major deciding factors for this metal in the mangroves.

Both monsoon and premonsoon seasons recorded much lower concentrations than the postmonsoon period. Desorption of Cd with increase in salinity due to the formation of stable chlorocomplexes have been reported (Comans and van Dijk, 1998; Liu *et al.*, 1990; Che *et al.*, 2003). Complexation of metals with organic or inorganic ligands was found to increase their dissolved component. Hence decrease in particulate Cd in the premonsoon season can be due to the increased desorption associated with increasing ionic strength. Monsoon showers bring with it large 'mega' particles as well as metal–deficient fine particles to the creek waters. Here, they get mixed with resuspended, metal-rich particles causing a reduction in the net particulate Cd concentration. Piatina and Hering (2000) reported that Cd were associated with finer particles such as clay minerals.

The riverine site exhibited highest annual mean concentration. Here also the postmonsoon period exhibited the maximum concentration. High concentration shown by Cd at the time of low river flow condition points to an anthropogenic input from industrial effluents. Zwolsman and van Eck (1999) observed high particulate Cd levels at low salinity and related this to the anthropogenic inputs. In this study, particulate Cd showed significant correlation with other trace metals. According to Sholkovitz (1976), a fraction of dissolved Cd is present in the colloidal state associated with hydrous Fe oxides. This fraction is removed from solution with colloids at low salinity when flocculation occurs due to the augmentation of the divalent cation activity. Particle concentration effect may be possible for this metal also since it has a strong particulate component (Horowitz *et al.*, 1996).

Adsorption onto particles was found to-be highly favoured in the low river flow conditions. The large soluble fraction of Cd brought in by the heavy monsoon run-off might have adsorbed onto suspended solids in the postmonsoon period. Kinetic studies have shown that adsorption of Cd take place at longer time periods (Ciffroy, 2003). Lead *et al.* (1999) opined that removal of Cd from solution in the presence of natural suspended particulate matter was probably due to the rapid uptake of the .metal to the binding sites of the particle surfaces and the pH dependence of this process was attributed to competition between metals and protons for the binding sites. At this site also Cd showed though negative, less significant correlation with pH. The low concentration level in the monsoon season may due to the increases in suspended matter content. Dilution of the solid pool of the metal with suspended matter that has few complexation sites was observed by Noriki and Tsunogai (1992). There could be large 'mega' particles and they may have small specific surface area or they could be composed of materials with intrinsically low abundance of particulate sites.

The estuarine site (station R) recorded the lowest concentration among the aquatic systems studied. As pointed out by Zwolsman *et al.* (1993), there is overwhelming evidence both from laboratory experiments and field investigations that Cd bound to suspended matter (partially) was desorbed when river water mixes with seawater (Lead *et al.*, 1999; Shulkin and Bogdanova, 2003; Regnier and Wollast, 1993). The removal is explained as due to the formation of chlorocomplexes. Thus the low concentration levels observed in the Cochin estuary compared to that in the polluted river draining to this estuary is due to the desorption of Cd from riverine particulate matter. Cd was found to be desorbed from particulate matter at the Bang Pakong estuary, Thailand also (Windom *et al.*, 1988). In the Rhine River estuary, Duinker and Nolting (1977,1978) noticed a 90% removal of dissolved Cd whereas Liu *et al.* (1990) and Che *et al.* (2003) observed a re-adsorption of these desorbed Cd onto newly introduced marine particles.

At this site Cd showed high correlation with dissolved oxygen (Table C.4). According to Drever (1997), Fe and Mn oxides are ubiquitous in the estuarine environment. Increasing dissolved oxygen levels favour the formation of insoluble Fe and Mn oxyhydroxides. These amorphous oxides might have scavenged more Cd onto them transforming it to the particulate form. Highly significant correlation between particulate Cd and particulate Mn was observed in this estuary (Table C.9). Lead *et al.* (1999) found out that Mn oxide fractions showed higher affinity for Cd than Fe oxides.

Postmonsoon season recorded the maximum concentration at this estuarine site. This may be due to the adsorption of Cd onto re-suspended particles facilitated by the increased residence time of particles in the water column. Ion exchange processes might have led to this adsorption. Resuspension of particles was favoured at this site by the dredging of the shipping channel. Ouseph (1992) also observed an increase in particulate metal content in the non-monsoon months. Desorption of Cd from particles with increasing salinity may be the reason for the metal-impoverishment during the premonsoon period. During monsoon, the high energy input due to increased river discharge may cause resuspension of bottom sediments with low metal content accounting for the reduced levels of the element in the particulate matter. Mixing of metal-rich riverine particles with metal-impoverished marine particles may account for the general low level of cadmium in particulate matter in Cochin estuary.

## ➢ Lead

Trace metals are added to the sea mainly *via* riverine input, weathering, Aeolian transport and remobilization from sediments (Chester 1986; Jickells *et al.*, 1987). Removal is principally controlled by the aquatic cycles of particulate matter through reactions in the water columns and sediments. For metals such as lead that bind strongly to particle surface and have no biological functions, the dominant removal process is by adsorption on to particulate materials, which then sinks and transport the metal to the bottom (Fowler and Knauer, 1986).

Station 3, the polluted riverine site, recorded the maximum concentration in this study and the minimum was observed at the mangrove site (station 2). The order of abundance of lead was station 3 > station 1> station R > station 2. This order was same as that of the dissolved component. However seasonal distributions of the two fractions presented a different picture (Figure 5.18). Postmonsoon season was dominant in lead content at all stations whereas monsoon dominated in the case of dissolved phase. Pb, which is introduced to the aquatic systems in the soluble form by the monsoon showers, gets precipitated on to particles later, in the postmonsoon period. ANOVA calculations revealed a significant variation between seasons but not between stations (Table B.7).

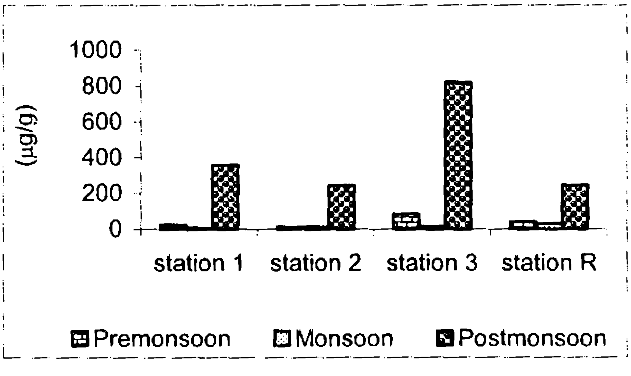


**Figure 5.18:- Seasonal mean variation of particulate lead**

Of the two mangrove stations, station 2 showed lower values of particulate Pb than station 1. The concentration ranged from 5.27 µg/g to 392.14µg/g at Mangalavanam (station 1) and from 5.83µg/g to 438.1µg/g at station 2 (Table A.48). At both the stations, correlation with other trace metals was very significant

(Table C.9). pH was found to have an influence on Pb distribution at station 1, while no hydrographical parameters had any influence at station 2 (Table C.4).

Under anaerobic conditions, iron sulphides may be formed through the interaction of Fe with $H_2S$, which is formed by the biological reduction of $SO_4^{2-}$ ions. Co-precipitation of Pb with FeS may occur in the system (Evans, 1989). In addition, iron oxides (and/or hydroxides) may also play a role in the retention of Pb (Forstner *et al.*, 1990; Izquierdo *et al.*, 1997). In this study also, a significant correlation was observed between Fe and Pb. Fernex (1992) has shown that Pb co-precipitated with Mn oxides as well.

Organic matter remineralization was found to release metal to the water column (Regnier and Wollast, 1993). Once released to solution, dissolved lead is removed from the water column by readsorption on to settling inorganic particles, leading to a low dissolved metal concentration. Besides, adsorption on to particles is an irreversible process as evidenced from scavenging models of the metals (Cotte Krief, 2002).

A good positive correlation was found between almost all heavy metals and Pb shows that there were common source or at least one major source for all of them. Hakanson and Jansson (1983) suggested that even metals with quite different chemical properties might appear with similar distribution in nature due to the fact that they are linked to carrier particles with similar properties.

The riverine site exhibited the highest concentration in all the three seasons. The high affinity of Pb to the solid phase is confirmed by experimental (Shulkin and Bogdanova, 1998) and field (Westerlund *et al.*, 1986) studies. Further more, in a study by Jarvie *et al.* (2000) it was found that Pb showed relatively low tendency to become associated with particles by scavenging and thus had a relatively high particulate component. The anthropogenic input of the metal to the river may be the reason for the elevated metal level at this site. Another mechanism, which affects the particulate Pb concentration, is the readsorption of dissolved Pb, which is released from the sediments on to the suspended particles. Readsorption of Pb in heavily contaminated suspensions was also reported by Regnier and Wollast (1993).

Colloidal aggregations can be another reason for the observed elevated Pb concentration at this site. According to Zhang and Liu (2002), concentration of Pb in rivers may exceed two fold depending on the water discharge, sediment origin and content and also anthropogenic activities of the drainage basin. Rivers of industrialized areas bring suspended matter enriched with trace metals. Benthic fluxes of particulate Pb was considered as the main source of Pb in the overlying water by Brugmann *et al.*, (1992). The positive relationship of Pb with Fe further points to the sediment transport effects. Significant correlations with other trace metals such as Cu, Zn, Co etc. indicate high similarities in the environmental distribution and chemical behaviour of these metal species.

Estuarine reactivity of Pb is well understood (Shulkin and Bogdanova, 2003; Martin *et al.*, 1993; Regnier and Wollost, 1993). Factors controlling the regional distribution of particulate Pb to the depositional environments are different discharges from petroleum basin, shipping wastes, land–based sources, biological activities and effects of wind. Pb can be released from the antifouling paints and equipments like solders used in ships. The released Pb ions are adsorbed or co-precipitated on to suspended matter found in abundance in the estuary. In the Cochin estuary, shipping activity is high and emanations from these ships constitute one of the major sources for this metal.

In an experimental study on the mobilization of metals from riverine suspended matter on mixing with seawater, Shulkin and Bogdanova (2003) found that Pb remained preferentially in the particulate phase. In the Bang Pakong estuary, Thailand and in the Gota river estuary, Sweden (Danielsson *et al.*, 1983) particulate Pb distribution implied an estuarine removal (Windom *et al.*, 1985).

Pb can have an atmospheric source also (Westerlund *et al.*, 1986; Rojas *et al.*, 1993; Veron *et al.*, 1994; Ferrand *et al.*, 1999). The air-borne particulate Pb contributes either directly to the make up of particulate population, or to a lesser degree, indirectly via dissolution and rapid readsorption on to pre-existing particles. In this study, Pb exhibited preference for particulate Mn as evidenced from its strong correlation with Mn (Table C.9). Fernex (1992) has also shown that Pb co-precipitated with Mn oxides. The observed correlation with dissolved oxygen (Table C.4) also supports this argument. Mn oxide formation is promoted with increasing dissolved oxygen and these oxides can further scavenge additional metal ions on to them. Thus the main contributors of Pb to this estuarine system are the riverine particles brought in by the rivers flowing through the industrialized areas and the atmospheric input together with contribution from resuspended sediments.

## 5.4 Sedimentary Trace Metals

The capacity of the sediments to accumulate compounds makes them one of the most important components for the evaluation of contamination levels in aquatic ecosystems. The sediment, after fine particle deposition and adsorption processes, is the main depository of heavy metal accumulation (Silva and Rezende, 2002). Lake sediments can serve as information archive of environmental changes through time (Haworth and Lund, 1984); where each layer of buried sediment would represent a particular record of the past environmental conditions (Von Guten *et al.*, 1997). Elevated metal concentration associated with long-term pollution caused by human activities has been recorded in mangrove sediments (Lacerda *et al.*, 1993; Mackay *et al.*, 1992; Mackay and Hodgkinson, 1995; Tam and Yao, 1998). Mangrove sediment can act as a sink for many heavy metals released to the environment as well as a source of them to the nearby aquatic system (Harbison, 1986). Sediments have thus proved to be excellent indicators of environmental pollution. Thus the determination of trace metals in the sediments becomes an integral part of any hydrogeochemical evaluation of the aquatic environment.

### ➢ Iron

Iron is a trace metal with very important biological and biochemical functions. Iron oxyhydroxides can act as a major carrier phase for other trace metals in the aquatic environment. Seasonal variations in hydrological flows, in redox conditions, in particle loading, in speciation all significantly influence the distribution of Fe (Davison, 1985).

In this study, Fe in the sedimentary phase exhibited a unique distribution pattern at each site. At station 1, the monsoon period recorded maximum Fe content and minimum concentration was noted during postmonsoon. The other mangrove site, station 2, showed a monsoon maximum and a premonsoon minimum. The riverine and estuarine sites presented similar seasonal variation with a premonsoon hike and a postmonsoon minimum (Figure 5.19). The order of abundance of sedimentary Fe was station 3 > station 2 > station 1 > station R. ANOVA calculations also showed highly significant variation within the systems (Table B.8).

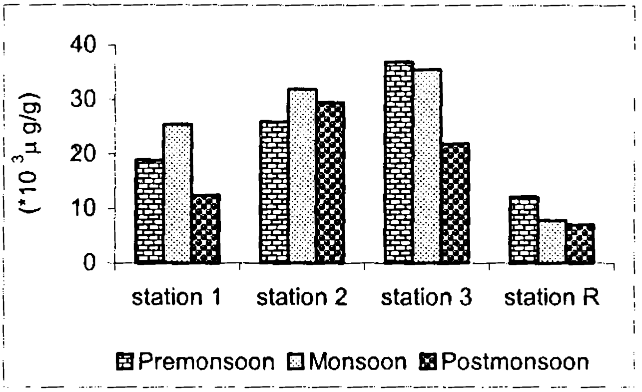


**Figure 5.19 Seasonal mean variation of sedimentary iron**

Among the mangrove habitats analyzed, the 'Fisheries' station (station 2) exhibited higher Fe content than station 1 (Mangalavanam). At station 1, Fe ranged from 7.006x10$^3$ to 38.58x10$^3$ µg/g, whereas station 2 showed Fe in the range 15.90x10$^3$ to 46.08x10$^3$ µg/g (Table A.49). The higher concentration of Fe at station 2 could be related to its environmental setting. Surface sediment sample was collected from the vegetated area at station 1 whereas at station 2, samples were collected from the creek waters. The ability of mangrove plants in modifying the observed geochemistry of many trace metals is well understood (Vale and Sundby, 1994). According to Ross (1994), the fine roots of mangrove plants can affect small changes in soil condition in the rhizosphere, which can influence metal bioavailability and their transfer from soil to plants. Many marsh and mangrove plants have aerenchyma tissues, which can supply oxygen to the roots buried in the anaerobic soils. The amount of oxygen transported to the roots often exceeds the demand of the root tissue, resulting in radial oxygen loss into the rhizosphere (Otte, 1991). Because of this phenomenon, sediments at the vegetated sites have higher redox potential. The reduced state of the bulk sediment might have favoured the mobilization of the metal by the formation of metal sulphides but oxidation processes in the rhizosphere might have immobilized the metal. Cacador (1994) has reported that metal oxides have been observed to coat the roots of a number of aquatic plant species. The metal oxide plaque on the roots of many marsh plants has the form of thin coatings or stains. In regions where the plants are active most of the year, much thicker FeO coatings around the roots have been reported. These coatings, which have the shape of hollow cylinders, are called rhizoconcretions. Such coatings were seen on the plant roots of the 'Fisheries' station (station 2). Thus, presence of such coatings would have significantly affected the sediment Fe concentration at this site.

Seasonally, the monsoon period recorded peak concentration at both the mangrove sites. Heavy influx of runoff water would have brought huge amount of fine sediments rich in trace metals to the creek waters. Non-monsoon periods exhibited lowest concentration at these sites. Resuspension of metal-rich fine sediments may cause an elevation in metal concentration in the water column. The observed increased metal levels in the dissolved and particulate compartments during the same period further augmented this possibility. Another explanation is the intense evapo-transpiration characteristic of the summer periods. Due to this, the reducing condition is intensified in the mangrove sediments and Fe bound to the sediments are released to the water column as $Fe^{2+}$ ions. Correlation analysis of iron and dissolved oxygen also supports this argument (Table C.3). Fe varied inversely with dissolved oxygen. In contrast to many metals, reduced form of Fe is more soluble in water and, as dissolved oxygen increases, more and more Fe gets precipitated as iron oxides. Fe showed inverse relationship with temperature at station 2, which too can be related to the reducing conditions developed that is intensified with increasing evaporation rates. Hence, hydrodynamic factors can have a decisive role in the distribution of Fe at this site.

Almost all metals exhibited positive correlation with Fe at station 1, while, Cd showed an inverse relationship at station 2 (Table C.10). Thus at station 1, Fe may have acted as the major carrier phase for other metal ion or both of them may have undergone similar geochemical reaction mechanisms. Organic carbon was also found to have significant positive relationship with Fe at both sites. Enrichment of the metal with organic matter in sediments reflects the diagenetic origin of the metal. Vezina and Cornett (1990) have shown that high concentration of Fe and organic matter are characteristic of fulvic and humic acid colloids, which are very abundant in the mangroves. Humic and fulvic acids are reported to have high Fe content (Hung *et al.*, 2000).

At station 1, Fe correlated well with Zn, Cu, Co and Pb and less significantly with Cr, Ni and Mn. However, Cr and Ni were found to be highly correlated to Mn (Table C.10). Thus, except for these two metals, Fe oxides appeared to be acted as the adsorbents. Although laboratory studies showed hydrous Fe oxides to be excellent adsorbers of other trace metals, at station 2, no such correlation was observed except for Cd, which showed an inverse relationship with Fe (Table C.10). This indicates the purely anthropogenic origin of Cd. In a study by Velde *et al.* (2003) in the French salt marshes, Fe correlated well with Ni, Co, Cr while, poor correlation was observed with Co and Mn.

Among the trace metals, Fe was the most abundant metal in this study and the Fe concentration observed in this study were similar to those reported by Rini (2002). Several studies (Harbison, 1986; Lacerda *et al.*, 1993; Tam and Wong, 1993,1995; Ong Che, 1999) have shown that mangrove sediments have a high capacity to retain heavy metal from tidal water and storm water run-off, and therefore often act as sinks for heavy metals. Church and Scudlark (1998) have pointed out that trace metals are trapped as oxides at the surface and as sulphides below with limited release in the marsh sediments. Redox sensitive elements like Fe precipitate above as ferric hydrates and are recombined below as mono or pyretic sulphides. Furthermore, elevated metal concentration related to long-term pollution caused by human activities has been recorded in mangrove sediments (Lacerda *et al.*, 1993; Mackay *et al.*, 1992; Mackay and Hodgkinson, 1995; Tam and Yao, 1998).

The riverine station (Chitrapuzha) recorded highest annual mean iron concentration than other systems in this study. Premonsoon season recorded maximum concentration here, while minimum was observed during the postmonsoon period. The overall high metal content and the premonsoon maximum characteristic of the station point to the severe contamination of the river. During the dry season, the river sediments absorb trace metals and organic pollutants discharged freely from domestic and industrial sources without much treatment. Since many industries are located on the banks of this river, contamination from effluents discharged from these industries may significantly contribute to the Fe pool of the river. In a previous metal speciation study, Joseph (2001) noted a premonsoon maximum in a nearby site. In the highly polluted Subarnarekha River, east coast of India, premonsoon hike in sedimentary iron was reported (Senapathy and Sahu, 1996).

Immediately after the monsoon, trace metals in the river sediments are released to the overlying water and then discharged to the estuarine and coastal environments resulting in a reduction of the metal levels in the sediments during the postmonsoon season. Abnormally high metal concentration in the particulate matter collected during the same period further reflects the resuspension process occurring during the period. Enrichment of Fe in suspended sediments was also reported in other Indian rivers. In the Godavary River, Fe was enriched by a factor of 2-3 times than the bed sediments (Biksham *et al.*, 1991), whereas in the Krishna River, suspended sediments contained as much as 25 times more Fe than the sediments (Ramesh *et al.*, 1990). The suspended solids are finer in nature and are richer in multiple hydroxide coatings, organics and trace metal scavenging clays (Forstner and Wittman, 1981). In addition, hydrodynamic conditions, which influence the movement of bed and suspended sediments are different. Hence particulates in most rivers show heavy metal enrichment relative to bed sediments. Subramaniam, *et al.* (1987) reported that suspended solids were 5-10 times richer than the bed sediments in the Ganges and Brahmaputra rivers.

Fe did not exhibit any correlation with hydrographical parameters (Table C.3). This fact again emphasizes the anthropogenic source of Fe in this riverine system. Here, Fe showed significant positive correlation only with Ni, though Cu exhibited a less significant correlation (Table C.10). This indicates a common fate of these metals in this river sediment. Total organic carbon was also found to be highly correlated to Fe (Table C.12), pointing to the complexation of the metal in the sedimentary environment presumably with humic substances. Diagenetic enrichment of Fe in the surface sediments is well documented (Zwolsman *et al.*, 1993; Valette-Silver, 1993; Brecker, 1993; Spencer, 2002). In the upstream stations of a Taiwan River, Fe content in humic and fulvic acids were high compared with the coastal locations (Hung, *et al.*, 2000). Another reason for the extremely high Fe content may be the nature of sediment in this study area. Silt and clay mineral particles are well known for adsorption of the metal cations onto them due to the increased specific surface area. The concentration range observed in this study was in accordance with those reported by Joseph (2001) in the same river.

The estuarine site recorded much lower sedimentary Fe than the riverine and mangrove habitats in this study. Here, iron ranged from $5.427 \times 10^3$ to $15.29 \times 10^3$ μg/g. Seasonally, premonsoon period recorded highest concentration, while, monsoon and postmonsoon exhibited similar concentration. The distinct low content of Fe in the estuarine sediments can be related to the sand dominance of the substratum. Due to the intense tidal action, dilution of the metal-rich fluvial sediments with the metal-impoverished marine sediments would have occurred, which was reflected in the lower metal content.

However, Fe at this site too was present in much large amount compared to the other elements. Diagenetic enhancement of Fe and Mn in the surface sediments of the estuaries is well documented (Zwolsman *et al.*, 1993; Valette-Silver, 1993; Brecker, 1993; Spencer, 2002). With burial, microbial degradation of organic matter take place resulting in bacterial utilisation of oxygen and other inorganic oxidizing agents (Santschi, *et al.*, 1990; Buckley, *et al.*, 1995). The reduction of $Fe^{3+}$ species results in the mobilization of the metal and diffusion to oxic surface sediments where they get precipitated either as oxides or occasionally as carbonates (Farmer and Lovell, 1984). Enhancement of Fe oxides at surface sediments occurs at lower depths than Mn (Cochran *et al.*, 1998). Fe showed significant positive correlation with organic matter (Table C.12) in this study, supporting its possible diagenetic pathway.

In the Beypore estuary, Kerala, Fe was predominant in the clay mineral lattices, Fe bearing heavy minerals and also in the adsorbed state on the surfaces of other minerals and total organic carbon (Nair and Ramachandran, 2002). Positive loading of total organic carbon and $Fe_2O_3$ in this estuarine sediment was a reflection of difference in their chemical partitioning pattern. Silt, clay and total organic carbon control the distribution of Fe in this study. Another possible source of Fe is the industrial effluents discharged to the rivers draining into this estuary. During the high-energy periods of the monsoon, increased amount of polluted material might have reached the estuary.

Seasonally, premonsoon season recorded maximum Fe content. In accordance with the sediment enrichment, both the dissolved and particulate components were low, during the same period. Since residence time of particles was found to be high during the summer periods, adsorption and subsequent flocculation of particles would have favoured. The coagulated particles might have settled to the bottom. Furthermore, immediately after the heavy monsoon rain, sediments are highly disturbed and resuspension of metal-rich finer fraction was possible. The depletion of metals from sediments during the postmonsoon period and subsequent enrichment in the particulate and dissolved segments point to the fact that resuspension of sediment was occurring in the estuary during this period.

In a geochemical study of Fe in the Vembanad Lake, of which Cochin estuary forms a part, Padmalal and Seralathan (1991) found that as soon as the reducing condition is developed in the sediment column, $Fe^{2+}$ in the oxidized zone of overlying waters might get precipitated as ferric complexes. Fe showed strong relationship with organic carbon suggesting that the major source of the element is the organic matter decay.

Fe showed, though less significant, a positive correlation with salinity at this site (Table C.3). This can be due to flocculation and precipitation of colloidal particles to the bed sediment as salinity increases. Of the metals studied, Fe exhibited high positive correlation with Cu, Zn and Ni, while Cd was correlated with Mn (Table C.10). This indicates that for Cu, Zn and Ni, hydrous Fe oxides are the major adsorbing phases. Such correlations were seen in sediments of Laucula bay, Fiji, also (Morrison *et al.*, 2001). The sedimentary Fe concentration in the present study was much lower than those reported by Joseph (2001) in the Cochin bar mouth region, while in line with those observed in Kayamkulam estuary (Unnikrishnan, 2000).

### ➢ Manganese

The chemistry of manganese in aquatic sediments is highly influenced by the physico-chemical status of the system. Manganese is found to be relatively mobile in the aquatic environment. In this study, Mn showed large variation in concentration in the diverse systems analyzed. In the mangrove environments, Mn ranged from 66 to 444.3µg/g, from 47.08 to 627.4µg/g at the riverine site and the estuarine site recorded Mn in the range 34.19 to 171.9µg/g (Table A.50). ANOVA calculations also showed highly significant variation between stations (Table B.8). Highest annual mean concentration was recorded at station 3, Chitrapuzha River, while the lowest was recorded at the estuarine site. Both the mangrove habitats exhibited similar concentration levels.

Seasonal mean variation of dissolved manganese is depicted in Figure 5.20. In the mangrove environments, postmonsoon season recorded the lowest concentration. Though monsoon period recorded slightly higher Mn level at station 2 than the premonsoon period, both the seasons were found to have similar Mn content at station 1. Premonsoon hike in concentration was also seen for the dissolved fraction also whereas, the particulate metal at both the sites showed highest concentration during the postmonsoon period. Sediment resuspension, which results in reduction of the metal content of the sediments, may be taking place in the postmonsoon season. It may be noted that it was only during the monsoon season sedimentary Mn exceeded the particulate metal concentration at both the sites. Enormous load of sediments brought in by the increased land run off during the monsoon season might have explained this. Thus, during this season, the influx of runoff water, which is rich in fine-grained sediments may have resulted in elevated metal concentration.

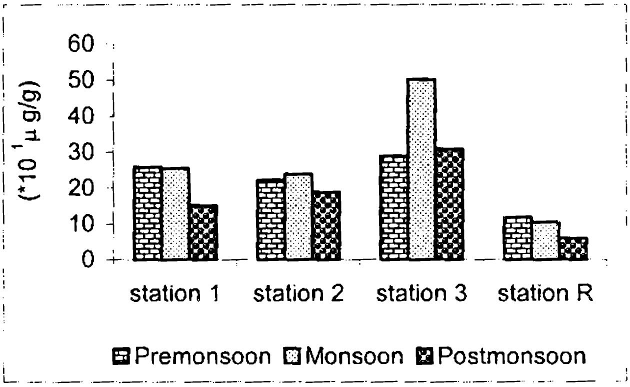


**Figure 5.20:- Seasonal mean variation of sedimentary manganese**

The enhanced levels of Mn in mangrove sediments compared to the estuary can be related to the environmental setting of the two systems. The muddy nature of the mangrove substratum can hold great quantities of metals onto them, and as Church and Scudlark (1998) have pointed out, metals were trapped as oxides at the surfaces and as sulphides below with limited sedimentary release in the marshes. However, more easily reduced element like Mn can be released to the tidal environment for export to the nearby estuary. Mn oxidation is accelerated by the presence of Fe oxides in the sediments. Since Fe was found to be present in huge quantity in these mangroves, precipitation of Mn as oxides is highly favoured.

The observed enrichment of Mn in the suspended particulate matter can be related to the reducing condition existing in the mangrove habitats. Unlike many metals, reduced species of Fe and Mn are more soluble than their corresponding oxides. Hence, under the anoxic condition, $Mn^{2+}$ ions may form in the sediment pore waters and may have diffused into the overlying water column. This could ultimately result in a reduction of the metal in the sediments. However, rooted plants and burrowing animals can affect the accumulation rate of trace metals as well as their distribution within the sediment (Vale and Sundby, 1994). In the intertidal regions, presence of plants slows down the currents and favours the settling of fine-grained particulate matter. This increases the accretion rate as well as the trace metal accumulation rate because of the higher specific surface area of the fine-grained materials. Like wise, much of the accreting matter consists of high content of plant debris enriched in metals.

In addition to this, presence of oxygen at the root-sediment and burrow-sediment interfaces creates local oxidizing condition in other wise reducing sediments. This affects in particular, the chemistry of Fe and Mn, the soluble reduced forms of which diffuse back to the interface, where they get precipitated as insoluble Fe and Mn oxides. Mn accumulates at the burrow interface as a result of intense decomposition processes in the burrow lining and mobilization of the metal from the adjacent sediments.

Mn showed high degree of positive correlation only with pH at station 1 (Table C.3). Here, dissolved oxygen was, though less significantly, inversely correlated with Mn. In the sediments, due to the intense reducing condition, pH is lower and Mn may have migrated to the overlying water column as $Mn^{2+}$. But at the surface, due to the presence of oxygen, pH is increased and the reduced species precipitated as Mn oxides. Mn was correlated well with organic matter at this station (Table C.12). However, at station 2, no such correlation was observed, yet, the clay fraction showed enrichment of the metal (Table C.3).

At station 1, Mn exhibited significant correlation with metals such as Co, Cr, and Ni (Table C.10) indicating that major adsorbing surfaces for these metals were the Mn oxyhydroxides. For the rest of the metals studied, Fe may have acted as the major carrier phase. Little affinity for organic matter was observed for Mn at this site. Cauwet (1987) observed no enrichment of Mn in the finer fraction of the sediment. However, at station 2, no such relations were noted. Thus at this site, Mn would have experienced different geochemical pathways than at station 1.

The riverine site exhibited highest annual mean concentration among all the sites. Seasonally, the monsoon period was associated with a concentration hike, while, the other two seasons exhibited lower, but similar concentration levels. Only during the monsoon season, sedimentary Mn concentrations were higher than the corresponding particulate metal concentration. Dissolved metal also was highest during this season. All these clearly point to the fact that the major source of Mn in this system is the heavy terrestrial runoff during the monsoon period. Since many industries are located on the banks of this river, effluents discharged from them may be the single largest source of this metal. Moreover, Mn did not exhibit any correlation with hydrographical parameters at this site. In a previous study by Joseph (2001) also a monsoon hike in Mn concentration was observed.

During the non-monsoon periods, suspended particulate matter showed greater Mn content than the sediments. Ramesh *et al.* (1990) also observed such enrichment in the suspended solids of the Krishna River, India. The suspended solids are finer and are richer in multiple hydroxide coatings (Forstner and Wittman, 1981), organics and trace metal scavenging clays. Thus particulates of most rivers may show metal enrichment relative to the sediment. Studies done on other Indian rivers confirmed the particulate matter enrichment of the metal (Biksham *et al.*, 1991, Subramianiam, *et al.*, 1987).

In this study, Mn showed high correlation with sedimentary organic carbon. Scholkovitz (1976) reported significant metal association with organic matter. This fact is further exemplified by Hunt (1981), who suggested that trace metal enrichment was dictated by total organic carbon content in sediments possibly through exchange reactions. Organic flocculent coatings also greatly affect the adsorption capacities for trace metals of sediments. A high degree of positive correlation observed between sedimentary organic carbon and the metal, is a testimony to this. Hung *et al.* (2000) have pointed out that humic substances present in river sediments have a high complexing capacity with Mn.

Metals like Zn, Cd and Pb correlated well with Mn at the riverine site (Table C.10). The affinity shown by these metals towards Mn clearly reflects the co-precipitation of these metals with Mn oxyhydroxides in the river environment. In a study by Morrison *et al.* (2001), Mn was found to be correlated with Fe, Zn and Cu and inversely with Pb. However, in this study, no correlation with Fe was observed. According to Ambatsian *et al.* (1997), important transformations are occurring for Mn in the surficial sediments than for Fe since Mn is easily reduced than Fe and a great part of Mn is dissolved in the first stage of diagenesis.

At the estuarine site also, postmonsoon season recorded the lowest concentration. This site showed much lower annual mean Mn concentration than the other three sites. Here, the range of sedimentary Mn was from 34.19 to 169μg/g. Premonsoon season recorded slightly higher values than the monsoon period. Since the particulate fraction was observed with maximum concentration in the postmonsoon season, resuspension of sediments might have occurred during this period resulting in a subsequent reduction in sediment metal concentration.

The major contributors of Mn to this estuary may be the rivers draining into it. Since sedimentation rates are faster in estuaries, metal-rich riverine suspended matter gets incorporated to the estuarine sediments. In addition to this, diagenetic enhancement of Mn in the surface sediments of estuaries is suggested (Zwolsman, *et al.*, 1993; Valette-Silver, 1993; Bricker, 1993; Spencer, 2002). With burial, microbial decomposition of organic material takes place resulting in bacterial utilization of oxygen and other inorganic oxidizing agents (Santschi *et al.*, 1990; Buckley *et al.*, 1995). The reduction of $Mn^{4+}$ species results in the mobilization of this metal and diffusion to oxic surface sediments where they get re-precipitated as oxides or occasionally as carbonates (Farmer and Lovell, 1984). As Finney and

Huy (1989) have pointed out, diagenetic recycling may contribute to enhancement of trace metal concentration in the upper surface sediments.

Because of the thinness of the oxidized layer, some of the upward diffusing Mn escapes to the water column. Particulate Mn is also removed from the surface sediments by periodic resuspension. The larger, fast settling particles, which mainly include the weakly enriched aggregates quickly re-deposit. The finer, slower settling particles stay in suspension and serve as nuclei for the auto-catalytic oxidation-precipitation of the dissolved Mn, which reaches the water column (Sundby and Silverberg, 1981). Chester *et al.* (1988) described this process as 'Mn trap'. Studies done on estuaries elsewhere also pointed to similar conclusion (Chen *et al.*, 2000; Chester *et al.*, 1990).

Among the hydrographical parameters, only dissolved oxygen exhibited any correlation with Mn (Table C.3). Here, dissolved oxygen varied inversely with sedimentary Mn. This clearly indicates the diagenetic enrichment of the metal in the sediments. Sedimentary organic carbon also displayed significant correlation with Mn (Table C.12). It has been reported that many metals are strongly complexed by organic ligands. Thus, metals may interact in solution with dissolved organic matter by the chelation or complexation processes and are, in turn, concentrated by adsorption onto fine particulates such as clay minerals (Piatina and Hering, 2000). In this study also, significant correlation with the clay fraction of the sediment was observed (Table C.3). Hence the process undergone by Mn in this estuary may be the oxidative precipitation and subsequent incorporation into the finer sediments.

The sediments were mainly sandy in nature at the estuarine sampling site. Furthermore, due to the high tidal activity, considerable dilution of the fluvial sediments with the marine sediments may also have taken place. Thus the dominance of sand, which is a poor-adsorber of trace metals and the dilution of the marine sediments might account for the general reduction in the metal content observed in this estuary.

### ➤ Zinc

Zinc is considered as a biologically essential element. It plays a vital role in the biosynthesis of nucleic acids, RNA and DNA polymerases. In the aquatic environment, Zn is enriched in the sediments. According to Moore and Ramamoorthy (1992), total Zn in freshwater sediments of uncontaminated areas is <50µg/g. A similar range was reported for estuarine and coastal areas. However, in the vicinity of industries, Zn concentration often exceeded 100µg/g.

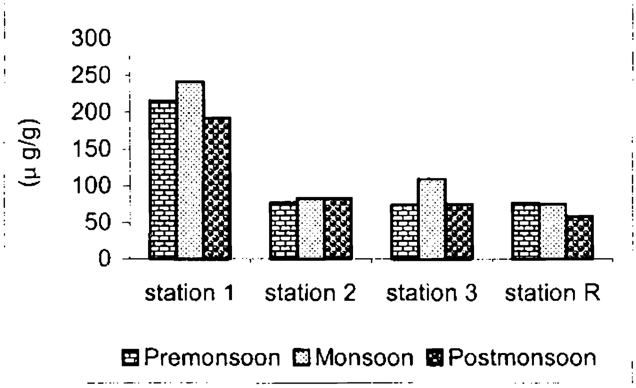


**Figure 5.21:- Seasonal mean variation of sedimentary zinc**

After Fe, Zn is the most abundant element in this study. This metal showed remarkably high concentration in the mangrove environment. The order of abundance of the metal in this study was, station 1 >> station 3 > station 2 > station R. At station 1, the concentration was as high as 362.98 µg/g. Monthly data showed Zn in the range 46.67 to 362.98 µg/g here (Table A.51). Seasonally also, Zn showed higher content in sediments than the other mangrove site (station 2) analyzed. Seasonal mean variation of dissolved zinc is depicted in Figure 5.21. Dissolved as well as the particulate concentration of this metal was quite high at this station indicating a point source of this metal. Contamination from petroleum storage tanks and cement storage facility located near the sampling site, may partly explain the elevated concentration of the metai in the sediments. Furthermore, sediments were collected from the vegetated area at station 1 and due to plant respiration and animal burrowing, local oxidizing microenvironments may be created in the sediment. Vale and Sundby (1994) have shown that Zn accumulates at the burrow interfaces as a result of intense decomposition processes occurring in the burrow linings and the mobilization of the metal from adjacent sediments.

Microbial degradation of the huge amount of organic matter in mangrove mud generally removes all oxygen from sediments below the surface layer, creating ideal condition for bacterial sulphate reduction (Berner, 1983). When photosynthetic oxygen production ceases in the night, hydrogen sulphide diffuses through the mud and escapes to the shallow water covering sediments (Hansen *et al.*, 1978). Metals dissolved in this water as free ions or metal-humate complexes are then deposited as sulphides (Pauli, 1975). Thus, incorporation into the sediments as metal sulphides may be another pathway for Zn in the anoxic environments. Moreover, many authors have opined that elevated metal concentration related with long-term pollution caused by human activities is recorded in mangrove sediments (Lacerda *et al.*, 1993; Mackay *et al.*, 1992; Mackay and Hedgkinson, 1995; Tam and Yao, 1998). Similarly, several studies (Harbison, 1986; Lacerda *et al.*, 1993; Tam and Wong, 1993, 1995) have shown that mangrove sediments have a high capacity to retain heavy metals from tidal water and therefore they often act as sink for heavy metals. The estuarine water flooding the mangrove sites was contaminated with Zn from the industrial effluents and hence adsorption of the metal from the tidal waters may also have contributed to the sediment metal concentration at station 1.

Seasonally, monsoon recorded peak concentration at station 1 and minimum was observed during postmonsoon period. However, at station 2, no significant seasonal variation was able to observe. At station 1, Zn exhibited higher concentration in all the three phases such as dissolved, particulate and sedimentary. This clearly indicates that leaching from 'Zn rich pockets' may be the reason for the elevated metal content at this site. At station 2, dissolved concentration was found to decrease as sedimentary metal increased. This may be due to the strong soluble complexes that Zn forms with reduced sulphur (Emerson *et al.*, 1983), which will increase the migration of Zn to the water column (Huerta-Diaz and Morse, 1992).

Dissolved oxygen was found to correlate inversely with Zn at station 1 (Table C.3). This may due to the increased precipitation of Zn as ZnS as dissolved oxygen diminishes. Salinity correlated negatively with Zn at station 2 and may be due to the dilution of the metal-rich sediment by the large quantity of incoming metal-deficient sediments in the monsoon runoff. Considering the relationship of Zn with other metals, highly significant correlations were seen between Zn and Fe, Cu, Co, Ni and Pb at station 1. Fe correlated positively, yet less significantly, at station 2. Ni showed positive correlation with Zn at this site also (Table C.10). These correlations point to the common geochemical processes undergone by these metals in the mangrove sediments. At both the mangrove habitats, Zn was enriched in the finer sediments to a considerable extent in this study (Table C.3). This may be due to the large surface area of the fine particles and due to the surface properties of clay minerals. Thus enrichment on fine particles shows the control of size over Zn concentration.

Zn concentration recorded in previous studies showed wide variations. In the study by Rini (2002), Zn varied from 43.56 to 940.46µg/g in the Vypeen mangroves; while, Badarudeen (1997) reported Zn in the range 15 to 91 ppm in the same area. In the Cauvery mangroves, Seralathan (1897) observed Zn to vary between 76-107ppm. However, studies done elsewhere showed much higher Zn concentration. In the mangrove sediments of southeast Gulf of California, Zn ranged between 46.4 to 347.8 mg/kg (Soto-Jimenez and Paez-Ozuna, 2001); whereas, Ong Che (1999) observed much higher Zn concentration in the Mai Po mangroves, Hong Kong. Here Zn varied between 148 to 513µg/g.

At the riverine site, Zn varied from 19.59 to 156.8µg/g with the peak concentration in the monsoon season. Non-monsoon seasons did not show much variation in concentration levels. The main source of Zn into this river may be the effluents discharged from various industries. Metal enrichment in the sediments can be related to the removal of the metal from solution by terrestrial organic matter, which eventually becomes incorporated to the sediment. Maximum concentration of the metal during the monsoon period may be the result of heavy influx of metal-rich particles associated with the runoff water. The increased amount of particulate matter along with suspended sediment load brought into the river may have settled at a faster rate enhancing the sediment metal concentration. Lower concentration during the summer period may be the result meagre terrestrial runoff. Positive correlation with the dissolved and sedimentary metal concentration also augmented this possibility.

At this site, Zn showed enrichment in sediments relative to the particulate matter only during the monsoon period. In the non-monsoon periods and especially during the postmonsoon season, Zn showed high concentration in the particulate fraction. In the suspended sediments of the Godavary River, India also, Biksham *et al.* (1991) found that Zn was enriched in particulates by a factor of 3-15 times than the bed sediments. They have related this to the finer nature of the suspended particles with multiple hydroxide coatings, which can efficiently adsorb metals. Sediment resuspension may partly explain the elevated particulate metal concentration in this season.

Zn exhibited high correlation with organic matter at this site (Table C.12). Sediment humic substances have high ability to complex with metals. According to Hong *et al.* (1994), Zn has moderate binding capacity with humic and fulvic acids and they observed that 93-98 percentage of Zn was complexed by organic matter in the interstitial water as a result of high ligand concentration. None of the hydrographical parameters exhibited correlation with the metal indicating its anthropogenic source (Table C.3). Zn showed highly significant positive correlation with Cd and Pb at this site. Since neither these two metals have a biogenic origin, association of Zn with them points to the anthropogenic source, presumably industrial effluents.

In a study on the modern deltaic sediments of the Cuavery River, Seralathan (1987) found that Zn was highest at the river channel rather than in the tidal channel, swamps or marine sediments. Here, Zn varied between 80-170 ppm. However, in the Vellar River, concentrations were lower than that of the estuary (Mohan, 1997). Joseph (2001) reported Zn in the Chitrapuzha river sediments in the range 137.89 to 352.1mg/kg.

At the estuarine site, Zn recorded the highest concentration among all metals studied except Fe. Zn ranged from 47.64 to 106.1µg/g with an annual mean value of 70.01µg/g. The minimum concentration was recorded during the postmonsoon season, while the monsoon and premonsoon periods exhibited almost similar concentration ranges. Zn was found to be present in higher concentration in the estuarine sediments than the river sediments (Mohan, 1997). In the present study, except for Zn, the river sediments were found to be enriched with all other metals relative to the estuarine sediments. The high concentration of Zn in the estuary can be related to the precipitation of Fe and Mn hydroxides to which Zn is adsorbed, which are high in the estuarine environment than in the river.

Zn exhibited significant correlation with Mn at this site (Table C.10). This indicates its probable association with Mn hydroxide in the transport to the estuary and co-precipitation with the hydroxide therein. The major source of sedimentary Zn in this estuary may be the rivers draining into it. Various chemical industries and in particular, a Zn refining factory is located on the banks of the Periyar River, which drain into this estuary. In addition to this, emanations from boats and ships are other possible source for Zn. The sacrificial anodes made up of Zn and the zinc chromate paint used in boats both may be significantly contributing to the Zn pool of this estuary. The low seasonal variation also points to this consistent source. Resuspension of sediments in the postmonsoon season may have facilitated desorption of the metal from the sediment and subsequently, increased the particulate metal levels. The enrichment of the metal in the particulate matter relative to sediments is a testimony to this.

Among the hydrographical parameters, dissolved oxygen showed a negative relationship with Zn (Table C.3). This indicates the increased precipitation of the metal as sulphides as dissolved oxygen level decreases. Zn was found to be correlated neither with the organic matter nor with the finer fraction of the sediment at this site. Therefore, diagenetic enrichment may not be feasible for this metal and thus, points to the purely anthropogenic sources.

In a study by Krishnakumar *et al.* (1998) Zn showed a concentration value of 68.8μg/g in the sediments collected from the vicinity of a chemical and fertilizer factory. In the Beypore estuary, Kerala, enrichment of Zn towards the bar mouth of the estuary was observed. Here, Zn varied between 25 to 75 ppm. In a previous study on the Cochin estuary, Joseph (2001) reported Zn in the range 23.52-271.25mg/kg. The present observations were in line with those reported in earlier studies.

## ➢ Copper

In the aquatic environment, copper occurs in many organic and inorganic forms. After entry into the aquatic system, Cu may remain dissolved or adsorbed onto particulates, sink to the sediments or be absorbed by organisms. Sediments are regarded as an important sink for the removal of Cu. Excess Cu from the water may get adsorbed onto particulates and settle to bottom sediments. If water is depleted of the metal, the adsorbed Cu may re-dissolve or desorb to increase its concentration in the interstitial waters. Thus sediments are involved in determining the fate of Cu in the aquatic environment.

Cu, in this study, exhibited comparable concentration in the mangrove and riverine locations, whereas the estuarine sediments recorded remarkably low concentration. Seasonal distribution of the metal too was quite unique for each site (Figure 5.22). Mangalavanam (station 1) displayed Cu in the range 4.780-52.38µg/g, while, the other mangrove site, the 'Fisheries' station recorded Cu in the range, 12.10-30.93µg/g. Chitrapuzha, the riverine site showed Cu in the range 3.848-40.49µg/g, whereas in the estuarine sediments Cu varied from 3.357-16.00µg/g (Table A. 52). The highest annual mean concentration was recorded at station 1 closely followed by station 3 and station 2.

Among the two mangrove habitats analyzed, station 1 was found to have high sediment Cu content than station 2. Seasonal distribution was different for the two stations. Monsoon season was characterized by peak concentration at station 1 and with a minimum in the postmonsoon period. However, at station 2, such distinct seasonal variation was difficult to observe. Slightly higher values were seen during the postmonsoon period.

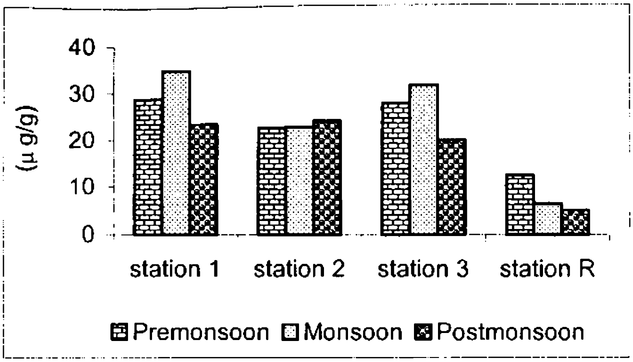


**Figure 5.22:- Seasonal mean variation of sedimentary copper**

Forstner *et al.* (1989) observed Cu to be present in large quantity in sediments in the anoxic condition than in oxic condition. In the anoxic sediments sulphides of Cu are found to be more stable (Haraldson and Westerlund, 1988). Tam and Wong (1996) have further shown that sulphide precipitation is very important in mangrove sediments. Low redox potential in the mangrove sediments indicates the presence of significant quantities of $H_2S$ that precipitates metals in insoluble sulphide forms (Huerta-Diaz and Morse, 1992). Hence the elevated Cu concentration in the mangrove sediments may be due to the increased precipitation of the metal as insoluble sulphides.

At both the sites, Cu exhibited an inverse relationship with dissolved oxygen (Table C.3). This clearly shows precipitation and incorporation of Cu into sediments. In the mangroves, oxygen is used up by the microbial community for the remineralization of organic matter eventually resulting in oxygen depletion in the sediments, creating ideal condition for bacterial sulphate reduction (Berner, 1983). The metal in this reduced environment may combine with sulphides forming stable metal sulphides. The simultaneous decrease in dissolved Cu may be an indication of its association with particulates and subsequent settling to sediments as Cu sulphides with decrease in dissolved oxygen levels. Haraldson and Westerlund (1988) also observed a rapid decrease in dissolved Cu in the anoxic zones of the Black Sea and Fram Varren fjord, Norway. However, at station 2, pH was found to be influencing Cu concentration (Table C.3).

At both the mangrove habitats, Cu did not show any significant correlation with sedimentary organic carbon (Table C.12). Such behaviour was reported earlier in the anoxic condition for Cu (Haraldson and Westerlund, 1988; Seralathan, 1987). They have reached in the conclusion that all organic compounds are not capable of complexing with Cu and that therefore total organic carbon measurements cannot be a good indicator of Cu complexing capacity. Another reason may be the non-availability of traces for concentration for Cu due to the presence of huge amount of organic matter in the mangroves. Sediments can be exposed to continuous disturbances such as bioturbation and resuspension, which can mark changes over small time span. Thus the non-correlation with sedimentary organic carbon may indicate other anthropogenic sources of this metal (Helland *et al.*, 2002). Cu was found to be enriched in the finer fraction of the sediments in this study (Table C.3). Excellent correlation with finer components of the sediments points to the increased adsorption of the metal facilitated by the greater surface area of the particles.

Cu exhibited remarkably high correlation with other metals such as Fe, Zn, Co and Pb at station 1 (Table C.10). However, at station 2, significant correlation was observed only with Cr. High correlation with Fe indicates that Cu is associated with Fe oxyhydroxides rather than Mn hydroxides. Shaw *et al.* (1990) pointed out that Cu is enriched in the sediments by transport with detrital biogenic material followed by adsorption onto sediments. Zn also is reported to have a biogenic origin. The excellent correlation exhibited by both the elements (Table C.10) reflects that they have a common source in these mangroves. Since at station 2, Cu correlated only with Cr, Cu can have other sources such as anthropogenic inputs.

In this study, particulate fraction showed higher concentration than the sediments. Thus, it can be inferred that Cu is enriched in the particulate matter rather than the sediments in these mangrove environments. The intense bioturbation occurring in the mangroves changes the chemistry of the sediments significantly. Animals can manipulate the sediment texture as they burrow into them. Substantial amount of particulate matter is created when they feed or burrow. Thus the observed depletion of Cu in sediments can be related to the bioturbative or bio-irrigative processes operating in the mangroves.

The concentration of sedimentary Cu reported in this study was much lower than those reported earlier. Badarudeen (1997) reported Cu in the range 15-91ppm in Cochin mangroves. Cu, in the Brazilian mangroves ranged from 18-80µg/g (Machado *et al.*, 2002), whereas the Mai Po mangroves, Hong Kong, recorded Cu in the range 51-87µg/g. In a study by Seralathan (1987) on the Cauvery mangroves, Cu was found to vary in a small range, i.e., from 70 to 78 ppm.

In the river sediments, Cu varied from 3.848 to 40.49µg/g. Here, the monsoon period was characterized by the highest concentration and the minimum was recorded during the postmonsoon season. The main source of Cu in this river may be the industrial effluents. Use of Cu as catalyst in many industrial processes result in large inputs of the metal into the aquatic environments (Moore and Ramamoorthy, 1992). Since Cu is an efficient biocide, urban runoff may also contain high metal content.

At this site also, Cu was found to be enriched in the particulate fraction. This might be due to the resuspension processes occurring in this season. Since the maximum concentration was observed in the rainy season, the main source of Cu into this system may be the runoff water. The heavy influx of freshwater might have leached the metal-rich particles from the effluent discharge points elevating the metal load in the monsoon season. During the summer season, stream flow is greatly reduced and during this season, the riverbed may absorb trace metals discharged from untreated/partially treated domestic and industrial wastes. Immediately after the heavy rain, trace metals from the river sediments are released to the overlying water by resuspension and discharged to the estuarine environment. The presence of higher Cu concentration in the particulate fraction during the non-monsoon period may be the result of the resuspension process. Biksham *et al.* (1991) also found enrichment of Cu in the suspended sediments of the Godavary River, India, by a factor of 2-4 times than the bed sediments. He has related this to the finer nature of the sediments, which are rich in multiple hydroxide coating thus facilitating increased metal adsorption.

Cu, at this site, showed remarkably high correlation with sedimentary organic carbon and with the silt and clay fraction of the sediment (Table C.3, C.10). Humic materials of freshwater are reported to bind >90 percentage of dissolved Cu, whereas those in seawater bind only 10 percentage of total Cu (Mantoura *et al.*, 1978). According to the Irwing-Williams series, Cu shows highest affinity for humic substances except Hg. Forstner *et al.* (1989) have further shown that Cu complexation with organic matter has a dominant role in the transfer of the metal to biologically inactive form. The strong correlation with the muddy fraction reflects the increased adsorbing capacity of the clay mineral particles (Table C.3). In the Vellar River, Mohan (1997) observed higher Cu content in the river than the estuary and related this to the high amount of fine sized particles.

Among the hydrographical parameters, only pH correlated with Cu at this site (Table C.3). Complexation with humic substances was found to be highly pH dependent, and in addition to this, sedimentary organic carbon also was found to have good positive relation with Cu (Table C.12). Thus, with increasing pH, adsorption of Cu onto humic substances might have increased. Cu exhibited correlation with Fe, Co and Ni in this river indicating a common source of these metals (Table C.10). Association with Fe indicates that Cu may have co-precipitated with Fe oxides rather than with Mn oxides.

The estuarine sediments showed remarkably low Cu concentration. Here, the premonsoon season recorded the maximum concentration and the minimum was observed during the postmonsoon period. Considerable dilution of the metal-rich fluvial sediments by the metal-deficient marine sediments might have occurred reducing the metal content. The sand dominance of the substratum can also be a reason for the low metal content. Sand particles are well known for their poor capacity to hold metals onto them and hence, even though flocculation of Fe and Mn oxides, to which Cu is preferably attached, occur in the estuary, they are exported to the sea by waves and currents. Another reason for the general reduction of the metal in estuaries is desorption of the metal adsorbed onto clay minerals when river water mixes with seawater. In a study by Helland (2001) in a micro tidal estuary, only a small amount of Cu was associated with particles and settled out. The low entrapment of the metal suggested that bulk of the metal stayed complexed, probably with humic substances and was transported out of the estuary.

Cu finds its way to this estuary mainly through anthropogenic inputs. Cu is used as a catalyst in many industrial processes, which has led to large inputs of Cu into the marine environment. Relatively high concentration of Cu was observed in the sediments collected from Thannirbavi River, Mangalore, from the vicinity of effluent discharge point of a chemical and fertilizer factory (Krishnakumar *et al.*, 1998). Since various industries release their effluent load directly or indirectly to the Cochin estuarine system, Cu contamination is indeed possible. In addition to this, since Cu is an efficient biocide, it is used as antifouling paints in boats and ships. The intense boat traffic in the estuary may also have contributed considerable amounts of Cu to the estuarine sediments. The observed non-correlation of the metal with hydrographical parameters also points to its anthropogenic sources.

At the estuarine site, Cu was positively correlated with organic carbon and with the finer fraction of the sediment (Table C.12, C.3). Cu is well known for its complexation capacity with organic compounds especially with humic substances. According to Moore and Ramamoorthy (1992), among the humic substances of different origin, marine sedimentary humic and fulvic acids have the greatest ability to form stable complexes with Cu. Another possible mechanism for this observed co-variance is the exchange reactions between clay minerals and the metal ions. Organic flocculent coatings on sediment particles also greatly affect the adsorption capacity for trace metals. Thus, metal association of sedimentary organic carbon suggests strong interaction of the metal ion with organic matter, which, in turn, is further concentrated by adsorption onto clays. Such a close relationship of Cu with total organic carbon was reported by many authors (Qu and Kelderman, 2001; Piatina and Hering, 2000; Monterrosso *et al.*, 2003; Fan *et al.*, 2002; Nair and Ramachandran, 2002; Li *et al.*, 2001; Wang *et al.*, 1997; Fu *et* al., 1992).

Cu, in this estuary, exhibited significant positive correlation with Fe, Co, and Cd (Table C.10). Correlation with Fe points to the association of the metal with Fe oxyhydroxides. Significant correlation with other metals indicates that there may by common sources or at least one single major source of these metals in this estuary. In a previous study by Joseph (2001), Cu was reported to vary from 11.8 to 37.09 mg/kg in the Cochin estuary. These values were higher than those in the present study. However, in the Beypore estuary, Kerala, Cu ranged from 2-17ppm (Nair and Ramachandran, 2002).

## ➢ Cobalt

Cobalt is an essential element to biological systems and is also toxic at quite low concentrations (Ghatak *et al.*, 2002). Anthropogenic input of Co is through the usage of fertilizers and the deposition pattern indicates enrichment in soils (Young, 1979). In this study, Co recorded highest annual mean concentration at station 2, the mangrove site. The order of abundance of the metal was station 2 > station 3 > station 1 > station R. Generally, estuarine sediments was characterized by low metal content. Seasonally, monsoon period was observed with maximum concentration at the river and mangrove sites (Figure 5.23). Premonsoon period recorded the highest concentration at the estuarine site. Except at station 2, minimum concentration was observed during the postmonsoon period.

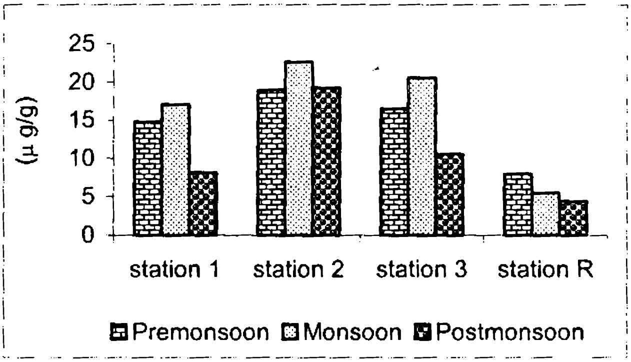


**Figure 5.23:- Seasonal mean variation of sedimentary cobalt**

In the present study, the mangrove sediments were characterized by high Co content. Of the two mangrove habitats, the 'Fisheries station' (station 2) recorded higher concentration. Co varied from 12.44 to 26.30μg/g at this site, whereas at station 1, a wider range was observed (4.630-23.01μg/g) (Table A.53).

Mangrove ecosystems have the capacity to act as sink or buffer and remove or immobilize trace metals before they reach nearby aquatic environments (Harbison, 1986). Because the sediments have a high proportion of fine particles, high organic content and low pH, they effectively trap trace metals often by immobilizing them in the anaerobic sediments either by adsorption on ion exchange sites of sediment particles, incorporation into lattice structures of the clay particles or precipitation as insoluble sulphides (Harbison, 1986; Macfarlane and Burchett, 2001). Mangrove ecosystems, although possessing enormous ecological and commercial importance, are often subject to effluent discharges, urban and agricultural runoff and solid waste dumping, due to the proximity to urban development (Macfurlane, 2002). Since Co has a significant anthropogenic origin elevated concentration observed in the mangroves may be due from the runoff waters.

Microbial degradation of the high content of organic matter in mangrove muds generally removes all oxygen from sediments below the surface layer, creating ideal condition for bacterial sulphate reduction (Berner, 1983). Metals dissolved in this water as free ions or as metal-humate complexes are then deposited as sulphides. Co showed significant negative correlation with dissolved oxygen at both the mangrove habitats. This clearly shows the reductive precipitation of the metal. As dissolved oxygen decreases, $H_2S$ production is enhanced facilitating the precipitation of the metal as sulphides.

Ghatak *et al.* (2002) have shown that humic substances play an important role both in the inactivation of toxicity and the mobilization/immobilization process of Co. They have also found that fulvic acid-Co complexes are much stable than the humic acid-Co complexes. Since humic substances were found to be present in great concentrations in the mangroves, Co may have got associated with them. The highly significant positive correlation observed between the metal and organic matter in the present study also indicates the metal-humic acid complexation in the sediments (Table C.12). At station 1, Co exhibited significant positive correlation with almost all the metals studied. This shows their common sink in the sediments. However, at station 2, Co displayed correlation only with Pb indicating the anthropogenic source of the metal at this site.

During the monsoon period, both the sites recorded maximum concentration indicating that the main pathway for the metal was through the runoff water. The finer sediments brought in by the heavy influx of freshwater may have got trapped in the tangled network of mangrove roots thus elevating the net metal concentration. At station 1, sediments recorded lowest concentration during the postmonsoon period, whereas the particulate metal concentration was highest during the same period. Resuspension processes may be the reason for this depletion of metal in this period. However, no such particulate matter enrichment was observed at station 2.

At the riverine site, Co varied from 3.341μg/g to 24.90μg/g. Monsoon period showed highest concentration and the minimum was observed in the postmonsoon season. Here, Co was found to be highly enriched in the finer sediments and organic carbon also showed positive correlation with Co (Table C.3, C.12). Both these observations clearly point to the association of Co with complexing polymeric molecules such as humic substances. Ghatak *et al.* (2002) also observed high affinity of Co for humic complexes. Another significant source of Co may be the industrial effluents.

Among the hydrographical parameters, only pH was found to have any influence on Co distribution (Table C.3). Metal-humic acid complexation is largely influenced by the change in pH (Moore and Ramamoorthy, 1992). Co, that may be associated with Fe and Mn oxides, is also found to precipitate at higher pH. Moreover, co-precipitation of Co with Fe and Mn oxides is reported (Zhang *et al.*, 2002; Hamilton-Taylor *et al.*, 1999; Lienemann *et al.*, 1997; Moffett and Ho, 1996; Ozturk, 1995; Balistrieri *et al.*, 1994; Shaw, *et al.*, 1990; Jacobs *et al.*, 1985). Thus the covariation of Co with pH may either be due to its complexation with sedimentary humic substances or due to increased precipitation of Fe and Mn oxides. In contrast with most of the metals studied, Co did not show any preference for the particulate matter at this site. Hence, it could be inferred that Co that may have entered the system either in the soluble or particulate form were rapidly incorporated to the sediment with limited release from them.

In this study, Co showed positive, though less significant correlation with Fe. However, highly significant correlation was observed with Cu and Ni (Table C10). Thus the close linear relationship between these metals points to their common fate in this aquatic system.

In the estuarine sediments, Co was present in very low concentrations ranging from 2.256 to 11.90μg/g. Premonsoon season was characterized by a concentration hike, while a minimum was observed during the postmonsoon period. A general decrease in Co concentration at the estuarine mouth was reported by Seralathan (1987) in the Cauvery delta sediments. He has related this general decrease to the desorption of Co, which may be concentrated in freshwater clay minerals or as due to the partial removal of the element from Fe and Mn oxides. However, a contrasting behaviour of Co was reported in the Vellar estuary (Mohan, 1997). Here, Co showed high content in the estuarine sediments than the river sediments.

Seasonally, Co exhibited highest concentration in the premonsoon period. This may be due to the increased co-precipitation of the metal with Fe and Mn oxyhydroxides, with increasing seawater cations. A corresponding decrease in the particulate metal concentration was also observed during the same period. In addition to this, Co co-varied with Fe. Considering all these facts, it can be inferred that Co was mainly associated with Fe oxides and hydroxides, which would have get precipitated with increasing salinity. Association of Co with Fe was observed in the Chennai estuaries, east coast of India, in a study by Achyuthan *et al.* (2002). In the present study, the observed reduced metal levels in the postmonsoon period can be due to the resuspension process occurring in the estuary. Particulate metal concentration showed a hike during this period augmenting the possible resuspension process.

The general lower concentration of the metal in the estuary can be due to the sandy nature of the substratum. However, Co was enriched in the clay fraction of the sediment and though less significantly, the element correlated positively with organic matter. The co-variance of Co with metals like Cu and Ni indicates their similar fate in the estuarine sediments.

Co varied from 11 to 35 ppm in the Beypore estuary, southwest coast of India, in a study by Nair and Ramachandran (2002). Joseph (2001) reported Co concentration in the range 6.7 to 20.92 mg/kg in the Cochin estuary. Co was found to vary from 3 to 12 µg/g in the sediments of Gulf of Mannar, India (Jonathan and Ram Mohan, 2003). The concentration of Co observed in the present study was similar to that reported earlier.

## ➢ Chromium

Chromium chemistry in aquatic environments is complex since many individually or simultaneously occurring reactions or processes can affect its chemical behaviour. Important among these are oxidation-reduction, precipitation or dissolution of a solid phase, adsorption or desorption of Cr in saline water, chemical speciation and biological interactions. The equilibrium tendencies of all these reactions regulate concentration and chemical behaviour of Cr in aquatic systems. Irrespective of the scavenging processes, sediments are considered as the ultimate sink for Cr in the aquatic systems (Sadiq, 1992 a).

Cr concentrations showed wide variations in each of the aquatic systems analyzed. The highest annual mean concentration was recorded in the mangrove sediments (station 2). Station 1, which is also a mangrove site and the river sediments recorded similar concentrations, while the estuarine sediments exhibited much lower Cr content. The order of abundance of the metal was station 2 > station 3 > station 1 > station R. Seasonal variation of dissolved chromium is depicted in Figure 5.24.

At Mangalavanam (station 1), Cr varied from 23.65-96.65µg/g whereas at station 2 (Fisheries station), the concentration range was 40.83 to114.8µg/g. River sediments showed Cr content in the range 26.93-117.94µg/g, while, Cr ranged from 22.97 to 48.70µg/g in the estuary (Table A.54). Seasonally, premonsoon season was characterized by highest Cr content at all stations except at station 2. Here, postmonsoon period recorded the highest concentration. Sedimentary Cr showed lowest metal concentration during the monsoon period in both the river and estuary. At Mangalavanam (station 1), minimum concentration was observed in the postmonsoon season while, the monsoon and premonsoon seasons showed very slight variation at station 2. ANOVA calculations also showed highly significant variation between the stations (Table B.8).

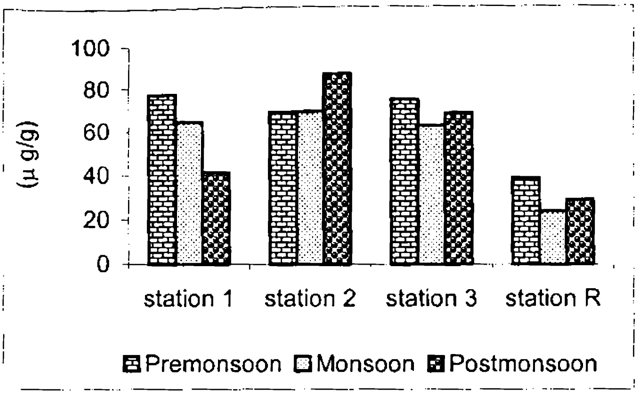


**Figure 5.24:- Seasonal mean variation of sedimentary chromium**

One of the most important factors for determining the valence state of Cr in natural waters is the oxygen content and redox potential of water. Concentration of Cr (III), which is the insoluble form, increased rapidly under reducing conditions (Florence and Batley, 1980). Concentrations of total dissolved Cr and Cr adsorbed on particles both reduced rapidly at the $O_2$-$H_2S$ interface (Emerson, 1979). Annual mean concentration was higher at station 2 than at station 1 among the mangroves. Since sampling was done in the vegetated area at station 1, interactions of fine roots of plants would have altered the sediment chemistry by creating oxic microenvironments. In this condition, Cr (III) is rapidly oxidized to the soluble form. Since intense anoxic conditions existed in the bulk sediments collected at station 2, Cr would be preferably remained in the sediments. Amdurer *et al.* (1983) have further shown that the residence time of $Cr^{3+}$ is much lower than $Cr^{6+}$ in the water column and is therefore, gets rapidly incorporated into the sediments.

Cr exhibited excellent correlation with pH at station1 (Tale C.3). Cr was found to be correlated well with organic matter also (Table C.12). These correlations point to the association of Cr with humic or fulvic acids, which are the dominant fraction of the sedimentary organic matter. Cr (III) is strongly sorbed on humic acids and the adsorption increases with increasing pH of the media. In the present study also pH was found to have high influence on Cr distribution (Table C.3). Cr also showed high correlation with Mn at this site (Table C.10). This indicates association of Cr with Mn hydroxides. In a study by Ong Che (1999) in the mangroves of Mai Po, Hong Kong, Cr showed highly significant correlation with Mn. This was attributed to the diagenetic processes associated with Mn, which mobilized a significant fraction of Cr. Co-variance of Cr with other toxic metals like Ni and Cd shows the similar geochemical processes undergone by these metals.

However, station 2, even though a mangrove site, presented a completely different picture. Cr exhibited poor correlation with organic matter, yet, it was enriched in fine sediments. Correlation with pH was also found to be less significant, although positive. Cr showed an inverse relationship with Mn. Velde *et al.* (2003) also observed non-correlation of Cr with Mn in the American and French salt marshes. This can be related to the redox nature of Cr. $Cr^{6+}$ is easily reduced by dissolved ferrous sulphides and by certain organic compounds with sulfhydryl groups. In contrast to this, $Cr^{3+}$ is oxidized rapidly by a large excess of $MnO_2$. Since Cr (VI) is the soluble form, with increasing Mn, release of sediment bound Cr (VI) may also have enhanced.

In the river, Chitrapuzha (station 3), Cr varied from 26.93 to 117.94µg/g. Here, postmonsoon season recorded the maximum concentration, while monsoon exhibited lowest metal content. Cr has wide industrial applications and is extensively used in plating industry and in paints. Hence the enormous quantity of the metal reaching the aquatic environment finally settles in the sediments. Apart from this industrial sources, municipal wastewaters release considerable amount of Cr (Moore and Ramamoorthy, 1992). In freshwaters, anthropogenically introduced soluble Cr (VI) is removed by reduction to Cr (III) and is precipitated. Hence, Cr is transported in rivers primarily in the solid phase. The premonsoon season recorded the maximum concentration of Cr at this site. During summer, when stream flow is considerably reduced, effluents from industries are released without much treatment to the river. The river sediments act as the ready reservoir for these effluents and accumulate large quantity of the metal in the sediments. The observed non-correlation of Cr with hydrographical parameters also points to its anthropogenic source (Table C.3).

Of the metals studied, Cr was the only one, which showed no significant correlation with any other metal indicating the distinctly different geochemical processes undergone by the metal. The dissolved fraction of the metal was found to increase as the sedimentary concentration diminished. This can be due to the differential solubility of the element in different chemical environments. Cr did not show any affinity either towards organic matter or to the finer sediments.

At the estuarine site, Cr ranged from 2.35 to 48.70μg/g. Comparing with other aquatic systems under study, estuarine sediments showed much low Cr content. In fact, the concentrations were half of that observed at the river site. The general reduction in concentration can be attributed to the nature of the substratum and the hydrodynamic features of the area. The sand particles dominant in the estuarine sediment show little affinity for trace metals and due to the high tidal activity dilution by metal-impoverished marine sediments were also possible.

Seasonally, premonsoon recorded the highest concentration, while the minimum was observed during monsoon. Cr was found to be associated with Fe and Mn hydroxides. Many authors have pointed out the transport of the metals associated with these hydroxides in freshwaters (Velde *et al.*, 2003; Seralathan, 1987; Mohan, 1997; Nair and Ramachandran, 2002). Flocculation and subsequent precipitation of these hydroxides in the estuarine environment was found to increase the concentration of the adsorbed metals also (Evans and Cutshell, 1973). Among the hydrographical parameters, both salinity and temperature showed significant positive correlation with Cr in this study (Table C.3). This clearly shows the increased precipitation of Fe and Mn hydroxides to which the metal is attached with increasing salinity. Cr exhibited high correlation with organic matter and with the fine sediment fractions. Apart from the surface area related enrichment of the metal, cation exchange capacity of sediments and affinity of metal ions for different types of clay minerals also contribute substantially to the metal-fine fraction proportionality of sediments.

The higher concentration observed during the non-monsoon period may be due to the increased adsorption of the metal to the particles facilitated by the longer residence time of the particles in the water column. Because of its industrial applications, anthropogenic inputs, especially from industrial effluents, are regarded as the major contaminant source of Cr in the marine environment (Nriagu and Nieboer, 1980). Since many industries are located near the estuary, contamination from the effluent discharges is a distinct possibility. Moreover, municipal wastewaters are reported to contain substantial portions of Cr (Moore and Ramamoorthy, 1992). Thus considerable amount of Cr found in this estuary could be traced to the effluent and sewage discharges. Apart from these sources, leakages from boats may also introduce Cr to this estuary since the paints used in boats have high Cr content.

### ➢ Nickel

Nickel is not a wide spread or significant contaminant of most freshwater and marine sediments (Moore and Ramamoorthy, 1992). Ni enrichment of nearshore sediments reflects anthropogenic inputs from industrial and municipal discharges and other sources such as urban storm water run off and sludge disposals.

In this study, Ni exhibited highest annual mean concentration in one of the mangrove environments. The lowest Ni concentration was observed in the estuary. At station 1, Ni ranged from 8.224 to 71.15 μg/g, whereas station 2, which is also a mangrove habitat, recorded much high level. Here, Ni varied from 40.61 to 86.82μg/g. The polluted river sediments showed Ni in the range 13.21 to 73.44μg/g and in the estuarine sediments, Ni was found to vary from 9.101 to 31.10μg/g (Table A.55).

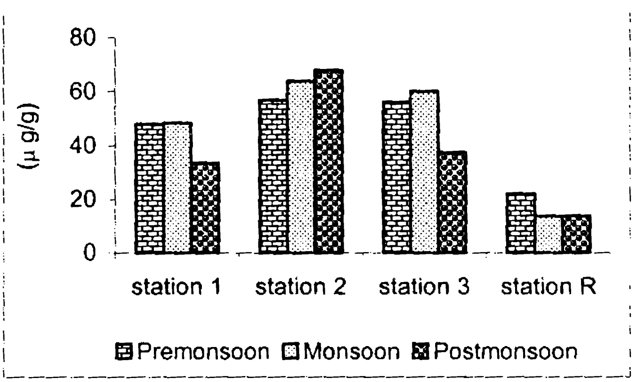


**Figure 5.25:- Seasonal mean variation of sedimentary nickel**

Of the two mangrove habitats, station 2 showed distinctly higher Ni content than station 1. Seasonally, the two stations behaved quite differently. Postmonsoon season recorded lowest concentration at station 1, while at station 2, this season showed the maximum concentration. The monsoon and premonsoon seasons showed little variation in Ni content at station 1. During the premonsoon period, Ni concentration in the sediments was lowest at station 2 (Figure 5.25).

Sediments are known to accumulate metals in several orders of magnitude more than water. Only very small amounts of metal are bio-available to plants, and in the mangroves, a large proportion is precipitated as sulphides in the sediments. Due to the enormous load of organic matter in the mangroves and the intense microbial degradation often result in permanent anoxic condition in the mangroves. Reduced sediments are found to accumulate more Ni (Lacerda and Abrado, 1984; Lacerda *et al.*, 1991). Dissolved Ni is also found to decrease under anoxic condition (Lu and Chen, 1977). $Ni^{2+}$ ion is found to form stable complexes with organic and inorganic ligands. Inorganic complexing ligands include halides, sulphates etc. Organic ligands with oxygen, nitrogen, and especially sulphur donor atoms form strong complexes with Ni (Moore and Ramamoorthy, 1992). Due to the intense sulphate reduction occurring in the mangroves, $H_2S$ is released from the sediments and Ni forms strong complexes with the sulphides (Tam and Wong, 1996; Huerta-Diaz and Morse, 1992). Precipitation of Ni as sulphides may be the reason for the observed high concentration of Ni in the mangrove sediments.

Ni was found to be enriched in the humic and fulvic acids and in a study by Nriagu and Coker (1980), 10 percentage of the total Ni was bound to the organic matter. According to Moore and Ramamoorthy (1992), complexes of Ni with humic or fulvic acids are of moderate stability. Since, humic substances were abundant in the mangroves under study, complexation with them would have increased the Ni content in the sediments.

Among the hydrographical parameters, Ni showed significant positive correlation with pH, while, dissolved oxygen showed an inverse, though less significant correlation (Table C.3). Complexation of Ni with humic or fulvic acids are found to increase with pH. At both the sites Ni showed highly significant correlation with organic carbon also. Thus, complexation with sedimentary humic substances may partly explain for the elevated metal content at this site.

Ni exhibited significantly high correlation with Mn and Co and moderately strong relationship with Fe, Cr, and Cu at station 1 (Table C.10). Good correlation with Ni and Mn was reported earlier (Luminez and Paes-Ozuna, 2001). They related this association to the peculiarities in Mn cycling. When reducing conditions are dominant as in the mangrove sediments, soluble Mn is the dominant form migrating through the pore water to the overlying water column. When oxidizing conditions predominate, Mn is present in solid form, which is retained in the sediment column. Thus, the resuspension-deposition pattern of Mn affects the mobilization of other metals (Shaw *et al.*, 1990; Huerta-Diaz and Morse, 1992). Correlation with other metals denotes the common sink for these metals in the mangrove sediments. Several authors (Forstner and Wittman, 1981; Sing and Subramanian, 1984) have reported the role of sediments as the sink for trace metals. However, at station 2, Ni showed significant correlation only with Zn and moderately with Cu.

Seasonally, station 1 recorded lowest concentration during the postmonsoon period. Resuspension of fine sediments, which are rich in metals, may be the reason for this low metal content in the sediments. Intense reducing condition, facilitated by the increased rate of evapo-transpiration during the summer periods would have resulted in elevated concentration of the metal in the premonsoon season. However, this trend was reversed at station 2. Here, postmonsoon season recorded the maximum concentration and premonsoon, the minimum. The finer fraction of the sediment brought in by the monsoon runoff starts to settle in the quieter postmonsoon period in the creek waters resulting in elevated metal concentration. Ni is found to have affinity for inorganic ligand like $Cl^-$ (Moore and Ramamoorthy, 1992). In the premonsoon season, as the chloride concentration increases, sediment-bound Ni is released as they form chloride complexes.

In a study by Saifulla *et al.* (2002) on the mangrove sediments of the Indus Delta, Ni concentration in the sediments was very high (48.3 to 71.2µg/g) when compared to the water. They have attributed the high concentration in sediments to the clayey loam texture of the sediments with relatively high silt and clay fraction, which are known to bind heavy metals. However, in the mangrove sediments of the Cauvery Delta, Ni varied from 85 to 156 ppm. Ni, in the mangrove sediments elsewhere, showed wide variation in concentration. In the Mai Po mangroves, Ni was present in the range 44-87µg/g (Ong Che, 1999) whereas the Brazilian mangroves, Machado *et al.* (2002) recorded Ni in the range, 1.8 to 12.7µg/g.

Chitrapuzha, station 3, recorded Ni in the range 13.21 to 73.44µg/g. The monsoon season was characterized by the peak concentration and the minimum was observed during the postmonsoon. The major polluting sources for Ni are chemical industries, tanneries, cement, shipyard, and refineries (Khan, 1995). Since, this river receives effluents from various industries, Ni contamination is highly possible here. According to Moore and Ramamoorthy (1992), anthropogenic inputs from municipal discharges, urban storm water runoff and automotive combustion of Ni-containing diesel oil also contribute Ni to the coastal water bodies. The observed non-correlation with hydrographical parameters also augments the possible anthropogenic source in this system. Monsoon season was found to be dominating in Ni content. Metal-rich sediments brought in by the heavy land runoff may be reason for this sudden hike in metal concentration. The observed postmonsoon minimum can be attributed to the resuspension of sediments occurring in this season. A corresponding increase in particulate metal concentration in the same season emphasizes the possibility for the resuspension process.

Ni showed high correlation with Fe in this river sediment. Association of Ni with Fe and Mn hydroxides are widely recognized. According to Moore and Ramamoorthy (1992), association of Ni with Fe and Mn oxides is an important mode of transport for the metal. In a study by Ambatsian *et al.* (1997), it was shown that Ni was transported from the land with Mn oxides but was released to water and a major fraction of this was associated with Fe oxides in the sediment. Nair and Ramachandran (2002) related the strong positive relationship to the sorbing or co-precipitation of the metal onto Fe and Mn oxyhydroxides. Metals like Cu and Co also correlated with Ni (Table C.10). Hence it can be inferred that for these elements, Fe oxides are the major adsorbents rather than Mn oxides in this river.

Ni showed enrichment in the fine sediments and this may be due to the increased specific surface area and due to the ion exchange capacity of the clay particles. This clearly shows the size control of the sediment over Ni concentration. Moderate correlation with organic matter shows the complexation of the metal with humic substances present in the sediment.

Considerably low metal content characterized the estuarine sediments. Here, the variation was from 9.101 to 30.10µg/g. Premonsoon season recorded the peak concentration, while little variation was seen between the monsoon and postmonsoon concentrations. Low metal concentration at this site can be related to the general textural characteristics of the sediments. Sand dominating sediments have poor ability to hold pollutants onto them and due to the high tidal activity; considerable dilution of the metal by metal-deficient marine sediments is possible.

Seasonally, premonsoon recorded the maximum concentration. Since Fe and Mn oxides are the chief carriers of Ni in the fresh water, increasing salinity would result in their flocculation and subsequent incorporation into sediments. In addition to this, Ni showed highly significant correlation with salinity and Fe at this site (Table C.3, C.10). Thus salinity induced co-precipitation of Fe oxyhydroxides seems to the major mechanism controlling the Ni cycle of this estuary.

In a study by Nair and Ramachandran (2002) in the Baypore estuary, Ni concentration was found to increase from upstream to bar mouth of the estuary. Mohan (1997) also reported that the Vellar estuarine sediments registered higher concentration than the river sediments. They have related this to the complexation with organic matter, since, according to the Irwing-Williams series, after Cu and Hg, Ni forms stable complexes with humic substances. Since surface area of fine particles are high, adsorption onto them take place very efficiently in aquatic systems. In addition to this, cation exchange capacity of sediments and affinity of the metal ions for different types of clay surfaces also contribute substantially to the metal-fine fraction proportionality of sediments. In this study also, Ni exhibited high positive relationship with organic matter and fine silt fraction of the sediments. Ni exhibited remarkably high correlation with other metals such as Cu, Co and Cr indicating a common fate for these metals.

The main source of Ni to this estuary is the industrial effluent discharged to the adjoining rivers. Emanations from Ni containing diesel oil from intense boat traffic may have contributed a substantial portion of the metal. In the Cauvery River estuary, Ni was found to vary from 96 to 156ppm (Seralathan, 1987), whereas in the Baypore estuary, Kerala, Ni varied from 25-98ppm (Nair and Ramachandran, 2002). In the nearby Kayamkulam estuary, Unnikrishnan (2000) noted Ni in the range 8.89 to 91.55 mg/kg. In a previous study by Joseph (2001) in the Cochin estuary, Ni was found to vary between 38.54 to 92.70mg/kg. In the present study, considerably lower concentration of the metal was observed in the estuarine sediments.

### ➢ Cadmium

Cadmium is probably the most bio-toxic element and is regarded as the priority pollutant. It is widely used in various industrial products and processes. Because of its wide variety of use, anthropogenic inputs into aquatic environments are considered as a principal source of Cd contamination. It is therefore expected that human activities in the estuarine and coastal areas may result in relatively high concentration of Cd (Sadiq, 1992 b). In general, Cd enters the aquatic environments *via* atmospheric deposition and through effluent discharges from point sources in nearshore areas (Nriagu, 1980).

Among the trace metals studied, Cd showed lowest concentration in sediments at all sites. However, seasonal distribution was different at each site. The highest annual mean concentration was recorded in one of the mangrove sites, station 1. Here, Cd ranged from 1.584-8.876µg/g. An abnormally high value was observed in the month of April. At station 2, the mangrove nursery, the concentration range was relatively small. Sediments showed Cd in the range 0.436-2.528µg/g (Table A. 56). If the high value observed at station 1 is excluded as an outlier, then monsoon season displayed highest metal content (Figure 5.26). However, seasonal changes appeared to have little influence on sedimentary Cd dynamics at station 2. Here, in all the three seasons Cd concentration remained similar. At the riverine station, Cd varied from 0.149 to 4.029µg/g, with a monsoon maximum. The non-monsoon periods exhibited similar metal content. Sediments of the estuary recorded the lowest metal content of all the systems under study. Cd varied from 0.437 to 2.700µg/g at this site. Monsoon season dominated in metal content here with a postmonsoon minimum.

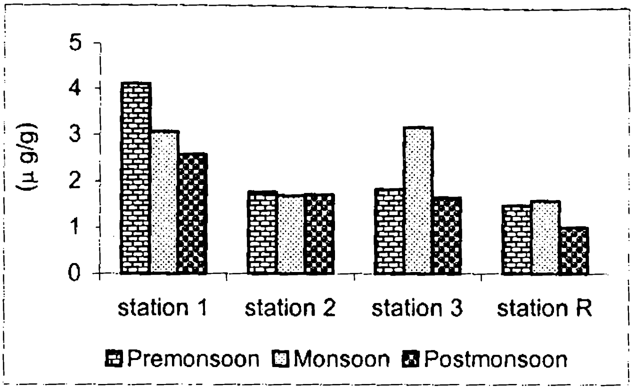


**Figure 5.26:- Seasonal mean variation of sedimentary cadmium**

In all the three aquatic systems analyzed in this study, Cd was found to be preferably associated with particulate matter, especially during the postmonsoon period. Affinity of Cd for particulate matter was reported in many studies. (Martin and Maybeck, 1979; Martin and Whitefield, 1983; Dyressen and Kremling, 1990; Horowitz *et al.*, 1996; Lead *et al.*, 1999; Ciffroy *et al.*, 2003). Fine clay particles, biogenic materials and numerous organic and inorganic ligands enrich the suspended sediments. Cd remains solely in the +2 oxidation state and has a natural affinity for the negatively charged clay mineral particles and organic matter (Sadiq, 1992b). Adsorption take place rapidly due to the increased stability of the complexes formed. Thus, both physical and chemical factors favour concentration of the metal in particulate matter.

Of the two mangrove environments studied, station 1 recorded higher value in all the three seasons. Generally, Cd is not affected by fluctuations in oxidation-reduction conditions since it remains in the divalent solo oxidation state. In anoxic sediments where pH and pE are very low, there are plenty of sulphides available, and formation of CdS can be anticipated. Luther *et al.* (1980) speculated on the formation of CdS, while, Salomons *et al.* (1987) concluded that trace metals like Cd might occur as sulphides in anoxic sediments. Since mangrove sediments are highly anoxic, Cd may precipitate as CdS in the sediments. Lu and Chen (1977) have further shown that dissolved Cd concentration was decreased under reducing conditions. Chemically, Cd is a sulphophilic element.

Sediments serve as important sink for dissolved Cd (Lyons and Fitzgerald, 1980; Santschi *et al.*, 1980). Sadiq (1992 b) has further shown that adsorption is an important removal mechanism for Cd from water. The most important adsorbents are organic matter, hydroxides of Fe and Mn, clays and particles of biogenic minerals. Cd forms moderately stable complexes with organic matter found in natural waters, including amino acids, amino sugars, polysaccharides, hydroxyl and carboxylic acids of aliphatic and aromatic nature etc., which contain suitable donor atoms for complexation with Cd (Moore and Ramamoorthy, 1992). Since the mangrove sediments contain huge amount of plant debris, large varieties of organic compounds are present in them. Hence, complexation with these compounds increases the metal concentration in mangroves. Positive correlation of Cd with organic matter (Table C.12) emphasizes such complexation reactions. However, Cd displayed a negative correlation with organic matter at station 2. In a study by Morrison *et al.* (2001) Cd showed no correlation with organic matter.

Cd exhibited significant correlation only with Fe at station 2 (Table C.10). This shows that Cd accumulated in sediments through adsorption of freshly precipitated Fe oxides (Mc Corkle and Klinkhammer, 1991). At station 1 no correlation with any other metal was observed indicating the purely anthropogenic origin of the metal. In this study, Cd was not enriched in fine sediments either (Table C.3). Cauwet (1987) also observed little enrichment of Cd onto finer sediments. Thorne and Nickless (1981) reported a weak correlation between Cd and the size of clay particles in the intertidal sediments of the Severn estuary.

Seasonally, except for the high value in April, concentration was generally high in the monsoon season at station 1. The abnormally high value in April can be due to some point discharges, which occurred at the time of sampling. Monsoon hike in concentration can be related to the increase in metal-rich sediments brought in by the run-off waters. Since sediments act as a perfect sink for the metal, immediate settling of dissolved Cd also is highly favoured. However, at station 2, seasonal changes did not exert any influence on metal distribution. According to Sadiq (1992b), if physical or chemical conditions change in a system, sediment-bound Cd may be regenerated to supply the interstitial and overlying waters. Due to this equilibration process, Cd showed little variation with respect to seasonal changes. Temperature exerted significant influence on metal distribution at both the sites (Table C.3). This may be due to increased evapo-transpiration creating more intense reducing conditions, which in turn, favours the precipitation of the metal as sulphides.

In the river sediments, Cd varied from 0.144 to 4.029µg/g with a distinct monsoon maximum, while the non-monsoon periods recorded similar concentrations. Cd is widely used in industrial applications and hence anthropogenic inputs are considered as a principal source of the metal to the river sediments. In general, Cd enters the environment through atmospheric deposition and through effluent discharges from point sources near the sampling site. The observed monsoon hike in concentration further strengthens its possible anthropogenic source. Due to the heavy influx of land runoff increased amount of particulate matter as well as suspended solids rich in metal enter the river and settles to the bottom elevating the metal content in sediments. Lower concentration during the summer period can be due to the meagre runoff.

Among the hydrographical parameters, only pH was found to have any influence on Cd distribution (Table C.3). Moore and Ramamoorthy (1992) have shown that adsorption of Cd onto sediments increases with pH and beyond a threshold value (≥7) virtually all the metal ions are sorbed. Cd showed moderate correlation with silt and clay fraction of the sediment and this could be related to the adsorption of $Cd^{2+}$ on negatively charged clay mineral particles. Cd, in this study, correlated well with organic matter (Table C.12). Poultron and Simpson (1988) observed an unusually high abundance of organic-bound Cd in Lake Ontario sediments and Rosental *et al.* (1986) found a strong association between Cd and organic matter of the sediments of the False Bay. In a study by Monterosso *et al.* (2003) also Cd showed strong positive relationship with organic matter. The metal may interact in solution with dissolved organic matter by complexation or chelation processes that are in turn, concentrated by adsorption onto fine particulates such as clay minerals.

Cd exhibited excellent correlations with Mn, Zn and Pb in these river sediments (Table C.10). Adsorption of Cd onto Mn hydroxides is indicative of its possible co-precipitation with Mn oxyhydroxides. Since Cd and Pb can find their way to this river through aerial discharges from industrial emanations, their association is highly probable.

Sediments of the estuary recoded low Cd content. Cd ranged from 0.437 to 2.614 µg/g. The low metal content can be related to the sandy nature of the substratum. Palanichamy and Rajendran (2000) in a study on the Gulf of Mannar sediments observed the release of Cd from sediments to the overlying water due to the coarser nature of the sediment.

The main source of Cd in this estuary may be the effluent discharge. Cd is extensively used in at least one of the industries located on the banks of river Periyar, the major river draining into Cochin estuary. Flocculation of Fe and Mn oxides to which a certain portion of Cd is adsorbed is also possible when freshwater mixes with seawater. Excellent correlation exhibited by Cd and Mn also supports this (table C.10). Among the hydrographical parameters, dissolved oxygen showed significant inverse relationship with Cd. When dissolved oxygen levels decline, increased amount of Cd gets precipitated as sulphides.

No enrichment of Cd either in organic matter or in the fine sediment fraction was observed in the estuarine sediments. This points to the association of the metal with Fe and Mn oxyhydroxides. In a study by Morisson *et al.* (2001) also Cd did not correlate with organic carbon and Cauwet (1987) observed no enrichment of the metal in the fine sediments.

Seasonally, monsoon period was characterized by peak concentration and this can be related to the influx of metal-rich freshwater and increased land runoff characteristic of this season. The increased particulate matter along with suspended sediment load brought in by the rivers would also be a possible reason for the abnormally high Cd concentration. Lower concentration during summer may be due to the meagre runoff during this period.

Release of Cd from suspended particles and sediments has been reported in several estuaries (Salomons and Forstner, 1984; Ahlf, 1983; Calmano *et al.*, 1985; Mart *et al.*, 1985). Remobilization has been explained by complexing reactions with chloride and/or ligands from decomposing organic matter in water. In this way, uptake by suspended matter or precipitation onto it may be inhibited. Forstner *et al.* (1989) suggested that significant amount of Cd is leached from surface sediments by the process of 'oxidative pumping'. Since chloride complexes of Cd are very strong, during the premonsoon season, concentrations of these complexes are increased resulting in low metal concentration in sediments. Remobilisation of Cd in the postmonsoon season from surface sediments is possible as the particulate metal concentration was high during this season. Forstner *et al.* (1989) have further shown that salinity-influenced remobilisation was high for Cd. Hence, due to the increased complexation and remobilisation processes Cd concentration in the estuarine sediments are low in the non-monsoon periods.

### ➢ Lead

Lead appears to be ubiquitous in the aquatic environment and generally does not bioaccumulate in aquatic organisms. Anthropogenic activities are responsible for most of the lead pollution (Scoullos, 1986). Combustion of oil and gasoline alone accounts for 50 percentage of all anthropogenic emission and thus constitute a major component in the global cycle of Pb. Pb accumulate in sediments (Zabel, 1989), therefore sediments serve as a Pb reservoir. Excess Pb, from water, as a result of contamination, may adsorb onto settling particulates and transport to sediments. In addition to adsorption, solid phase in which Pb may be present in sediments can regulate concentration of dissolved Pb. Because sediments play an important role in regulating Pb concentration in the interstitial waters and overlying waters, the investigation of its sediment content is necessary.

In this study, highest annual mean concentration was observed at one of the mangrove station closely followed by the riverine site. The highest concentration was recorded at Mangalavanam (station 1) where Pb concentration ranged from 17.99 to 94.11µg/g. At station 2, which is also a mangrove station, Pb varied from 22.71 to 52.17µg/g (Table A.57). However, at both these sites monsoon recorded the maximum concentration (Figure 5.27). In the river sediments, Pb varied from 14.18 to 86.41 µg/g and in the estuarine sediments, the variation was from 6.363 to 46.55 µg/g. Here also, monsoon season dominated in Pb content. ANOVA calculations also showed significant variation between stations (Table B.8).

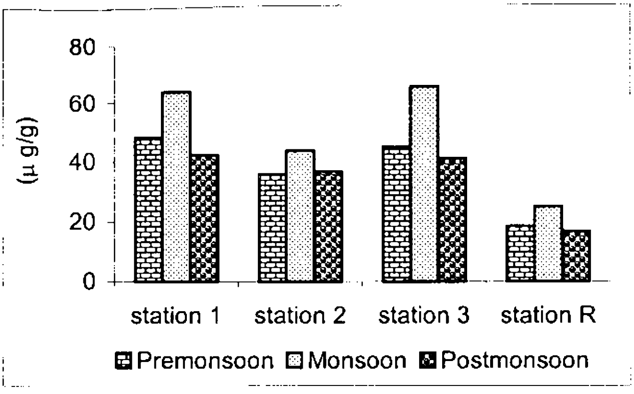


**Figure 5.27:- Seasonal mean variation of sedimentary lead**

Pb occurs only in divalent form $Pb^{2+}$ in marine environments and hence it is not directly affected by fluctuating redox conditions. However, it can be influenced by secondary reactions such as sulphide concentrations. Significant drop in dissolved metal concentrations are observed when conditions changed from oxidized to highly reduced (Bragmann, 1988; Lu and Chen, 1977). Dryseen (1985), by comparing the data on dissolved trace metals in anoxic waters pointed out the possible role of precipitating Fe(II) sulphides as a scavenger for other trace metals including Pb. Under anaerobic conditions FeS may be formed (Forstner and Wittman, 1979). Evans (1989) has also speculated on the co-precipitation of Pb with FeS. Fernex (1994) also opined that under anoxic condition, Pb could be bound to sediments as sulphides thus elevating the concentration. Intense anoxic conditions prevail in the mangroves due to the enormous load of organic matter in the system. Remineralization of this organic load wipes out all the oxygen that may be present in the system creating ideal condition for the metal to precipitate as sulphides. The very fine nature of mangrove sediments facilitates adsorption onto them and Pb bound in this way would remain unaffected by physical processes such as tides and currents.

Station 1 showed significantly higher values than station 2. At this station, Cd concentration was also very high. This points to a common source for these two metals presumably from leakages from petroleum storage place. Besides, Pb can have an atmospheric source through the emissions from automobiles. Since this site was located near the metropolis of Cochin, contamination from this source may be significant.

Seasonally, monsoon recorded maximum concentration of Pb. Pb, present in automobile fuels are identified as the single largest source of this metal to the atmosphere (Renner *et al.*, 1998; Fernex, 1992). Pb, present in the atmospheric particulates is brought down by the heavy monsoon showers and they are rapidly settled to the sediments adding up the Pb pool of the system. In addition to this, increased land runoff of the season would also bring with it metal-rich particles eventually elevating the sediment Pb levels.

Among the hydrographical parameters, dissolved oxygen exhibited highly significant inverse relationship with the metal (Table C.3). This can be due to the increased precipitation of the metal as sulphides with decreasing dissolved oxygen levels. Highly significant correlation exhibited by Pb with Fe also augments this argument. As Forstner and Wittman (1979) have pointed out, under anoxic condition, FeS may form and Pb would have co-precipitated with FeS. Other than Fe, Pb was found to correlate with Zn, Cu and Co in the mangroves indicating their common fate in these sediments.

At both the stations, Pb was enriched in the finer sediments (table C.3). The increased specific surface area and the cation exchange capacity of the clay minerals both may have facilitated adsorption of the metal onto them. Many authors reported the affinity of Pb to clay minerals (Velde *et al.*, 2003) in the mangroves. Organic matter did not appear to have any influence on metal concentration in the present study (Table C.12). In a study by Qu and Kelderman (2001), organic carbon showed negative correlation with Pb. Rosental *et al.* (1986) found no correlation between organic matter and Pb concentration in the sediments. The non-correlation indicates that there is different geochemical pathway for Pb other than diagenetic enrichment. Co-precipitation with FeS seems to be the main reaction mode for this metal in these highly anoxic systems.

In a previous study by Badarudeen (1997) Pb was reported in the range 11 to 49 ppm. Considering studies done elsewhere, the Brazilian mangrove sediments showed Pb in the range 1 to 8.9μg/g (Machado *et al.*, 2002). However, Ong Che (1999) reported Pb in the range 72 to 195μg/g in the Mai Po mangroves, Hong Kong.

Pb exhibited high concentration in the sediments of the Chitrapuzha River. Here, Pb varied from 14.18 to 86.41 μg/g, with a monsoon maximum and a postmonsoon minimum. Pb was found to be enriched in the suspended particulate matter in the non-monsoon periods. Moore and Ramamoorthy (1992) have shown that in rivers, Pb was associated mainly with particulate matter. The increased particulate fraction of the metal may be the result of resuspension of sediments and the atmospheric fallouts. However, due to the increased runoff characteristic of the monsoon period would have facilitated leaching of metal-rich particles from the effluent discharge points and the leaching of atmospheric particulates.

The main contributor of Pb into this river may be effluent discharges. Nriagu (1979) has pointed out that environmental contamination of Pb arises from various sources such as manufacturing processes, paints and pigments, emission from motor vehicles, incineration of municipal solid wastes, combustion of coal and hazardous wastes. Effluent discharges from the various industries located near the sampling site may contribute Pb into this system. Anthropogenic Pb is mainly transported through the atmosphere (Martin *et al.*, 1989; Guieu *et al.*, 1991; Migon, 1993) and it is easily solubilized in water (Bethoux *et al.*, 1990; Chester *et al.*, 1990). In the water body, Pb divides into three — one part remains soluble, another becomes assimilated by plankton organisms and the third, bound to other trace metals, settles to the bottom.

Pb was found to be correlated well with organic matter in this river sediment. Moore and Ramamoorthy (1992) also observed that sorption of Pb by river sediments and correlation with organic content. Humic acids also sorb Pb and the process is found to be pH dependent. Positive correlation observed between Pb and pH (Table C.3) in this study reflects the association of Pb with humic substances, which forms a substantial portion of sedimentary organic matter. Many authors have speculated on the adsorption of Pb by sedimentary organic matter (Campbell and Evans, 1987; Seralathan, 1987; Nair and Ramachandran, 2002; Fan *et al.*, 2001).

Pb showed significant correlation with other metals such as Mn, Zn and Cd at this site (Table C.10). Relatively high correlation with Mn suggests that Pb was trapped in the sediments during Mn precipitation. According to Fernex (1994), a trace metal like $Pb^{2+}$ can co-precipitate with a major dissolved metal like $Mn^{2+}$

during Mn oxide formation if this major ion is present in apparent over-saturation with respect to its oxides. Another possible way to enrichment of Pb with Mn in surficial sediments is due to the dissolution of Mn oxides in the deeper levels and ion migration to the upper levels where dissolved Mn precipitated. Adsorption of Pb on surfaces of oxides and hydroxides of Mn and Fe is well documented (Balistrieri and Murray, 1982, 1984; Scoullos, 1986). Balikangeri and Haerdi (1988) have pointed out that with increasing pH, Pb (II) binds more strongly with $MnO_x$ surfaces. Krauskopf (1956) has stated that Pb is adsorbed consistently by hydrated $Fe_2O_3$ and $MnO_2$ is a good scavenger of trace elements in freshwater environments. Thus co-precipitation of the metal with Mn oxides seems to be the main mode of transfer of Pb in this river.

The estuarine sediments exhibited lower metal concentration than the river or mangrove sediments. Pb varied from 6.363 to 31.17 µg/g in the estuary. The general low values in the sediments can be related to the sandy nature of the substratum, which cannot hold metal ions effectively onto them. Another reason for the observed reduction in metal content at the estuarine mouth can be due to desorption of the metal that is concentrated in freshwater clay minerals. Partial removal of the element that is associated with oxides of Fe and Mn was also reported (Seralathan, 1987).

The main source of Pb into this estuary is presumably from anthropogenic activities. The rivers draining into this estuary carry with them effluents discharged from various industries. Since Pb is well known for aerial deposition, contribution from the Aeolian fallouts leads to elevated metal contents. Seasonally, monsoon season was characterized by the peak concentration. The heavy monsoon showers coupled with increased land run off contribute Pb-rich particles from atmosphere and effluent discharge points respectively to the estuary. Pb, in this study, did not exhibit any correlation with the hydrographical parameters reflecting its purely anthropogenic source (Table C.3). Other metals studied also showed no correlation with Pb in this estuary. Thus, Pb might have followed a different geochemical processing since it has a purely anthropogenic source. However, Pb was found to be enriched in the silt fraction of the sediment showing its preferential adsorption onto finer sediments.

## 5.5 Statistical Analysis

The assessment of pollution is based upon the determination of the concentration of the pollutants in the concerned environment. The enormous size of the data set usually present a problem in interpreting the results and in reaching a consistent conclusion. To avoid the errors that might have occurred during the analytical and/or sampling procedures, statistical analysis is necessary.

Correlation coefficients are indices that measure the strength of the linear relationship between variables. Emphasis is on the degree to which two sets of values vary together around their respective means and on the direction of co-variation of the variables.

If the sediment samples from the four different aquatic environments are considered as objects and the determined chemical parameters as variables, a correlation matrix can be obtained. This was studied in order to find the internal structure and assist in identification of pollutant sources not accessible at first glance. Since, in the present study, the calendar year was divided into three seasons with respect to monsoon, correlation study was carried out using seasonal data only.

Hydrographical parameters are the signature of aquatic systems. The four primary factors, salinity, dissolved oxygen levels, pH and temperature together determine the ultimate fate of a pollutant in the highly dynamic hydrosphere. Correlation study reveals the influence of each of them on the metal distribution. To understand the cumulative effect of these physico-chemical parameters, canonical regression analyses were carried out. In this, monthly data were adopted to evaluate the combined influence of these parameters by transforming them to a single linear function.

In all the systems analyzed, hydrographical parameters have an upper hand in determining the metal distribution as evidenced by their extremely significant regression coefficients (Tables D.1 to D.12). In all the three major fractions almost all metals correlated with the hydrographical parameters. Among the dissolved metals only Fe and Zn did not correlate well with physico chemical parameters at the reference station. This indicate the purely anthropogenic source of these metals.

In the particulate fraction also Fe displayed non-correlation with hydrographical parameters at station 3 and at station 1, both Zn and Pb showed a similar behaviour. Besides Fe, Cu and Ni also exhibited less significant correlation with hydrographical parameters in the estuarine sediments. The non-correlation of Fe can be attributed to the relative abundance of the metal. Due to the enrichment of Fe in all the three phases, changes in the physico-chemical condition of the system have limited influence on the distribution of this element. Thus from the canonical regression analysis, it can be inferred that hydrographical parameters have an upper hand in regulating the trace metal chemistry in the mangrove, riverine and estuarine environments.

### 5.5.1 Principal component analysis

Due to the large number of variables and study locations, it was necessary to use some statistical technique to understand the results of the study. The multivariate analysis (principal component analysis or factor analysis) was adopted on the data matrix with columns representing the variables of a set and rows representing the observations. This approach helped to find the 'latent' variable that, in numbers smaller than the original ones, could explain the original variance and simultaneously reduce the dimensionality of the problem (Hpoke, 1983; Wenchuan *et al.*, 2001). By extracting the eigen values and eigen vectors of the matrix, the number of significant factors could be defined, the percentage of variance explained by each of them and the participation of the old variables in the new latent ones (Hopke, 1983; Pardo *et al.*, 1990). The explained variance of some factors can be defined as the percentage of sum of the variance of these factors as a function of the total variance. Factors with eigen values greater than one were selected (Davis *et al.*, 1973).

Trivial factors were eliminated by normalizing during rotation factor loadings by the Varimax method (Borovec, 1996). In this way, two factors were accounted in this study and the remaining factors did not give significant contribution to the information included in the data matrix. The composition of the first two principal components was referred to as 'principal component loadings' is reported in the table.

By using the multivariate methods, the dimensionality of the problem was reduced from the original 120 chemical variables to only two key factors. These variables are built by means of a linear combination of the original ones and the eigen vectors and can be plotted to obtain a graphical picture of the overall situation. The principal component score plot was used to interpret the spatial distribution by clustering the samples. It was also used to describe their different characteristics and help to find out the sources of heavy metal in the surficial sediments. Only sediment samples were selected for this analysis as they record pollution for considerably longer times.

| | Factor | Factor |
|---|---|---|
| | 1 | 2 |
| Fe | **0.7077** | 0.5733 |
| Mn | **0.9354** | 0.0849 |
| Zn | **0.7254** | 0.6252 |
| Cu | 0.6203 | **0.7517** |
| Co | 0.6229 | **0.7369** |
| Cr | 0.1677 | **0.7643** |
| Ni | 0.5921 | **0.7879** |
| Cd | **0.9284** | 0.0586 |
| Pb | 0.6336 | **0.7078** |
| Org. C | -0.1336 | **0.8888** |
| Expl.Var | 4.3346 | 4.3340 |
| Prp.Totl | 0.4335 | 0.4334 |

**Table 5.28:- Factor loadings of metals at station 1**

| | Factor | Factor |
|---|---|---|
| | 1 | 2 |
| Fe | **0.9028** | 0.1264 |
| Mn | **0.7955** | -0.1248 |
| Zn | **0.8882** | 0.4015 |
| Cu | 0.6244 | **0.7103** |
| Co | **0.8633** | 0.3090 |
| Cr | 0.6500 | 0.2124 |
| Ni | **0.8353** | 0.4780 |
| Cd | **0.7149** | 0.4687 |
| Pb | **0.9356** | -0.0325 |
| Org. C | -0.0794 | **0.9140** |
| Expl.Var | 5.8847 | 2.1224 |
| Prp.Totl | 0.5885 | 0.2122 |

**Table 5.29:- Factor loadings of metals at station 2**

At station 1, the first factor showed positive loading with Fe, Mn, Zn and Cd (Table 5.28). The order of significant loading were Mn > Cd > Zn > Fe. The second factor showed positive loading with organic C, Ni, Cr, Cu and Co. Hence, at this site Cd and Zn were mainly associated with Fe and Mn oxides while, the rest were associated with organic matter. The principal component score plot distinctly showed two groups of elements. Cd and Mn formed one group, while Fe and Zn, Ni, Cu, Co and Pb formed another cluster (Figure E.1). Thus, from this score plot, it is very clear that Cd was present mainly associated with Mn oxides rather than Fe oxides whereas for Zn, the reverse seems to be true. Cr and organic carbon were separated from the rest in the mangroves. Enormous load of organic mater degraded in the mangroves may have led to the abundance of large organic molecules, leaving limited chances of complexation with the metals. However, due to the natural affinity of the metal cations to the negatively charged organic coatings, in turn, leads to the observed positive loading of some metals with this variable. At station 2 also, organic C was found to have a positive loading with Cu (Table 5.29). Rest of the metal was concentrated in the first factor. At this site too, organic C was separated from the rest in the factor score plot (Figure E.2).

| | Factor | Factor |
|---|---|---|
| | 1 | 2 |
| Fe | **0.9582** | 0.0243 |
| Mn | 0.1086 | **0.9334** |
| Zn | 0.3210 | **0.9244** |
| Cu | **0.8498** | 0.4850 |
| Co | **0.7378** | 0.5762 |
| Cr | 0.2918 | 0.5267 |
| Ni | **0.8687** | 0.4591 |
| Cd | 0.5979 | 0.6454 |
| Pb | 0.6128 | **0.7459** |
| Org. C | **0.7124** | 0.3771 |
| Expl.Var | 4.3799 | 3.8970 |
| Prp.Totl | 0.4380 | 0.3897 |

**Table 5.30:- Factor loadings of metals at station 3**

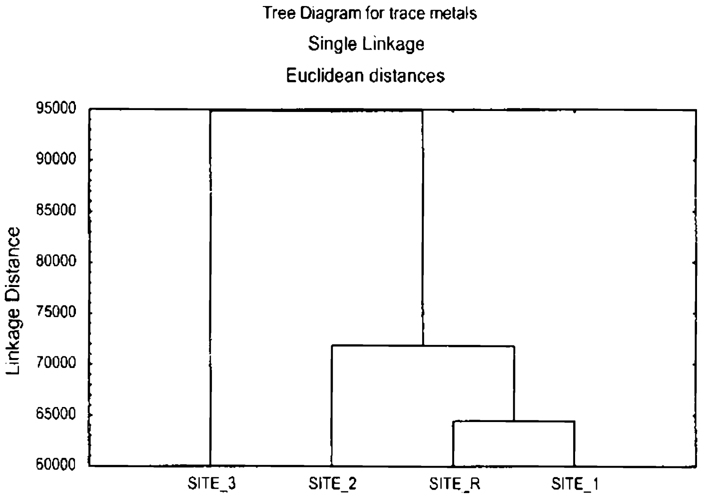
| | Factor | Factor |
|---|---|---|
| | 1 | 2 |
| Fe | **0.8368** | 0.4742 |
| Mn | 0.2464 | **0.8884** |
| Zn | **0.7389** | -0.0728 |
| Cu | **0.8424** | 0.4293 |
| Co | 0.6890 | 0.5716 |
| Cr | **0.7676** | -0.0132 |
| Ni | **0.8840** | 0.4105 |
| Cd | -0.2740 | **0.8303** |
| Pb | 0.2525 | 0.2532 |
| Org. C | **0.8618** | -0.0438 |
| Expl.Var | 4.7436 | 2.4546 |
| Prp.Totl | 0.4744 | 0.2455 |

**Table 5.31:- Factor loadings of metals at station R**

However, at the riverine site, factor 1 displayed positive loading with Fe, Cu, Co, Ni and organic matter (Table 5.30). Here, Mn was found to positively loaded with Zn and Pb. Hence, it can be inferred that Cu, Co and Ni were adsorbed either onto Fe oxides or organic matter, while Mn seems to be primary carrying phase for Zn and to a lesser extent, Pb. Another combination of metals was seen at the estuary. Here, Fe, Zn, Cu, Cr, Ni and organic matter showed positive loading with factor 1, while, Mn and Cd were loaded with factor 2 (Table 5.31). Score plots of factors showed a combination of Fe, Cu, Co and Ni and another group of Zn, Cr and organic matter (Figure E.4). Association of Zn and Cr in these estuarine sediments points to their common source in these estuarine sediments, presumably from the leakage from boats.

### 5.5.2 Cluster analysis

A simple model was obtained for the relationship amongst the test elements by cluster analysis, based on the weighted pair-group method with arithmetic averages. The single linkage method was used. The most similar sites are grouped together. The resultant dendrograms depict the sequence in the associations of sites, similar to the correlation matrix, but in a more lucid form. Trace metals in all the three phases were put together to get the dendrogram by the 'joining tree' diagram. This analysis revealed that the estuarine as well as station 1 were the most similar in the processes that determine the fate of trace metals in these aquatic systems. The other mangrove station (station 2) behaved differently, since the physicochemical environment was severely influenced y human interferences. The riverine site, exhibited dissimilar hydrogeochemical processes.



Tree Diagram for trace metals
Single Linkage
Euclidean distances

**Figure 5.28:- Dendrogram of trace metals**

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# Chapter 6

# Conclusion

The hydrogeochemical investigation on the three pivotal modules of the hydrosphere — mangrove, river and estuary — presented highly variable, yet, unique characteristics. Spatial and monthly variations of hydrographical parameters, which are the signature of each ecosystem, were determined. The life nourishing nutrient compounds and bioorganic compounds along with the toxic heavy metals were analyzed with a view to assess the peculiarities of these diverse aquatic systems in the processing of these entities.

The nutrient compounds analyzed in this study exhibited similar spatial distribution. The general order of abundance of the nutrients was river > mangroves >> estuary. The generally high value of nutrient concentration at the riverine site can be attributed to the influence of effluents discharged from various chemical and fertilizer industries. On the other hand, the extremely low record of nutrients in the estuarine system can be the result of the dilution of the estuarine waters by the nutrient-deficient marine water.

Among the mangroves, Mangalavanam (station 1) recorded higher concentration of dissolved and sedimentary nutrients than station 2 ('Fisheries' station). Due to regular semi-diurnal tidal flushing, nutrient and organic compounds may occur at relatively higher proportions at this particular mangrove habitat. Furthermore, this site is a bird sanctuary as well and the bird-droppings would further add to the nutrient load. The relatively higher concentration of nutrients in the mangroves can be due to the rapid mineralization processes occurring in the mangroves. Aerobic as well as anaerobic oxidation of organic matter together with the peculiar physico-chemical setting of the mangroves may be responsible for the increased nutrient concentration.

The dominance of ammonium in the mangroves can be the result of intense anaerobic oxidation of bulk organic matter. Denitrification reactions can also be a dominant process in the anoxic mangrove sediments. N/P ratio revealed that though the individual nutrient concentration was low in the estuary, this system exhibited N/P ratio closest to the theoretical value. River water, which recorded the highest nutrient concentration, on the other hand, exhibited the elements in the assimilative proportion to the planktonic organisms. The two mangrove habitats can be considered as severely affected by anthropogenic perturbations.

In this study, the two extreme environments, river and estuary, recorded the highest and lowest sediment nutrient concentrations. However, total organic carbon was highest in the mangroves. Plant litter may be the chief contributor of organic carbon in the mangroves. The fine-grained mangrove sediments could have adsorbed nutrients on to them. The low coefficient of adsorption of the sandy sediments of the estuary may be the reason for the relatively low nutrient concentration in this system.

The sedimentary C/N ratio suggested that there was net immobilization of nutrients taking place in the mangrove habitats and in the river. In the estuary, on the other hand, mineralization processes were dominant. Among the mangrove habitats, C/P ratio was higher at station 2 indicating that phosphorus present in this system may be of biogenic origin whereas at station 1, phosphorus was supplied in greater proportion through some external sources. At the estuarine site also, the low C/P ratio points to the contribution of phosphorus from domestic and aquaculture waste disposals.

N/P ratio was also higher at station 2, though the individual nutrient concentration was low at this site. This can be attributed to the relatively higher proportion in which phosphorus was present there. In fact, the ratio was low in all the systems analyzed revealing the dominance of phosphorus over nitrogen nutrients. Cluster analysis revealed that both the mangrove stations processed the nutrient compounds in analogous pathways. The estuary showed similarity to the mangroves, while the riverine site behaved in an entirely distinct manner. Indeed the physico-chemical characteristics of each aquatic system determine the ultimate fate of the nutrient compounds.

In this study, the bioorganic compounds recorded lowest concentration at the estuarine site. The sandy nature of the substratum may be the reason for the least abundance of these compounds in the estuarine system. The most labile compounds, dissolved monosaccharides, were found to be in greater proportion at the riverine station. The rest of the aquatic systems did not vary much in the dissolved monosaccharide concentration. In the mangroves, the first stage of decomposition of mangrove litter involves the leaching of soluble materials mainly carbohydrates. Bacterial mineralization of organic matter may also be the reason for the increased levels of monosaccharides. At the riverine site, enzymatic hydrolysis of particulate carbohydrates by soil microbes releases simple mono and oligo saccharides into the soil solution, which are flushed from the soil during wet season into the river.

Dissolved concentration of tannin and lignin were highest at the mangrove sites. Mangrove plants contain high amount of tannin and these compounds are leached from the plant biomass during bacterial degradation. Among the mangroves, station 2 recorded higher concentration of dissolved tannin and lignin probably due to the accumulation of organic matter since tidal flushing was quite limited at this site. At the riverine site, terrestrially driven organic matter may be the source of tannin and lignin whereas in the estuary, contribution from the adjoining mangroves and land runoff may be the major sources.

Sedimentary organic compounds exhibited unique distribution pattern in this study. The river sediments recorded the highest concentration of total carbohydrates and proteins, while the mangrove habitats dominated in total lipid, tannin and lignin contents. This kind of distribution is in accordance with the biochemical characteristics of the resident flora. Mangrove plants have fleshy leaves with thick cuticle, which is known to be a lipid membrane. The decomposition of plant biomass may be the primary source for this compound in this environment. Tannins are abundant in mangrove plants and many of the plant parts are complex structures of polymeric lignocelluloses. The very abundance of tannins in the mangroves may be responsible for the low sediment protein content by making them inactive through complexation reactions. Aquatic macrophytes were abundant in the riverine sites and leaching from the dead plant biomass may be the reason for the observed elevated concentration of carbohydrates and proteins

Among the two mangrove habitats, individual bioorganic compound concentration was higher at station 2. Tidal inundation was not regular at this site as the entrance for floodwaters was physically restricted to prevent the escape of the prawn larvae since this site is an aquaculture farm also. Hence organic matter would have accumulated and get preserved in the creeks leading to enhanced levels of organic entities. The estuarine sediments recorded invariably lowest concentration of all the analyzed compounds. The sandy sediments are considered to be poor adsorbers of organic matter and this may be the reason for the observed low concentration at this site.

Considering the CHO:SOC ratio, the mangroves and the estuarine organic matter was mainly autochthonous in nature, whereas in the river sediments, the organic matter was mainly allochthonous. At all the sites, proteins contributed highest to the SOC pool than any other compound followed by carbohydrates. Lipids contributed least to the SOC at all sites. At the riverine site, relative proportion of all labile compounds was high in the total organic matter and hence sediments at this site can be of greater quality. Among the two mangrove environments, station 2 was found to have higher ratios than station 1. Moreover, it must be noted that individual concentrations of these compounds too were higher at this site. Hydrodynamic features such as tidal activity may be the main factor determining the fate of organic matter at this site. Organic matter may be accumulated and preserved at this site due to the limited exchange with tidal water. Thus, it can be concluded that station 1 acted as a net exporter of organic matter, whereas station 2 can be a sink for organic matter. The estuarine sediments showed low relative proportion of all the analyzed compounds in the TOC pool. Dissolved humic substances, which are abundant in the river water flocculate as they meet with the brackish estuarine waters. Since many rivers drain into this estuary, major component of the TOC may be the humic substances. But, in this study, concentration of humic substances were not assessed hence contribution of these compounds can only be presumed. In summary, the river sediments appear to be of higher quality followed by the mangroves and then the estuary.

Cluster analysis revealed that two mangrove sites exhibited similar behaviour, as they are the most closely related ones in the "joining tree diagram". The river sediments were next related to the mangroves, while the estuarine sediments behaved in an entirely different way. The physicochemical characteristics of each system together with the anthropogenic perturbations is thus the primary factors determining the transport and fate of organic compounds.

In the present study, the toxic heavy metals exhibited unique distribution pattern in the three different aquatic systems. The most labile form, the dissolved metals recorded higher concentration in the river and mangrove environments than the estuarine system. River water recorded the highest proportion of metals such as Fe, Co, Cd, and Pb, while mangrove habitats dominated in the soluble fraction of biologically essential metals like Mn, Zn, Cu and Ni.

The extreme reducing conditions prevailing in the mangroves greatly modify the chemistry of metals, in particular Fe and Mn, the reduced forms of which are soluble. Among the two mangrove environments, station 2 recorded higher concentration of almost all the metals analyzed. Only Zn and Pb exhibited greater concentration at station 1. The dominance of Zn and Pb can be due to the input from point discharge sources, since this site was located near the metropolis of Cochin. The higher concentration of trace metals at station 2 may be the result of accumulation of metals in the creek water as the exchange with floodwater was limited at this site.

The primary source of trace metals in the river water may be the effluent discharges from various industries located on the banks of this river. Cd and Pb, the most toxic trace metals, recorded highest annual mean concentration at this site. Apart from the industrial effluents, runoff water from urban, aquaculture and agricultural areas significantly add to the trace metal load of this river. The observed low metal concentration in the estuary may be due to the dilution of the metal-rich estuarine waters with the metal-impoverished marine waters. However, Cr recorded higher concentration at the estuarine site. Since this estuary is used extensively for urban waste disposal, substantial amounts of Cr would have added to the waters, as Cr is present in significant amount in municipal wastewaters.

Trace metals associated with the suspended particulate matter exhibited analogous distribution pattern as the dissolved fraction. River water dominated in concentration of metals such as Fe, Cd and Pb whereas the mangroves recorded higher proportions of Mn, Zn and Cu. However, in contrast to the dissolved fraction, station 1 dominated in particulate trace metals over station 2. This can be expected from the natural distribution pattern of the metals. When the dissolved fraction was higher, particulate fraction was low.

In general, all trace metals analyzed in this study were found to be enriched in the particulate matter except for Fe and Co. Seasonally, postmonsoon period invariably recorded highest metal concentration. In fact, for many metals, concentrations in the other seasons were almost masked in the graphical representation. This postmonsoon-associated hike in concentration can be attributed to the readsorption of trace metals onto the resuspended sediments or due to the adsorption onto the newly introduced particles by the heavy monsoon runoff. The prolonged residence time of particles in the water column during the relatively calm postmonsoon period would also have favoured the readsorption process. Salinity-influenced desorption reactions would have limited the build up of metal ions onto suspended particulate matter in the premonsoon season even though the residence time of particles was high during this period also.

The general increase in particulate metal concentration can be due to the resuspension processes occurring in the aquatic systems. Resuspension of sediments was found to increase the metal concentration in the overlying water. In the estuary, regular dredging of the shipping channel greatly favours the resuspension processes. Burrowing animals can significantly modify the sediment structure. Particulate matter is produced in greater amounts when they feed or burrow. In addition to this, growing plant roots and the burrow linings creates oxidizing microenvironments in the otherwise reducing mangrove sediments. In these microenvironments, many metals are precipitated in insoluble form by oxidation. In the oxic waters of the estuary and river, oxidative precipitation of trace metals may be the reason for their greater concentration in the particulate phase. Association with Fe and Mn oxyhydroxides may be the reason for the observed highly significant positive correlation of metals with each other. Furthermore, in the river water, since the amount of particulate matter was high, modification of the colloidal particle dimensions would have occurred during the separation process as the filters were frequently clogged.

Adsorption of metals onto the humic and fulvic acid colloids can also enhance the particulate metal concentration. Certain metals such as Cr, Zn, Cu, Cd and Pb may have point discharge sources at the study sites. Shipping activity and boat traffic was found to be responsible for the elevated concentration levels of these metals. Effluents from the various chemical, petrochemical and metal refining industrial units together with the urban and agricultural waste disposals may also have significantly contributed to the trace metal load in the aquatic systems analyzed.

In this study, the sedimentary trace metals exhibited unique distribution patterns. Except Fe and Mn, all other metals analyzed recorded highest concentration in the mangrove sediments. The peculiar chemistry of Fe and Mn determined their fate in aquatic environments. The reduced forms of Fe and Mn are soluble while other metals precipitate in the reduced state. Due to the intense organic matter remineralization process mangrove sediments usually have low redox potential and as a consequence, Fe and Mn would have desorbed from the sediment surfaces and migrated to the upper water column. In the anoxic sediments of mangroves, sulphate reduction often results in substantial amount of sulphides both in the sediment and overlying water. Other trace metal cations, on the other hand, combine with these sulphide ions and get incorporated to the sediments.

Many of the trace metals studied have a natural ability to complex with the negatively charged organic matter. Since mangrove sediments are enriched in organic matter, complexation with it renders the metal ions immobile. Moreover, the muddy mangrove substratum adsorbs metals onto them effectively. The riverine sediments recorded highest concentration of Fe and Mn. The riverine sediments may have a high reduction potential and Fe and Mn are oxidatively precipitated in these sediments. The estuarine sediments, on the other hand, recorded low metal content in all the seasons. The sediments were composed mainly of sand, which has a low coefficient of adsorption. Dilution with metal-deficient marine sediments would have considerably reduced the metal content in this estuarine sediment.

Cluster analysis revealed that the estuarine and one of the mangrove sites were the closely related ones in the processing of trace metals. Station 2, which is also a mangrove habitat, formed another group, while the riverine site behaved in an entirely different way. The dissimilarity in the two mangrove environments in the trace metal abatement can be related to the unique environmental setting. Since station 1 is located near the metropolis of Cochin, whereby heavy discharges of urban and industrial effluents largely influence the chemical make up of this mangrove. Furthermore, this site is an open system with regular exchange of water and sediments with the surrounding estuary. Station 2, on the other hand, was a closed system and was located in a rural area. Thus, variations in the geographical setting influence the accumulation of toxic metals in these mangrove environments.

In all the systems analysed, hydrographical parameters were found to regulate metal distribution as revealed by their extremely significant canonical regression coefficients. In all the three major fractions, almost all metals correlated with the hydrographical parameters. Due to the large number of variables and study locations, it was necessary to use statistical techniques to analyse the results of the study. The multivariate analysis (principal component analysis or factor analysis) was adopted on the data matrix with columns representing the variables of a set and rows representing the observations. This approach helped to find the 'latent' variable that, in numbers smaller than the original ones, could explain the original variance and simultaneously reduce the dimensionality of the problem. In the Principal component score plot, at station 1, the first factor showed positive loading with Fe, Mn, Zn and Cd. The order of significant loading was Mn > Cd > Zn > Fe. The second factor showed positive loading with organic C, Ni, Cr, Cu and Co. Hence, at this site Cd and Zn were mainly associated with Fe and Mn oxides while, the rest were associated with organic matter. The principal component score plot distinctly showed three groups of elements. Cd and Mn formed one group, while Fe and Mn formed another; other metals such as Ni, Cu, Co and Pb grouped to form yet another cluster. Thus, from this score plot, it is very clear that Cd was mainly associated with Mn oxides rather than Fe oxides whereas for Zn, the reverse seemed to be true. Cr and organic carbon were separated from the rest in the mangroves. Enormous load of organic mater degraded in the mangroves may have led to the abundance of large organic molecules, leaving limited chances of complexation with the metals. However, the natural affinity of the metal cations to the negatively charged organic coatings, in turn, led to the observed positive loading of some metals with this variable. At station 2 also, organic C was found to have a positive loading with Cu. The other metals were found to be concentrated in the first factor. At this site too, organic C was separated from the rest in the factor score plot.

However, at the riverine site, factor 1 displayed positive loading with Fe, Cu, Co, Ni and organic matter. Here, Mn was found to be positively loaded with Zn and Pb. Hence, it can be inferred that Cu, Co and Ni were adsorbed either onto Fe oxides or organic matter, while Mn seemed to be the primary carrying phase for Zn and to a lesser extent, for Pb. Another combination of metals was seen in the estuary. Here, Fe, Zn, Cu, Cr, Ni and organic matter showed positive loading with factor 1, while, Mn and Cd were loaded with factor 2. Score plots of factors showed a combination of Fe, Cu, Co and Ni and another group of Zn, Cr and organic matter. Association of Zn and Cr in these estuarine sediments points to their common source in these estuarine sediments, presumably from the leachingfrom boats.

The overall analysis of data revealed that the riverine site was severely affected by the industrial influents as the concentrations of inorganic nutrients and pollutant metal ions were the highest at this site. The estuarine environment appeared to be the least polluted. The two mangrove sites were rich in inorganic nutrient and bioorganic compounds. However, the mangrove sediments were polluted in terms of trace metals. Among the two mangrove environments, though, the inorganic nutrient concentration was higher at station 1, organic compounds dominated at the 'Fisheries' station.

# *Appendix A*

## SPATIAL AND MONTHLY VARIATIONS

| Month | Station 1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 3.320 | 5.180 | 1.570 | 4.480 |
| March | 8.620 | 24.69 | 8.150 | 14.91 |
| April | 14.56 | 25.62 | 0.290 | 22.13 |
| May | 4.950 | 24.45 | 0.000 | 13.10 |
| June | 0.290 | 3.490 | 0.000 | 0.870 |
| July | 3.780 | 8.730 | 0.290 | 8.150 |
| August | 3.200 | 8.730 | 0.290 | 15.43 |
| September | 1.280 | 4.660 | 0.120 | 6.870 |
| October | 0.580 | 2.490 | 0.120 | 2.910 |
| November | 2.910 | 7.580 | 0.000 | 10.19 |
| December | 14.56 | 13.1 | 0.870 | 20.96 |
| January | 3.090 | 5.010 | 0.290 | 4.430 |
| **Mean** | **5.095** | **11.14** | **0.999** | **10.37** |

**Table A.1:- Spatial and monthly variation of salinity (‰)**

| Month | Station 1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 3.440 | 1.970 | 3.440 | 2.950 |
| March | 2.990 | 1.710 | 4.700 | 2.560 |
| April | 1.790 | 3.130 | 3.570 | 7.590 |
| May | 0.000 | 4.830 | 2.200 | 3.080 |
| June | 1.280 | 1.280 | 3.420 | 4.270 |
| July | 2.140 | 0.020 | 2.990 | 3.840 |
| August | 1.710 | 0.850 | 2.560 | 4.700 |
| September | 1.710 | 1.710 | 2.140 | 3.420 |
| October | 1.710 | 5.980 | 3.420 | 2.560 |
| November | 4.270 | 0.430 | 2.140 | 3.420 |
| December | 0.850 | 1.280 | 0.850 | 4.270 |
| January | 2.460 | 1.970 | 2.950 | 6.390 |
| **Mean** | **2.029** | **2.097** | **2.865** | **4.088** |

**Table A. 2:- Spatial and monthly variation of dissolved oxygen (ml/l)**

*Appendix A*

| Month | Station 1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 8.13 | 7.92 | 7.00 | 8.27 |
| March | 7.25 | 7.52 | 6.10 | 7.31 |
| April | 7.31 | 7.81 | 5.86 | 7.14 |
| May | 7.43 | 7.38 | 5.96 | 7.59 |
| June | 7.28 | 8.10 | 6.25 | 7.67 |
| July | 7.50 | 7.41 | 6.45 | 7.81 |
| August | 7.18 | 7.55 | 6.32 | 6.69 |
| September | 7.58 | 7.91 | 6.70 | 7.31 |
| October | 7.10 | 8.54 | 5.84 | 7.20 |
| November | 7.03 | 7.68 | 6.32 | 7.58 |
| December | 6.85 | 7.56 | 5.96 | 8.26 |
| January | 7.00 | 7.69 | 6.24 | 8.10 |
| **Mean** | **7.30** | **7.76** | **6.25** | **7.58** |

**Table A. 3:- Spatial and monthly variation of pH**

| Month | Station 1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 32.0 | 29.5 | 31.5 | 29.5 |
| March | 36.5 | 32.0 | 34.5 | 31.5 |
| April | 33.8 | 30.0 | 33.5 | 28.6 |
| May | 32.0 | 31.5 | 32.8 | 31.0 |
| June | 29.8 | 29.7 | 29.6 | 29.8 |
| July | 28.0 | 31.0 | 30.0 | 29.0 |
| August | 31.0 | 28.0 | 28.0 | 29.0 |
| September | 28.0 | 29.5 | 29.0 | 27.0 |
| October | 31.5 | 32.0 | 29.5 | 30.0 |
| November | 30.0 | 29.0 | 29.0 | 28.0 |
| December | 28.0 | 28.5 | 30.0 | 29.8 |
| January | 27.5 | 31.0 | 28.5 | 30.0 |
| **Mean** | **30.7** | **30.1** | **30.5** | **29.4** |

**Table A. 4:- Spatial and monthly variation of temperature ($^0$C)**

**Station 1**

| Season | % of sand | % of silt | % of clay |
|---|---|---|---|
| Premonsoon | 17 | 24 | 59 |
| Monsoon | 6 | 30 | 64 |
| Post monsoon | 22 | 22 | 56 |

**Station 2**

| Season | % of sand | % of silt | % of clay |
|---|---|---|---|
| Premonsoon | 26 | 17 | 57 |
| Monsoon | 1 | 40 | 59 |
| Post monsoon | 24 | 23 | 53 |

**Station 3**

| Season | % of sand | % of silt | % of clay |
|---|---|---|---|
| Premonsoon | 37 | 12 | 51 |
| Monsoon | 29 | 17 | 54 |
| Post monsoon | 52 | 5 | 43 |

**Station R**

| Season | % of sand | % of silt | % of clay |
|---|---|---|---|
| Premonsoon | 69 | 3 | 28 |
| Monsoon | 74 | 11 | 15 |
| Post monsoon | 81 | 2 | 17 |

**Table A. 5:- Seasonal variation of sediment composition**

| **Month** | **Station1** | **Station 2** | **Station 3** | **Station R** |
|---|---|---|---|---|
| February | 23.38 | 32.76 | 89.13 | 6.638 |
| March | 159.7 | 38.62 | 85.1 | 13.26 |
| April | 45.30 | 80.74 | 89.07 | 7.670 |
| May | 38.35 | 46.40 | 83.77 | 5.250 |
| June | 65.17 | 35.16 | 225.8 | 13.31 |
| July | 161.6 | 85.24 | 90.63 | 4.570 |
| August | 75.50 | 46.93 | 52.85 | 5.000 |
| September | 159.9 | 66.38 | 67.22 | 19.20 |
| October | 57.91 | 20.14 | 64.32 | 4.720 |
| November | 49.82 | 36.82 | 59.39 | 12.12 |
| December | 57.17 | 49.37 | 15.96 | 13.37 |
| January | 23.38 | 31.01 | 10.44 | 7.360 |
| **Mean** | **76.43** | **47.46** | **77.80** | **9.372** |

**Table A. 6:- Spatial and monthly variation of dissolved ammonium (µmol/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 1.720 | 0.580 | 28.13 | 0.800 |
| March | 1.410 | 0.380 | 31.02 | 0.810 |
| April | 0.900 | 2.540 | 4.510 | 1.360 |
| May | 0.790 | 0.280 | 17.08 | 1.220 |
| June | 3.990 | 0.590 | 2.920 | 0.930 |
| July | 3.560 | 0.860 | 3.560 | 0.650 |
| August | 2.776 | 0.990 | 3.984 | 0.590 |
| September | 2.511 | 2.040 | 2.040 | 0.530 |
| October | 1.690 | 0.430 | 1.400 | 0.630 |
| November | 0.880 | 0.810 | 1.120 | 0.956 |
| December | 1.320 | 0.930 | 4.290 | 0.931 |
| January | 1.720 | 0.570 | 9.060 | 0.826 |
| **Mean** | **1.939** | **0.917** | **9.093** | **0.853** |

**Table A. 7:- Spatial and monthly variation of dissolved nitrite (μmol/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 1.823 | 1.260 | 32.26 | 9.000 |
| March | 2.013 | 2.900 | 18.24 | 5.374 |
| April | 1.007 | 1.362 | 13.58 | 3.581 |
| May | 2.827 | 1.211 | 10.54 | 4.213 |
| June | 3.462 | 0.554 | 7.518 | 3.564 |
| July | 1.006 | 2.654 | 9.583 | 2.579 |
| August | 0.652 | 1.001 | 10.25 | 4.615 |
| September | 0.091 | 0.051 | 13.65 | 5.879 |
| October | 1.021 | 2.153 | 13.14 | 7.850 |
| November | 2.316 | 1.587 | 12.19 | 17.91 |
| December | 2.009 | 2.136 | 14.61 | 18.71 |
| January | 2.956 | 1.800 | 13.76 | 12.11 |
| **Mean** | **1.765** | **1.556** | **14.11** | **7.949** |

**Table A. 8:- Spatial and monthly variation of dissolved nitrate (μmol/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 4.300 | 1.120 | 1.570 | 0.930 |
| March | 28.85 | 0.000 | 3.140 | 0.040 |
| April | 10.03 | 0.000 | 36.56 | 1.360 |
| May | 9.090 | 4.160 | 0.790 | 0.950 |
| June | 3.480 | 1.470 | 0.550 | 0.128 |
| July | 69.13 | 15.35 | 12.66 | 10.06 |
| August | 2.680 | 3.030 | 1.810 | 2.370 |
| September | 17.71 | 2.270 | 1.220 | 0.980 |
| October | 2.860 | 0.460 | 0.510 | 0.670 |
| November | 1.110 | 0.000 | 0.590 | 0.380 |
| December | 2.420 | 2.270 | 0.990 | 0.740 |
| January | 3.560 | 0.110 | 0.780 | 1.740 |
| **Mean** | **12.935** | **2.520** | **5.098** | **1.696** |

**Table A. 9:- Spatial and monthly variation of dissolved urea (µmol/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 26.92 | 34.60 | 149.5 | 16.44 |
| March | 163.1 | 41.90 | 134.4 | 19.44 |
| April | 47.21 | 84.64 | 107.2 | 12.61 |
| May | 41.97 | 47.89 | 111.4 | 10.68 |
| June | 72.62 | 36.30 | 236.2 | 17.80 |
| July | 166.2 | 88.75 | 103.8 | 7.799 |
| August | 78.93 | 48.92 | 67.08 | 10.21 |
| September | 162.5 | 68.47 | 82.91 | 25.61 |
| October | 60.62 | 22.723 | 78.86 | 13.20 |
| November | 53.02 | 39.22 | 72.70 | 30.99 |
| December | 60.50 | 52.44 | 34.86 | 33.01 |
| January | 28.06 | 33.38 | 33.26 | 20.30 |
| **Mean** | **80.14** | **49.94** | **101.0** | **18.17** |

**Table A. 10:- Spatial and monthly variation of total dissolved nitrogen (µmol/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 8.430 | 7.170 | 32.56 | 0.590 |
| March | 28.97 | 10.18 | 110.0 | 3.784 |
| April | 57.25 | 26.74 | 40.39 | 2.830 |
| May | 40.15 | 30.55 | 39.60 | 2.440 |
| June | 13.54 | 26.07 | 10.23 | 3.290 |
| July | 69.13 | 15.35 | 12.66 | 10.06 |
| August | 8.350 | 16.23 | 36.88 | 2.500 |
| September | 67.52 | 10.36 | 45.82 | 2.860 |
| October | 13.29 | 10.18 | 15.50 | 2.040 |
| November | 42.68 | 23.46 | 24.34 | 3.740 |
| December | 23.74 | 10.19 | 36.71 | 3.130 |
| January | 13.48 | 9.380 | 58.77 | 1.390 |
| **Mean** | **32.21** | **16.32** | **38.62** | **3.221** |

**Table A. 11:- Spatial and monthly variation of dissolved inorganic phosphorus (μmol/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 10.02 | 12.64 | 68.23 | 6.716 |
| March | 36.19 | 18.09 | 119.0 | 7.782 |
| April | 63.29 | 33.02 | 54.03 | 6.797 |
| May | 51.81 | 55.81 | 42.01 | 8.268 |
| June | 21.09 | 34.57 | 25.01 | 23.13 |
| July | 72.74 | 17.66 | 23.00 | 29.64 |
| August | 32.21 | 28.71 | 42.44 | 9.962 |
| September | 74.07 | 18.64 | 67.36 | 13.53 |
| October | 59.62 | 21.02 | 42.08 | 5.102 |
| November | 49.51 | 32.83 | 37.19 | 7.080 |
| December | 39.67 | 13.81 | 40.58 | 6.266 |
| January | 18.08 | 12.02 | 69.82 | 4.947 |
| **Mean** | **44.03** | **24.90** | **52.56** | **10.77** |

**Table A. 12:- Spatial and monthly variation of total dissolved phosphorus (μmol/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 3.19 | 4.83 | 4.59 | 27.86 |
| March | 5.63 | 4.12 | 1.22 | 5.14 |
| April | 0.82 | 3.17 | 2.65 | 4.46 |
| May | 1.05 | 1.57 | 2.81 | 4.38 |
| June | 5.36 | 1.39 | 23.09 | 5.41 |
| July | 2.40 | 5.78 | 8.20 | 0.78 |
| August | 9.45 | 3.01 | 1.82 | 4.08 |
| September | 2.74 | 6.61 | 1.81 | 8.95 |
| October | 4.56 | 2.19 | 5.09 | 6.47 |
| November | 1.24 | 1.67 | 2.99 | 8.29 |
| December | 2.55 | 5.15 | 0.95 | 10.55 |
| January | 2.08 | 3.56 | 0.57 | 14.60 |
| **Mean** | **3.42** | **3.59** | **4.65** | **8.41** |

**Table A. 13:- Spatial and monthly variation of N/P ratio**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 3.050 | 1.703 | 1.971 | 1.240 |
| March | 1.745 | 1.743 | 4.889 | 1.340 |
| April | 3.360 | 2.489 | 4.808 | 1.808 |
| May | 1.887 | 4.552 | 5.363 | 0.872 |
| June | 4.134 | 1.435 | 3.347 | 1.034 |
| July | 2.636 | 1.934 | 2.824 | 0.843 |
| August | 5.275 | 2.474 | 6.880 | 0.728 |
| September | 0.928 | 1.913 | 1.717 | 1.318 |
| October | 0.850 | 3.140 | 0.860 | 0.773 |
| November | 1.888 | 1.769 | 1.758 | 0.724 |
| December | 0.821 | 1.480 | 11.55 | 0.763 |
| January | 1.285 | 1.226 | 2.553 | 1.174 |
| **Mean** | 2.322 | 2.155 | 4.044 | 1.051 |

**Table A. 14:- Spatial and monthly variation of exchangeable ammonium (µmol/g)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 2.910 | 1.601 | 2.745 | 1.642 |
| March | 1.102 | 3.183 | 3.512 | 1.551 |
| April | 2.599 | 2.852 | 1.075 | 1.007 |
| May | 2.198 | 3.709 | 3.612 | 1.474 |
| June | 3.578 | 4.075 | 4.664 | 2.640 |
| July | 3.764 | 6.421 | 2.626 | 0.917 |
| August | 3.890 | 6.714 | 3.382 | 0.738 |
| September | 1.809 | 1.358 | 3.332 | 1.726 |
| October | 2.046 | 1.111 | 0.806 | 0.968 |
| November | 3.903 | 4.577 | 3.687 | 0.837 |
| December | 1.528 | 1.438 | 2.969 | 0.798 |
| January | 2.711 | 4.072 | 5.721 | 2.029 |
| **Mean** | 2.670 | 3.426 | 3.177 | 1.360 |

**Table A. 15:- Spatial and monthly variation of total sedimentary nitrogen (mg/g)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 12.56 | 1.019 | 9.595 | 1.320 |
| March | 13.15 | 4.673 | 8.122 | 1.240 |
| April | 7.348 | 1.068 | 3.070 | 0.534 |
| May | 1.931 | 1.861 | 5.384 | 0.531 |
| June | 2.039 | 1.551 | 6.976 | 0.478 |
| July | 2.728 | 1.082 | 2.461 | 0.576 |
| August | 3.515 | 1.239 | 2.734 | 0.989 |
| September | 1.884 | 2.599 | 8.599 | 1.030 |
| October | 12.11 | 3.444 | 4.339 | 0.622 |
| November | 3.325 | 5.199 | 0.380 | 0.716 |
| December | 1.053 | 3.694 | 8.805 | 0.705 |
| January | 9.052 | 2.892 | 10.460 | 1.487 |
| **Mean** | 5.891 | 2.527 | 5.910 | 0.852 |

**Table A. 16:- Spatial and monthly variation of total sedimentary phosphorus (mg/g)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 81.16 | 68.85 | 16.93 | 12.59 |
| March | 86.61 | 76.95 | 29.92 | 13.07 |
| April | 82.06 | 82.27 | 47.83 | 15.99 |
| May | 79.38 | 79.08 | 28.47 | 14.21 |
| June | 77.44 | 80.03 | 32.5 | 15.93 |
| July | 79.21 | 68.53 | 46.62 | 11.65 |
| August | 73.18 | 58.75 | 51.96 | 11.38 |
| September | 69.39 | 65.24 | 37.11 | 12.99 |
| October | 81.66 | 81.93 | 7.662 | 12.89 |
| November | 80.18 | 102.39 | 16.43 | 13.46 |
| December | 112.7 | 82.74 | 39.49 | 12.38 |
| January | 83.21 | 73.02 | 42.80 | 14.15 |
| **Mean** | 78.55 | 76.65 | 33.14 | 13.39 |

**Table A. 17:- Spatial and monthly variation of total organic carbon (mg/g)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 27.89 | 43.00 | 6.17 | 7.67 |
| March | 78.59 | 24.18 | 8.52 | 8.43 |
| April | 31.58 | 28.84 | 44.50 | 15.89 |
| May | 36.11 | 21.32 | 7.88 | 9.64 |
| June | 21.64 | 19.64 | 6.97 | 6.03 |
| July | 21.04 | 10.67 | 17.75 | 12.70 |
| August | 18.81 | 8.75 | 15.36 | 15.43 |
| September | 38.37 | 48.03 | 11.14 | 7.53 |
| October | 39.92 | 73.76 | 9.51 | 13.32 |
| November | 20.54 | 22.37 | 4.46 | 16.08 |
| December | 73.74 | 57.53 | 13.30 | 15.51 |
| January | 30.69 | 17.93 | 7.48 | 6.98 |
| **Mean** | **36.58** | **31.33** | **12.75** | **11.27** |

**Table A. 18:- Spatial and monthly variation of C/N ratio**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 6.46 | 67.57 | 1.76 | 9.54 |
| March | 6.59 | 16.47 | 3.68 | 10.54 |
| April | 11.17 | 77.03 | 15.58 | 29.94 |
| May | 41.11 | 42.49 | 5.29 | 26.76 |
| June | 37.98 | 51.60 | 4.66 | 33.33 |
| July | 29.04 | 63.34 | 18.94 | 20.23 |
| August | 20.82 | 47.42 | 19.01 | 11.51 |
| September | 36.83 | 25.10 | 4.32 | 12.61 |
| October | 6.74 | 23.79 | 1.77 | 20.72 |
| November | 24.11 | 19.69 | 43.24 | 18.80 |
| December | 106.98 | 22.40 | 4.48 | 17.56 |
| January | 9.19 | 25.25 | 4.09 | 9.52 |
| **Mean** | **28.08** | **40.18** | **10.57** | **18.42** |

**Table A. 19:- Spatial and monthly variation of C/P ratio**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 0.23 | 1.57 | 0.29 | 1.24 |
| March | 0.08 | 0.68 | 0.43 | 1.25 |
| April | 0.35 | 2.67 | 0.35 | 1.88 |
| May | 1.14 | 1.99 | 0.67 | 2.78 |
| June | 1.76 | 2.63 | 0.67 | 5.52 |
| July | 1.38 | 5.93 | 1.07 | 1.59 |
| August | 1.11 | 5.42 | 1.24 | 0.75 |
| September | 0.96 | 0.52 | 0.39 | 1.68 |
| October | 0.17 | 0.32 | 0.19 | 1.56 |
| November | 1.17 | 0.88 | 9.70 | 1.17 |
| December | 1.45 | 0.39 | 0.34 | 1.13 |
| January | 0.30 | 1.41 | 0.55 | 1.36 |
| **Mean** | **0.84** | **2.03** | **1.32** | **1.83** |

**Table A. 20:- Spatial and monthly variation of N/P ratio**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 0.957 | 0.978 | 1.446 | 0.377 |
| March | 1.050 | 3.111 | 4.459 | 1.446 |
| April | 8.370 | 4.586 | 6.42 | 3.898 |
| May | 4.202 | 2.433 | 1.791 | 2.721 |
| June | 3.050 | 3.667 | 0.91 | 1.898 |
| July | 0.961 | 0.951 | 64.77 | 4.243 |
| August | 1.404 | 2.145 | 2.597 | 0.129 |
| September | 1.873 | 3.434 | 2.448 | 0.416 |
| October | 2.081 | 4.618 | 3.746 | 1.684 |
| November | 1.843 | 3.508 | 1.139 | 1.605 |
| December | 4.301 | 2.239 | 0.336 | 4.142 |
| January | 2.477 | 0.919 | 0.495 | 3.508 |
| **Mean** | **2.714** | **2.716** | **7.546** | **2.172** |

**Table A. 21:- Spatial and monthly variation of dissolved monosaccharides (ppm)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 0.984 | 0.56 | 1.195 | 0.711 |
| March | 0.711 | 1.377 | 1.831 | 0.499 |
| April | 0.58 | 0.364 | 0.246 | 0.01 |
| May | 0.711 | 1.195 | 0.711 | 0.802 |
| June | 0.364 | 1.424 | 1.108 | 0.01 |
| July | 0.514 | 1.14 | 0.573 | 0.186 |
| August | 0.335 | 2.91 | 0.46 | 0.81 |
| September | 1.407 | 1.922 | 0.651 | 0.893 |
| October | 0.53 | 2.043 | 0.59 | 0.469 |
| November | 0.53 | 1.377 | 0.923 | 0.469 |
| December | 0.651 | 1.68 | 0.741 | 0.287 |
| January | 0.469 | 1.165 | 0.62 | 0.499 |
| **Mean** | **0.649** | **1.430** | **0.804** | **0.470** |

**Table A. 22:- Spatial and monthly variation of dissolved tannin and lignin (ppm)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 11.09 | 8.75 | 10.26 | 1.350 |
| March | 12.54 | 14.10 | 8.530 | 2.160 |
| April | 10.10 | 7.520 | 13.55 | 0.190 |
| May | 4.500 | 7.760 | 6.910 | 0.400 |
| June | 7.330 | 9.730 | 11.53 | 0.340 |
| July | 8.480 | 7.470 | 13.82 | 0.320 |
| August | 8.840 | 5.600 | 22.13 | 0.180 |
| September | 3.310 | 9.480 | 8.420 | 0.280 |
| October | 5.250 | 8.040 | 2.340 | 0.280 |
| November | 9.240 | 9.540 | 5.960 | 0.160 |
| December | 4.350 | 13.19 | 13.74 | 2.160 |
| January | 7.210 | 8.630 | 13.21 | 0.260 |
| **Mean** | **7.69** | **9.15** | **10.87** | **0.673** |

**Table A. 23:- Spatial and monthly variation of sedimentary carbohydrates (mg/g)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 22.22 | 16.28 | 15.26 | 0.730 |
| March | 30.61 | 32.5 | 25.78 | 1.170 |
| April | 0.540 | 5.510 | 6.720 | 1.900 |
| May | 2.000 | 10.53 | 17.36 | 1.280 |
| June | 3.400 | 15.24 | 10.93 | 1.670 |
| July | 17.37 | 23.04 | 33.67 | 0.690 |
| August | 15.79 | 25.23 | 32.43 | 0.240 |
| September | 7.940 | 24.52 | 23.88 | 0.810 |
| October | 31.30 | 21.32 | 3.840 | 0.720 |
| November | 24.31 | 24.46 | 16.59 | 1.100 |
| December | 9.950 | 26.09 | 48.69 | 0.89 |
| January | 13.85 | 18.09 | 33.49 | 0.74 |
| **Mean** | **14.94** | **20.23** | **22.39** | **0.995** |

**Table A. 24:- Spatial and monthly variation of sedimentary protein (mg/g)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 2.06 | 1.21 | 1.44 | 0.21 |
| March | 2.06 | 2.68 | 2.78 | 0.31 |
| April | 2.37 | 5.51 | 2.51 | 0.46 |
| May | 4.14 | 3.27 | 3.29 | 0.45 |
| June | 3.56 | 1.99 | 3.06 | 0.77 |
| July | 3.06 | 2.56 | 4.04 | 0.38 |
| August | 3.81 | 4.39 | 3.05 | 0.26 |
| September | 0.88 | 2.63 | 3.15 | 0.24 |
| October | 1.82 | 2.54 | 0.99 | 0.35 |
| November | 3.53 | 2.47 | 1.65 | 0.25 |
| December | 1.09 | 1.99 | 2.25 | 0.24 |
| January | 1.91 | 1.86 | 2.65 | 0.22 |
| **Mean** | **2.524** | **2.758** | **2.572** | **0.345** |

**Table A. 25:- Spatial and monthly variation of sedimentary total lipid (mg/g)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 8.81 | 4.35 | 2.93 | 0.32 |
| March | 8.9 | 7.95 | 7.09 | 0.93 |
| April | 9.33 | 5.85 | 6.47 | 1.18 |
| May | 2.53 | 8.13 | 4.52 | 0.44 |
| June | 4.95 | 8.36 | 7.29 | 0.9 |
| July | 6.16 | 5.00 | 9.50 | 0.31 |
| August | 5.59 | 6.32 | 11.41 | 0.14 |
| September | 0.72 | 8.18 | 8.44 | 0.39 |
| October | 6.57 | 8.01 | 0.18 | 0.44 |
| November | 8.87 | 10.15 | 2.37 | 0.15 |
| December | 2.82 | 6.65 | 9.64 | 0.41 |
| January | 5.45 | 5.51 | 10.46 | 0.31 |
| **Mean** | **5.892** | **7.038** | **6.692** | **0.493** |

**Table A. 26:- Spatial and monthly variation of sedimentary tannin and lignin (mg/g)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 13.66 | 12.71 | 60.60 | 10.72 |
| March | 14.48 | 18.32 | 28.51 | 16.53 |
| April | 12.31 | 9.14 | 28.33 | 1.19 |
| May | 5.67 | 9.81 | 24.27 | 2.81 |
| June | 9.47 | 12.16 | 35.48 | 2.13 |
| July | 10.71 | 10.90 | 29.64 | 2.75 |
| August | 12.08 | 9.53 | 42.59 | 1.58 |
| September | 4.77 | 14.53 | 22.69 | 2.16 |
| October | 6.43 | 9.81 | 30.54 | 2.17 |
| November | 11.52 | 9.32 | 36.28 | 1.19 |
| December | 3.86 | 15.94 | 34.79 | 17.45 |
| January | 8.66 | 11.82 | 30.86 | 1.84 |
| **Mean** | **9.47** | **12.00** | **33.72** | **5.21** |

**Table A. 27:- Spatial and monthly variation of CHO/TOC ratio**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 27.38 | 23.65 | 90.14 | 5.80 |
| March | 35.34 | 42.24 | 86.16 | 8.95 |
| April | 0.66 | 6.70 | 14.05 | 11.88 |
| May | 2.52 | 13.32 | 60.98 | 9.01 |
| June | 4.39 | 19.04 | 33.63 | 10.48 |
| July | 21.93 | 33.62 | 72.22 | 5.92 |
| August | 21.58 | 42.94 | 62.41 | 2.11 |
| September | 11.44 | 37.58 | 64.35 | 6.24 |
| October | 38.33 | 26.02 | 50.12 | 5.59 |
| November | 30.32 | 23.89 | 100.97 | 8.17 |
| December | 8.83 | 31.53 | 123.30 | 7.19 |
| January | 16.64 | 24.77 | 78.25 | 5.23 |
| **Mean** | **18.28** | **27.11** | **69.71** | **7.21** |

**Table A. 28:- Spatial and monthly variation of protein/TOC ratio**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 2.54 | 1.76 | 8.51 | 1.67 |
| March | 2.38 | 3.48 | 9.29 | 2.37 |
| April | 2.89 | 6.70 | 5.25 | 2.88 |
| May | 5.22 | 4.14 | 11.56 | 3.17 |
| June | 4.60 | 2.49 | 9.42 | 4.83 |
| July | 3.86 | 3.74 | 8.67 | 3.26 |
| August | 5.21 | 7.47 | 5.87 | 2.28 |
| September | 1.27 | 4.03 | 8.49 | 1.85 |
| October | 2.23 | 3.10 | 12.92 | 2.72 |
| November | 4.40 | 2.41 | 10.04 | 1.86 |
| December | 0.97 | 2.41 | 5.70 | 1.94 |
| January | 2.30 | 2.55 | 6.19 | 1.55 |
| **Mean** | **3.15** | **3.69** | **8.49** | **2.53** |

**Table A. 29:- Spatial and monthly variation of lipid/TOC ratio**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 10.86 | 6.32 | 17.31 | 2.54 |
| March | 10.28 | 10.33 | 23.70 | 7.12 |
| April | 11.37 | 7.11 | 13.53 | 7.38 |
| May | 3.19 | 10.28 | 15.88 | 3.10 |
| June | 6.39 | 10.45 | 22.43 | 5.65 |
| July | 7.78 | 7.30 | 20.38 | 2.66 |
| August | 7.64 | 10.76 | 21.96 | 1.23 |
| September | 1.04 | 12.54 | 22.74 | 3.00 |
| October | 8.05 | 9.78 | 2.35 | 3.41 |
| November | 11.06 | 9.91 | 14.42 | 1.11 |
| December | 2.50 | 8.04 | 24.41 | 3.31 |
| January | 6.55 | 7.55 | 24.44 | 2.19 |
| **Mean** | **7.22** | **9.20** | **18.63** | **3.56** |

**Table A. 30:- Spatial and monthly variation of tannin and lignin/TOC ratio**

| **Month** | **Station1** | **Station 2** | **Station 3** | **Station R** |
|---|---|---|---|---|
| February | 56.73 | 63.18 | 114.3 | 36.45 |
| March | 95.88 | 117.9 | 252.0 | 37.68 |
| April | 53.15 | 34.05 | 104.7 | 25.60 |
| May | 121.0 | 49.23 | 249.9 | 115.3 |
| June | 39.33 | 118.9 | 53.83 | 107.9 |
| July | 44.05 | 108.6 | 143.7 | 72.33 |
| August | 38.38 | 81.53 | 26.60 | 88.43 |
| September | 47.58 | 93.58 | 65.38 | 90.00 |
| October | 133.2 | 105.8 | 260.3 | 99.50 |
| November | 129.3 | 189.7 | 173.6 | 37.35 |
| December | 93.05 | 118.3 | 72.05 | 76.53 |
| January | 217.6 | 88.48 | 51.30 | 95.50 |
| **Mean** | **89.09** | **97.43** | **130.64** | **73.55** |

**Table A. 31:- Spatial and monthly variation of dissolved iron (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 12.69 | 23.02 | 3.200 | 6.110 |
| March | 11.63 | 3.060 | 12.83 | 8.800 |
| April | 244.7 | 253.5 | 9.660 | 15.52 |
| May | 30.55 | 30.65 | 12.48 | 10.11 |
| June | 18.59 | 17.83 | 20.71 | 9.000 |
| July | 27.05 | 19.18 | 6.250 | 23.89 |
| August | 8.040 | 7.560 | 8.600 | 4.620 |
| September | 10.12 | 41.38 | 20.68 | 23.30 |
| October | 18.16 | 8.610 | 12.53 | 11.91 |
| November | 43.28 | 88.03 | 6.930 | 21.16 |
| December | 8.180 | 38.60 | 15.46 | 6.680 |
| January | 19.67 | 36.40 | 7.360 | 5.980 |
| **Mean** | **37.72** | **47.32** | **11.39** | **12.26** |

**Table A. 32:- Spatial and monthly variation of dissolved manganese (μg/l)**

| **Month** | **Station1** | **Station 2** | **Station 3** | **Station R** |
|---|---|---|---|---|
| February | 68.15 | 50.90 | 20.40 | 23.75 |
| March | 76.40 | 88.25 | 14.53 | 16.13 |
| April | 32.90 | 26.25 | 10.28 | 10.25 |
| May | 45.88 | 33.63 | 22.38 | 7.750 |
| June | 80.50 | 32.38 | 86.00 | 18.50 |
| July | 70.00 | 68.75 | 42.25 | 22.00 |
| August | 56.50 | 24.00 | 13.70 | 28.75 |
| September | 36.63 | 51.50 | 13.25 | 10.50 |
| October | 111.0 | 80.65 | 19.93 | 8.125 |
| November | 104.8 | 37.50 | 12.45 | 10.25 |
| December | 65.75 | 32.63 | 18.53 | 9.125 |
| January | 58.90 | 76.15 | 8.575 | 12.88 |
| **Mean** | **67.28** | **50.21** | **23.52** | **14.83** |

**Table A. 33:- Spatial and monthly variation of dissolved zinc (μg/l)**

| **Month** | **Station1** | **Station 2** | **Station 3** | **Station R** |
|---|---|---|---|---|
| February | 16.90 | 16.30 | 14.50 | 6.300 |
| March | 7.100 | 6.000 | 1.800 | 5.100 |
| April | 7.600 | 7.900 | 11.30 | 8.200 |
| May | 9.500 | 6.900 | 9.000 | 6.200 |
| June | 10.00 | 7.800 | 7.500 | 14.80 |
| July | 4.900 | 8.700 | 7.400 | 17.60 |
| August | 1.000 | 5.000 | 4.300 | 2.300 |
| September | 3.700 | 11.70 | 6.000 | 4.200 |
| October | 9.700 | 10.30 | 13.00 | 6.500 |
| November | 12.30 | 5.700 | 5.600 | 4.200 |
| December | 5.200 | 3.900 | 4.100 | 10.00 |
| January | 7.900 | 10.20 | 4.700 | 11.90 |
| **Mean** | **7.983** | **8.367** | **7.433** | **8.108** |

**Table A. 34:- Spatial and monthly variation of dissolved copper (μg/l)**

| **Month** | **Station1** | **Station 2** | **Station 3** | **Station R** |
|---|---|---|---|---|
| February | 1.330 | 1.190 | 1.860 | 3.900 |
| March | 1.080 | 1.310 | 1.660 | 1.540 |
| April | 0.680 | 0.470 | 0.490 | 0.270 |
| May | 0.610 | 0.660 | 0.820 | 0.170 |
| June | 0.200 | 0.880 | 0.130 | 0.710 |
| July | 0.750 | 1.070 | 0.760 | 0.800 |
| August | 0.300 | 0.970 | 0.340 | 0.390 |
| September | 0.800 | 1.560 | 0.550 | 0.590 |
| October | 0.640 | 1.440 | 1.480 | 1.540 |
| November | 0.530 | 1.280 | 2.330 | 1.540 |
| December | 1.200 | 1.090 | 1.170 | 0.470 |
| January | 0.050 | 1.180 | 2.020 | 0.390 |
| **Mean** | **0.681** | **1.092** | **1.134** | **1.026** |

**Table A. 35:- Spatial and monthly variation of dissolved cobalt (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 3.620 | 8.290 | 2.210 | 1.970 |
| March | 4.840 | 4.550 | 5.480 | 14.140 |
| April | 2.130 | 3.700 | 1.950 | 3.220 |
| May | 2.040 | 3.630 | 1.600 | 3.010 |
| June | 2.520 | 5.030 | 3.520 | 2.360 |
| July | 5.270 | 4.260 | 2.040 | 2.870 |
| August | 6.500 | 2.960 | 7.470 | 4.630 |
| September | 1.260 | 3.310 | 2.340 | 2.890 |
| October | 1.930 | 3.920 | 3.160 | 2.690 |
| November | 5.040 | 2.540 | 3.650 | 1.650 |
| December | 2.460 | 4.020 | 3.080 | 14.530 |
| January | 3.720 | 2.690 | 2.070 | 5.430 |
| **Mean** | **3.444** | **4.075** | **3.214** | **4.949** |

**Table A. 36:- Spatial and monthly variation of dissolved chromium (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 19.53 | 28.85 | 23.46 | 13.56 |
| March | 24.60 | 28.01 | 19.59 | 14.95 |
| April | 6.233 | 9.653 | 8.771 | 7.723 |
| May | 12.98 | 8.683 | 7.519 | 7.946 |
| June | 8.504 | 7.791 | 7.194 | 10.13 |
| July | 4.991 | 11.43 | 11.20 | 14.81 |
| August | 1.857 | 6.158 | 5.599 | 3.486 |
| September | 6.147 | 9.059 | 16.40 | 13.41 |
| October | 16.11 | 8.214 | 11.40 | 15.79 |
| November | 7.741 | 8.909 | 11.37 | 8.716 |
| December | 6.741 | 9.902 | 12.45 | 9.909 |
| January | 8.388 | 24.86 | 13.19 | 5.050 |
| **Mean** | **10.32** | **13.46** | **12.34** | **10.46** |

**Table A. 37:- Spatial and monthly variation of dissolved nickel (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 1.400 | 0.320 | 0.550 | 2.660 |
| March | 0.330 | 0.170 | 2.520 | 0.300 |
| April | 0.260 | 2.110 | 0.330 | 1.670 |
| May | 0.010 | 6.740 | 2.050 | 7.740 |
| June | 0.280 | 1.270 | 0.910 | 0.770 |
| July | 1.600 | 0.110 | 2.670 | 0.330 |
| August | 0.060 | 0.000 | 2.130 | 0.040 |
| September | 0.050 | 0.000 | 0.000 | 0.000 |
| October | 0.000 | 1.140 | 0.070 | 0.240 |
| November | 0.830 | 0.120 | 0.140 | 0.710 |
| December | 4.580 | 2.420 | 1.280 | 1.040 |
| January | 0.790 | 19.090 | 16.830 | 0.530 |
| **Mean** | **0.849** | **2.791** | **2.457** | **1.336** |

**Table A. 38:- Spatial and monthly variation of dissolved cadmium (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 11.03 | 4.050 | 15.26 | 12.91 |
| March | 7.680 | 8.040 | 17.39 | 9.000 |
| April | 4.750 | 6.430 | 4.830 | 6.700 |
| May | 18.92 | 8.660 | 4.620 | 16.64 |
| June | 14.89 | 13.33 | 33.13 | 11.60 |
| July | 19.28 | 18.24 | 42.76 | 14.77 |
| August | 19.36 | 11.18 | 22.71 | 9.250 |
| September | 20.62 | 8.900 | 11.21 | 19.89 |
| October | 20.11 | 22.30 | 17.27 | 25.01 |
| November | 25.96 | 8.930 | 12.85 | 4.590 |
| December | 1.460 | 7.030 | 4.960 | 2.420 |
| January | 8.300 | 1.100 | 18.35 | 7.550 |
| **Mean** | **14.36** | **9.849** | **17.11** | **11.69** |

**Table A. 39:- Spatial and monthly variation of dissolved lead (µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 0.639 | 3.216 | 5.449 | 1.307 |
| March | 0.568 | 1.281 | 1.235 | 2.921 |
| April | 10.05 | 5.918 | 41.67 | 24.79 |
| May | 2.778 | 25.64 | 0.858 | 0.719 |
| June | 10.46 | 24.86 | 0.893 | 14.53 |
| July | 3.581 | 0.012 | 3.636 | 31.18 |
| August | 4.350 | 4.571 | 4.648 | 16.65 |
| September | 6.315 | 7.356 | 3.111 | 2.999 |
| October | 3.119 | 0.670 | 4.042 | 3.399 |
| November | 55.80 | 78.29 | 92.58 | 48.76 |
| December | 20.59 | 46.85 | 52.90 | 23.93 |
| January | 7.154 | 9.072 | 65.91 | 1.526 |
| **Mean** | **10.45** | **17.31** | **23.08** | **14.39** |

**Table A. 40:- Spatial and monthly variation of particulate iron (*$10^3$ µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 2460.4 | 676.5 | 311.4 | 88.84 |
| March | 72.17 | 131.0 | 10.69 | 147.1 |
| April | 104.0 | 320.2 | 940.9 | 416.5 |
| May | 269.1 | 496.6 | 166.0 | 492.3 |
| June | 117.9 | 244.6 | 273.1 | 338.2 |
| July | 336.5 | 15.69 | 81.33 | 138.3 |
| August | 586.9 | 318.5 | 107.7 | 808.1 |
| September | 42.70 | 24.23 | 35.53 | 43.37 |
| October | 51.89 | 593.9 | 88.55 | 28.96 |
| November | 517.2 | 938.5 | 2966.4 | 2218 |
| December | 2032.4 | 5352.5 | 672.5 | 1355.3 |
| January | 7023.4 | 882.3 | 964.1 | 249.7 |
| **Mean** | **1134.6** | **832.9** | **551.5** | **527.1** |

**Table A. 41:- Spatial and monthly variation of particulate manganese (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 522.7 | 714.3 | 42.11 | 42.89 |
| March | 381.9 | 96.97 | 16.87 | 36.21 |
| April | 143.2 | 39.63 | 164.2 | 790.6 |
| May | 192.1 | 43.15 | 150.8 | 314.0 |
| June | 48.31 | 30.45 | 63.34 | 337.7 |
| July | 114.8 | 16.7 | 60.4 | 141.3 |
| August | 732.8 | 34.32 | 16.32 | 103.0 |
| September | 28.19 | 16.66 | 35.53 | 30.86 |
| October | 49.24 | 33.50 | 12.32 | 86.34 |
| November | 1994.3 | 464.3 | 264.7 | 379.8 |
| December | 2352.6 | 1271.5 | 855.4 | 198.7 |
| January | 1937.0 | 364.7 | 1536 | 44.92 |
| **Mean** | **708.1** | **260.5** | **268.2** | **208.9** |

**Table A. 42:- Spatial and monthly variation of particulate zinc (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 65.31 | 6.090 | 4.220 | 21.24 |
| March | 16.83 | 3.110 | 1.600 | 21.14 |
| April | 64.14 | 3.160 | 20.58 | 54.65 |
| May | 13.73 | 2.580 | 24.72 | 28.98 |
| June | 5.010 | 9.490 | 5.230 | 8.690 |
| July | 2.270 | 0.680 | 6.210 | 15.44 |
| August | 8.620 | 15.79 | 14.12 | 24.77 |
| September | 0.950 | 1.340 | 7.600 | 1.600 |
| October | 884.9 | 500.1 | 800.1 | 410.4 |
| November | 1923.3 | 2089.4 | 3369.8 | 1560.8 |
| December | 714.0 | 369.1 | 1231.0 | 252.4 |
| January | 166.4 | 423 | 453.9 | 109.9 |
| **Mean** | **322.1** | **285.3** | **494.9** | **209.2** |

**Table A. 47:- Spatial and monthly variation of particulate cadmium (µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 30.78 | 15.76 | 146.5 | 53.79 |
| March | 31.02 | 22.54 | 57.23 | 38.47 |
| April | 29.42 | 5.830 | 113.4 | 41.46 |
| May | 11.33 | 7.620 | 21.76 | 28.13 |
| June | 8.570 | 13.34 | 16.92 | 41.67 |
| July | 6.640 | 30.90 | 4.600 | 24.03 |
| August | 8.740 | 63.40 | 17.49 | 35.76 |
| September | 5.270 | 9.520 | 17.70 | 15.95 |
| October | 214.8 | 103.5 | 433.4 | 189.1 |
| November | 550.0 | 336.0 | 595.6 | 221.5 |
| December | 280.4 | 438.1 | 556.6 | 360.9 |
| January | 392.1 | 93.03 | 1696.9 | 205.3 |
| **Mean** | **130.8** | **95.0** | **306.5** | **104.7** |

**Table A. 48:- Spatial and monthly variation of particulate lead (µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 10.70 | 15.90 | 32.42 | 7.425 |
| March | 10.27 | 16.86 | 34.81 | 12.82 |
| April | 25.68 | 33.48 | 49.76 | 15.29 |
| May | 28.90 | 37.45 | 30.88 | 13.29 |
| June | 38.58 | 27.71 | 33.80 | 8.657 |
| July | 22.59 | 28.11 | 37.96 | 7.806 |
| August | 37.09 | 30.73 | 43.04 | 5.427 |
| September | 3.469 | 41.27 | 27.31 | 9.397 |
| October | 6.890 | 30.53 | 25.77 | 6.882 |
| November | 24.51 | 46.08 | 7.604 | 7.484 |
| December | 7.006 | 21.54 | 30.14 | 6.325 |
| January | 11.38 | 19.73 | 24.18 | 7.678 |
| **Mean** | **18.92** | **29.12** | **31.47** | **9.040** |

**Table A. 49:- Spatial and monthly variation of sedimentary iron (*$10^3$ µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 15.94 | 13.02 | 5.751 | 5.041 |
| March | 15.81 | 19.45 | 40.72 | 8.183 |
| April | 44.43 | 31.59 | 15.98 | 16.90 |
| May | 27.27 | 25.28 | 53.28 | 17.19 |
| June | 31.49 | 28.18 | 63.54 | 7.044 |
| July | 22.51 | 21.16 | 40.75 | 12.88 |
| August | 25.17 | 21.88 | 47.49 | 11.91 |
| September | 22.93 | 24.53 | 48.95 | 10.03 |
| October | 13.44 | 20.52 | 24.23 | 3.419 |
| November | 27.26 | 22.13 | 4.708 | 6.125 |
| December | 6.600 | 16.14 | 31.74 | 8.564 |
| January | 13.38 | 16.46 | 62.74 | 5.873 |
| **Mean** | **22.186** | **21.695** | **36.657** | **9.430** |

**Table A. 50:- Spatial and monthly variation of sedimentary manganese (*$10^1$µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 163.5 | 56.73 | 41.89 | 66.17 |
| March | 191.5 | 77.13 | 88.78 | 81.78 |
| April | 317.3 | 86.92 | 68.63 | 76.70 |
| May | 191.3 | 87.90 | 97.98 | 81.14 |
| June | 348.5 | 82.33 | 156.8 | 106.1 |
| July | 282.4 | 69.36 | 83.95 | 83.70 |
| August | 289.9 | 75.01 | 107.5 | 47.64 |
| September | 46.67 | 104.1 | 88.29 | 63.54 |
| October | 160.1 | 99.87 | 66.70 | 50.89 |
| November | 362.9 | 104.6 | 19.59 | 67.77 |
| December | 101.7 | 63.58 | 101.5 | 48.66 |
| January | 145.8 | 64.32 | 112.55 | 66.06 |
| **Mean** | **216.8** | **80.98** | **86.18** | **70.01** |

**Table A. 51:- Spatial and monthly variation of sedimentary zinc (µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 24.65 | 12.10 | 17.75 | 5.922 |
| March | 25.93 | 29.58 | 24.00 | 15.28 |
| April | 34.22 | 22.94 | 40.49 | 16.00 |
| May | 29.81 | 24.33 | 27.50 | 12.18 |
| June | 52.38 | 21.72 | 36.89 | 7.773 |
| July | 42.87 | 17.65 | 29.37 | 6.912 |
| August | 38.87 | 20.70 | 32.47 | 3.679 |
| September | 4.780 | 29.80 | 26.57 | 7.631 |
| October | 17.07 | 28.53 | 18.75 | 4.820 |
| November | 49.80 | 30.93 | 3.848 | 6.076 |
| December | 9.240 | 17.66 | 29.05 | 3.357 |
| January | 16.21 | 18.01 | 27.21 | 6.088 |
| **Mean** | **28.82** | **22.83** | **26.16** | **7.976** |

**Table A. 52:- Spatial and monthly variation of sedimentary copper (µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 14.24 | 12.44 | 9.865 | 3.377 |
| March | 11.58 | 18.91 | 17.01 | 8.238 |
| April | 17.31 | 23.48 | 19.15 | 11.90 |
| May | 16.13 | 21.04 | 19.93 | 8.475 |
| June | 23.01 | 23.22 | 24.90 | 7.530 |
| July | 19.33 | 19.28 | 20.79 | 6.770 |
| August | 21.19 | 21.71 | 23.74 | 5.422 |
| September | 4.729 | 26.30 | 12.83 | 2.256 |
| October | 4.630 | 22.73 | 8.811 | 3.475 |
| November | 15.90 | 21.95 | 3.341 | 4.100 |
| December | 4.925 | 14.30 | 15.48 | 4.720 |
| January | 7.169 | 18.11 | 14.58 | 5.496 |
| **Mean** | **13.34** | **20.29** | **15.87** | **5.98** |

**Table A. 53:- Spatial and monthly variation of sedimentary cobalt (µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 81.55 | 71.97 | 78.62 | 36.81 |
| March | 96.95 | 45.33 | 89.26 | 44.06 |
| April | 73.57 | 76.97 | 65.80 | 48.70 |
| May | 56.64 | 82.82 | 66.60 | 27.18 |
| June | 61.79 | 56.46 | 92.14 | 30.51 |
| July | 96.61 | 40.83 | 47.67 | 16.43 |
| August | 70.76 | 61.43 | 70.67 | 21.35 |
| September | 28.58 | 119.4 | 42.24 | 28.17 |
| October | 23.65 | 114.8 | 29.97 | 24.99 |
| November | 68.16 | 94.31 | 26.93 | 33.39 |
| December | 29.90 | 60.88 | 117.9 | 22.97 |
| January | 44.94 | 77.60 | 100.2 | 36.53 |
| **Mean** | **61.09** | **75.23** | **69.01** | **30.92** |

**Table A. 54:- Spatial and monthly variation of sedimentary chromium (µg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 48.02 | 40.61 | 46.00 | 14.10 |
| March | 44.61 | 56.74 | 47.86 | 22.60 |
| April | 53.70 | 64.33 | 73.44 | 30.10 |
| May | 45.39 | 66.16 | 57.11 | 21.67 |
| June | 71.15 | 60.36 | 71.99 | 17.34 |
| July | 57.12 | 52.20 | 55.69 | 13.44 |
| August | 57.47 | 59.75 | 64.72 | 9.101 |
| September | 8.224 | 83.42 | 47.98 | 14.78 |
| October | 26.48 | 80.46 | 28.79 | 12.78 |
| November | 65.54 | 86.82 | 13.21 | 13.24 |
| December | 15.43 | 49.39 | 57.51 | 13.19 |
| January | 26.75 | 55.02 | 50.16 | 16.00 |
| **Mean** | **43.32** | **62.94** | **51.21** | **16.53** |

**Table A. 55:- Spatial and monthly variation of sedimentary nickel (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 2.888 | 0.436 | 0.149 | 1.321 |
| March | 0.584 | 1.876 | 1.002 | 0.897 |
| April | 8.876 | 2.239 | 3.474 | 2.700 |
| May | 4.131 | 2.493 | 2.674 | 0.974 |
| June | 4.343 | 1.351 | 4.029 | 0.437 |
| July | 2.741 | 1.335 | 2.443 | 1.988 |
| August | 4.342 | 1.515 | 2.836 | 2.614 |
| September | 0.874 | 2.528 | 3.381 | 1.248 |
| October | 3.136 | 2.212 | 0.871 | 1.457 |
| November | 4.678 | 1.889 | 0.456 | 0.543 |
| December | 0.812 | 0.812 | 3.051 | 0.924 |
| January | 1.684 | 1.912 | 2.205 | 1.078 |
| **Mean** | **3.257** | **1.716** | **2.214** | **1.349** |

**Table A. 56:- Spatial and monthly variation of sedimentary cadmium (μg/l)**

| Month | Station1 | Station 2 | Station 3 | Station R |
|---|---|---|---|---|
| February | 43.33 | 27.59 | 27.27 | 6.363 |
| March | 37.46 | 22.71 | 33.73 | 8.671 |
| April | 56.21 | 44.78 | 63.02 | 28.00 |
| May | 56.24 | 48.36 | 56.00 | 31.17 |
| June | 94.11 | 49.55 | 86.41 | 23.80 |
| July | 72.44 | 30.16 | 53.94 | 16.57 |
| August | 70.81 | 43.20 | 64.50 | 14.04 |
| September | 17.99 | 52.17 | 56.89 | 46.55 |
| October | 27.88 | 42.03 | 29.71 | 14.57 |
| November | 93.56 | 51.35 | 14.18 | 22.23 |
| December | 21.83 | 28.16 | 63.30 | 14.11 |
| January | 26.46 | 26.03 | 57.63 | 16.70 |
| **Mean** | **51.53** | **38.84** | **50.55** | **20.23** |

**Table A. 57:- Spatial and monthly variation of sedimentary lead (µg/l)**

# Appendix B

## ANOVA

**Salinity**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 1109.73 | 11 | 100.8845 | 5.554131 | 5.84E-05 | 3.974947 |
| Stations | 817.511 | 3 | 272.5037 | 15.00251 | 2.49E-06 | 6.883056 |
| Error | 599.4077 | 33 | 18.16387 | | | |
| Total | 2526.648 | 47 | | | | |

**DO**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 16.89344 | 12 | 1.407787 | 0.745088 | 0.699257 | 2.723155 |
| Stations | 35.71155 | 3 | 11.90385 | 6.300256 | 0.001509 | 4.377114 |
| Error | 68.01924 | 36 | 1.889423 | | | |
| Total | 120.6242 | 51 | | | | |

**pH**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 2.358367 | 11 | 0.214397 | 1.789164 | 0.096655 | 3.974947 |
| Stations | 16.35308 | 3 | 5.451028 | 45.48937 | 7.99E-12 | 6.883056 |
| Error | 3.954417 | 33 | 0.119831 | | | |
| Total | 22.66587 | 47 | | | | |

**Temperature**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 102.2873 | 11 | 9.298845 | 4.843132 | 0.000199 | 3.974947 |
| Stations | 10.81229 | 3 | 3.604097 | 1.877128 | 0.152657 | 6.883056 |
| Error | 63.36021 | 33 | 1.920006 | | | |
| Total | 176.4598 | 47 | | | | |

**Table B. 1:- Two way-ANOVA of hydrographical parameters.**

*Appendix B*

## DIP

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 3490.541 | 11 | 317.322 | 0.968599 | 0.492465 | 3.974947 |
| Stations | 9168.221 | 3 | 3056.074 | 9.32841 | 0.00013 | 6.883056 |
| Error | 10811.11 | 33 | 327.6093 | | | |
| Total | 23469.87 | 47 | | | | |

## TDP

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 2418.088 | 11 | 219.8262 | 0.577984 | 0.832581 | 3.974947 |
| Stations | 12767.89 | 3 | 4255.962 | 11.1901 | 3.2E-05 | 6.883056 |
| Error | 12550.98 | 33 | 380.3327 | | | |
| Total | 27736.95 | 47 | | | | |

## Ammonium

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 22272.88 | 11 | 2024.807 | 1.477826 | 0.186777 | 3.974947 |
| Stations | 37176.17 | 3 | 12392.06 | 9.044466 | 0.000163 | 6.883056 |
| Error | 45214.15 | 33 | 1370.126 | | | |
| Total | 104663.2 | 47 | | | | |

## Nitrite

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 265.7687 | 11 | 24.1608 | 0.546926 | 0.856335 | 2.093252 |
| Stations | 565.2597 | 3 | 188.4199 | 4.265248 | 0.011884 | 2.891568 |
| Error | 1457.795 | 33 | 44.1756 | | | |
| Total | 2288.823 | 47 | | | | |

## Nitrate

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 251.1854 | 11 | 22.83503 | 1.374733 | 0.230583 | 3.974947 |
| Stations | 1281.355 | 3 | 427.1182 | 25.71371 | 9.16E-09 | 6.883056 |
| Error | 548.1472 | 33 | 16.61052 | | | |
| Total | 2080.687 | 47 | | | | |

**Urea**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 2472.542 | 11 | 224.7765 | 2.332732 | 0.029704 | 2.093252 |
| Stations | 945.3502 | 3 | 315.1167 | 3.270283 | 0.033329 | 2.891568 |
| Error | 3179.802 | 33 | 96.35764 | | | |
| Total | 6597.694 | 47 | | | | |

**TDN**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 21032.52 | 11 | 1912.048 | 1.209424 | 0.319261 | 3.974947 |
| Stations | 48515.42 | 3 | 16171.81 | 10.22912 | 6.51E-05 | 6.883056 |
| Error | 52171.61 | 33 | 1580.958 | | | |
| Total | 121719.5 | 47 | | | | |

**Table B. 2:- Two-way ANOVA of dissolved nutrient compounds.**

**Ex.Ammonium**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 33.39878 | 11 | 3.036252 | 1.045568 | 0.431582 | 2.83967 |
| Stations | 55.03975 | 3 | 18.34658 | 6.317856 | 0.001659 | 4.436799 |
| Error | 95.82955 | 33 | 2.903926 | | | |
| Total | 184.2681 | 47 | | | | |

**Total Nitrogen**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 33.4427 | 11 | 3.040246 | 2.522422 | 0.019705 | 2.093252 |
| Stations | 30.51852 | 3 | 10.17284 | 8.440174 | 0.000266 | 2.891568 |
| Error | 39.77451 | 33 | 1.205288 | | | |
| Total | 103.7357 | 47 | | | | |

**Total Phosphorus**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 134.8785 | 11 | 12.26169 | 1.621403 | 0.138297 | 3.974947 |
| Stations | 229.644 | 3 | 76.54799 | 10.12219 | 7.06E-05 | 6.883056 |
| Error | 249.5589 | 33 | 7.562392 | | | |
| Total | 614.0814 | 47 | | | | |

**Total Organic Carbon**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 1012.823 | 11 | 92.07483 | 0.81223 | 0.628143 | 3.974947 |
| Stations | 40352.58 | 3 | 13450.86 | 118.6556 | 9.43E-18 | 6.883056 |
| Error | 3740.896 | 33 | 113.3605 | | | |
| Total | 45106.3 | 47 | | | | |

**Table B. 3:- Two-way ANOVA of sedimentary nutrient compounds**

**Carbohydrate**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 910.804 | 11 | 82.80037 | 0.979444 | 0.483602 | 2.093252 |
| Stations | 228.4422 | 3 | 76.14741 | 0.900747 | 0.451231 | 2.891568 |
| Error | 2789.758 | 33 | 84.53811 | | | |
| Total | 3929.004 | 47 | | | | |

**Tannin & Lignin**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 2.742061 | 11 | 0.249278 | 1.346363 | 0.24412 | 3.974947 |
| Stations | 6.266636 | 3 | 2.088879 | 11.28213 | 3E-05 | 6.883056 |
| Error | 6.109929 | 33 | 0.185149 | | | |
| Total | 15.11863 | 47 | | | | |

**Table B. 4:- Two-way ANOVA of dissolved bioorganic compounds.**

**Carbohydrates**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 122.7148 | 11 | 11.15589 | 1.150152 | 0.357053 | 3.974947 |
| Stations | 720.4775 | 3 | 240.1592 | 24.75997 | 1.41E-08 | 6.883056 |
| Error | 320.0833 | 33 | 9.699493 | | | |
| Total | 1163.276 | 47 | | | | |

**Protein**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 1444.97 | 11 | 131.3609 | 1.885098 | 0.078577 | 3.974947 |
| Stations | 3330.979 | 3 | 1110.326 | 15.93376 | 1.41E-06 | 6.883056 |
| Error | 2299.568 | 33 | 69.68388 | | | |
| Total | 7075.517 | 47 | | | | |

**Total Lipid**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 14.93372 | 11 | 1.357611 | 2.092965 | 0.050032 | 2.093252 |
| Stations | 46.86877 | 3 | 15.62292 | 24.08512 | 1.92E-08 | 2.891568 |
| Error | 21.4056 | 33 | 0.648655 | | | |
| Total | 83.2081 | 47 | | | | |

**Tannin & Lignin**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 28.14748 | 11 | 2.558861 | 0.369396 | 0.959098 | 3.974947 |
| Stations | 337.4202 | 3 | 112.4734 | 16.23661 | 1.17E-06 | 6.883056 |
| Error | 228.5959 | 33 | 6.927148 | | | |
| Total | 594.1635 | 47 | | | | |

**Table B. 5:- Two-way ANOVA of sedimentary bioorganic compounds.**

**Iron**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 46041.08 | 11 | 4185.553 | 1.463031 | 0.192568 | 2.093252 |
| Station | 20906.87 | 3 | 6968.957 | 2.435951 | 0.082158 | 2.891568 |
| Error | 94408.95 | 33 | 2860.877 | | | |
| Total | 161356.9 | 47 | | | | |

**Manganese**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 50072.19 | 11 | 4552.018 | 2.962645 | 0.007715 | 2.093252 |
| Station | 11864.19 | 3 | 3954.73 | 2.573906 | 0.070622 | 2.891568 |
| Error | 50703.53 | 33 | 1536.471 | | | |
| Total | 112639.9 | 47 | | | | |

**Zinc**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 5905.971 | 11 | 536.9064 | 1.501384 | 0.17788 | 3.974947 |
| Station | 20989.3 | 3 | 6996.433 | 19.56454 | 1.81E-07 | 6.883056 |
| Error | 11801.06 | 33 | 357.6078 | | | |
| Total | 38696.33 | 47 | | | | |

**Copper**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 330.5323 | 11 | 30.04839 | 2.544338 | 0.018796 | 2.093252 |
| Station | 5.575625 | 3 | 1.858542 | 0.157371 | 0.92418 | 2.891568 |
| Error | 389.7269 | 33 | 11.80991 | | | |
| Total | 725.8348 | 47 | | | | |

**Cobalt**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 10.32881 | 11 | 0.938982 | 3.096463 | 0.005832 | 1.773344 |
| Station | 1.53359 | 3 | 0.511197 | 1.685763 | 0.189045 | 2.257742 |
| Error | 10.00704 | 33 | 0.303243 | | | |
| Total | 21.86943 | 47 | | | | |

**Chromium**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 100.5524 | 11 | 9.141128 | 1.433697 | 0.204529 | 1.773344 |
| Station | 21.69391 | 3 | 7.231302 | 1.134159 | 0.349551 | 2.257742 |
| Error | 210.4052 | 33 | 6.375914 | | | |
| Total | 332.6515 | 47 | | | | |

**Nickel**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 1176.152 | 11 | 106.9229 | 6.027104 | 2.69E-05 | 3.974947 |
| Station | 83.49167 | 3 | 27.83056 | 1.568772 | 0.215465 | 6.883056 |
| Error | 585.4314 | 33 | 17.74035 | | | |
| Total | 1845.075 | 47 | | | | |

**Cadmium**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 295.4265 | 11 | 26.85696 | 2.60836 | 0.016379 | 2.093252 |
| Station | 30.22779 | 3 | 10.07593 | 0.978579 | 0.414656 | 2.891568 |
| Error | 339.7842 | 33 | 10.29649 | | | |
| Total | 665.4385 | 47 | | | | |

**Lead**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Month | 1539.898 | 11 | 139.9907 | 3.313885 | 0.003724 | 2.093252 |
| Station | 361.6582 | 3 | 120.5527 | 2.853745 | 0.052086 | 2.891568 |
| Error | 1394.042 | 33 | 42.24369 | | | |
| Total | 3295.598 | 47 | | | | |

**Table B. 6:- Two-way ANOVA of dissolved trace metals.**

**Iron**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 16483.67 | 11 | 1498.515 | 8.20326 | 1.12E-06 | 3.974947 |
| Stations | 1017.714 | 3 | 339.2379 | 1.857076 | 0.156112 | 6.883056 |
| Error | 6028.214 | 33 | 182.6731 | | | |
| Total | 23529.6 | 47 | | | | |

**Manganese**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 31888940 | 11 | 2898995 | 1.964606 | 0.066136 | 1.773344 |
| Stations | 2919953 | 3 | 973317.7 | 0.659603 | 0.582772 | 2.257742 |
| Error | 48695172 | 33 | 1475611 | | | |
| Total | 83504065 | 47 | | | | |

**Zinc**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 6624469 | 11 | 602224.4 | 3.188011 | 0.004824 | 2.093252 |
| Stations | 1947998 | 3 | 649332.8 | 3.43739 | 0.02793 | 2.891568 |
| Error | 6233794 | 33 | 188902.9 | | | |
| Total | 14806261 | 47 | | | | |

### Copper

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 860968.7 | 11 | 78269.88 | 2.133586 | 0.045799 | 2.093252 |
| Stations | 116056.5 | 3 | 38685.51 | 1.054542 | 0.381579 | 2.891568 |
| Error | 1210594 | 33 | 36684.67 | | | |
| Total | 2187619 | 47 | | | | |

### Cobalt

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 729.8781 | 11 | 66.35255 | 3.579161 | 0.002177 | 2.093252 |
| Stations | 161.841 | 3 | 53.94701 | 2.909987 | 0.049015 | 2.891568 |
| Error | 611.7731 | 33 | 18.53858 | | | |
| Total | 1503.492 | 47 | | | | |

### Nickel

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 50291.8 | 11 | 4571.982 | 6.124951 | 2.31E-05 | 3.974947 |
| Stations | 3120.341 | 3 | 1040.114 | 1.39341 | 0.262091 | 6.883056 |
| Error | 24632.91 | 33 | 746.4519 | | | |
| Total | 78045.05 | 47 | | | | |

### Cadmium

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 18508765 | 11 | 1682615 | 25.60441 | 4.95E-13 | 3.974947 |
| Stations | 526089.6 | 3 | 175363.2 | 2.668508 | 0.063691 | 6.883056 |
| Error | 2168622 | 33 | 65715.82 | | | |
| Total | 21203477 | 47 | | | | |

### Lead

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 1861804 | 11 | 169254.9 | 3.676375 | 0.001794 | 2.093252 |
| Stations | 355296.2 | 3 | 118432.1 | 2.572455 | 0.070735 | 2.891568 |
| Error | 1519272 | 33 | 46038.54 | | | |
| Total | 3736372 | 47 | | | | |

**Table B. 7:- Two-way ANOVA of particulate trace metals**

### Iron

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 1.32E+09 | 11 | 1.2E+08 | 1.511661 | 0.174121 | 3.974947 |
| Stations | 3.81E+09 | 3 | 1.27E+09 | 16.00509 | 1.35E-06 | 6.883056 |
| Error | 2.62E+09 | 33 | 79401991 | | | |
| Total | 7.75E+09 | 47 | | | | |

### Manganese

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 217799.5 | 11 | 19799.96 | 1.622537 | 0.137966 | 3.974947 |
| Stations | 446378.7 | 3 | 148792.9 | 12.19305 | 1.57E-05 | 6.883056 |
| Error | 402701.9 | 33 | 12203.09 | | | |
| Total | 1066880 | 47 | | | | |

### Zinc

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 38430.17 | 11 | 3493.652 | 1.222456 | 0.311385 | 3.974947 |
| Stations | 172384 | 3 | 57461.34 | 20.10617 | 1.36E-07 | 6.883056 |
| Error | 94310.55 | 33 | 2857.895 | | | |
| Total | 305124.7 | 47 | | | | |

### Copper

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 1124.147 | 11 | 102.1952 | 1.0936 | 0.396128 | 3.974947 |
| Stations | 3119.13 | 3 | 1039.71 | 11.12603 | 3.35E-05 | 6.883056 |
| Error | 3083.797 | 33 | 93.44839 | | | |
| Total | 7327.074 | 47 | | | | |

### Cobalt

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 585.3869 | 11 | 53.21699 | 2.916169 | 0.008508 | 3.974947 |
| Stations | 1293.055 | 3 | 431.0183 | 23.61881 | 2.39E-08 | 6.883056 |
| Error | 602.2149 | 33 | 18.24894 | | | |
| Total | 2480.657 | 47 | | | | |

**Chromium**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 1928.46 | 11 | 175.3145 | 0.266504 | 0.988162 | 3.974947 |
| Stations | 13875.27 | 3 | 4625.09 | 7.03083 | 0.000878 | 6.883056 |
| Error | 21708.39 | 33 | 657.8299 | | | |
| Total | 37512.12 | 47 | | | | |

**Nickel**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 2223.501 | 11 | 202.1365 | 0.842197 | 0.601274 | 3.974947 |
| Stations | 13977.08 | 3 | 4659.026 | 19.41174 | 1.96E-07 | 6.883056 |
| Error | 7920.356 | 33 | 240.0108 | | | |
| Total | 24120.94 | 47 | | | | |

**Cadmium**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 33.67029 | 11 | 3.060935 | 1.886433 | 0.07835 | 3.974947 |
| Stations | 24.71688 | 3 | 8.23896 | 5.077614 | 0.005318 | 6.883056 |
| Error | 53.54596 | 33 | 1.622605 | | | |
| Total | 111.9331 | 47 | | | | |

**Lead**

| *Source of Variation* | *SS* | *df* | *MS* | *F* | *P-value* | *F crit* |
|---|---|---|---|---|---|---|
| Months | 5834.022 | 11 | 530.3656 | 1.889247 | 0.077874 | 3.974947 |
| Stations | 7630.655 | 3 | 2543.552 | 9.060536 | 0.000161 | 6.883056 |
| Error | 9264.045 | 33 | 280.7286 | | | |
| Total | 22728.72 | 47 | | | | |

**Table B. 8:- Two-way ANOVA of sedimentary trace metals.**

# *Appendix C*

## CORRELATION COEFFICIENTS

**Station1**

| | Salinity | DO | pH | Temp |
|---|---|---|---|---|
| Salinity | 1 | | | |
| DO | 0.6083 | 1 | | |
| pH | 0.2062 | -0.6512 | 1 | |
| Temp | 0.8413 | 0.0828 | 0.7024 | 1 |

**Station 2**

| | Salinity | DO | pH | Temp |
|---|---|---|---|---|
| Salinity | 1 | | | |
| DO | 0.7263 | 1 | | |
| pH | -0.7807 | -0.1374 | 1 | |
| Temp | 0.8971 | **0.9553** | -0.4242 | 1 |

**Station 3**

| | Salinity | DO | pH | Temp |
|---|---|---|---|---|
| Salinity | 1 | | | |
| DO | 0.7263 | 1 | | |
| pH | -0.1565 | 0.2856 | 1 | |
| Temp | **0.9994** | 0.9157 | -0.1236 | 1 |

**Station R**

| | Salinity | DO | pH | Temp |
|---|---|---|---|---|
| Salinity | 1 | | | |
| DO | -0.3124 | 1 | | |
| pH | 0.3004 | 0.8122 | 1 | |
| Temp | **0.9717** | -0.0792 | 0.5171 | 1 |

**Table C.1:- Correlation coefficients of hydrographical parameters with each other**

(Significant correlations are given in bold)

## *Appendix C*

### Station 1

| | Salinity | DO | pH | Temp. |
|---|---|---|---|---|
| DIP | -0.4118 | **-0.9738** | 0.8068 | 0.1461 |
| TDP | -0.9436 | -0.8368 | 0.1295 | -0.6149 |
| Ammonium | -0.7331 | **-0.9858** | 0.5144 | -0.2491 |
| Nitrite | -0.9299 | -0.8576 | 0.1682 | -0.5835 |
| Nitrate | 0.7894 | **0.9674** | -0.4379 | 0.3324 |
| Urea | -0.5396 | **-0.9965** | 0.7126 | 0.0011 |
| TDN | -0.7399 | **-0.9840** | 0.5056 | -0.2589 |
| MCHO | **0.9956** | 0.5313 | 0.2970 | 0.8883 |
| T & L | 0.4030 | -0.4812 | **0.9786** | 0.8337 |
| Fe | 0.4390 | **0.9802** | -0.7887 | -0.4390 |
| Mn | 0.8859 | 0.1707 | 0.6366 | **0.9960** |
| Zn | -0.1053 | 0.7252 | **-0.9947** | -0.6261 |
| Cu | **0.9948** | 0.6856 | 0.1060 | 0.7822 |
| Co | 0.9339 | 0.2843 | 0.5425 | **0.9790** |
| Cr | **-0.9558** | -0.8148 | 0.0906 | -0.6452 |
| Ni | **0.9885** | 0.4812 | 0.3519 | 0.9134 |
| Cd | 0.0594 | 0.8284 | **-0.9645** | -0.4896 |
| Pb | **-0.9995** | -0.6325 | -0.1759 | -0.8243 |

### Station 2

| | Salinity | DO | pH | Temp. |
|---|---|---|---|---|
| DIP | 0.7094 | 0.0307 | **-0.9943** | 0.3250 |
| TDP | 0.8446 | 0.2454 | **-0.9939** | 0.5212 |
| Ammonium | -0.0288 | -0.7080 | -0.6022 | -0.4675 |
| Nitrite | 0.0703 | -0.6346 | -0.6783 | -0.3776 |
| Nitrate | 0.2907 | 0.8689 | 0.3710 | 0.6835 |
| Urea | -0.4341 | -0.9345 | -0.2241 | -0.7875 |
| TDN | 0.1260 | -0.5904 | -0.7183 | -0.3252 |
| MCHO | 0.4025 | 0.9216 | 0.2578 | 0.7655 |
| T & L | **-0.9704** | -0.8709 | 0.6065 | **-0.9773** |
| Fe | -0.8907 | -0.3343 | **0.9795** | -0.5982 |
| Mn | 0.9406 | 0.9165 | -0.5222 | **0.9938** |
| Zn | -0.0211 | 0.6719 | 0.6413 | 0.4228 |
| Cu | 0.8778 | 0.3082 | **-0.9847** | 0.5758 |
| Co | -0.9122 | -0.3808 | **0.9682** | -0.6373 |
| Cr | 0.9270 | 0.4155 | **-0.9581** | 0.6659 |
| Ni | 0.9215 | 0.9362 | -0.4767 | **0.9983** |
| Cd | -0.1045 | 0.6078 | 0.7031 | 0.3457 |
| Pb | -0.8850 | **-0.9628** | 0.4000 | **-0.9996** |

**Station 3**

| | Salinity | DO | pH | Temp. |
|---|---|---|---|---|
| DIP | **0.9817** | 0.8032 | -0.3416 | **0.9749** |
| TDP | **0.9817** | 0.8032 | -0.3415 | **0.9749** |
| Ammonium | 0.1573 | 0.5686 | **0.9508** | 0.1901 |
| Nitrite | **0.9999** | 0.9068 | -0.1449 | **0.9998** |
| Nitrate | **0.9468** | 0.7148 | -0.4661 | 0.9355 |
| Urea | 0.9219 | **0.9988** | 0.2383 | 0.9343 |
| TDN | 0.4856 | 0.8156 | 0.7874 | 0.5144 |
| MCHO | -0.4441 | -0.0134 | **0.9544** | -0.4140 |
| T & L | **1.0000** | 0.8986 | -0.1640 | **0.9992** |
| Fe | 0.8217 | 0.4949 | -0.6915 | 0.8023 |
| Mn | -0.7159 | -0.3440 | 0.8016 | -0.6923 |
| Zn | -0.4819 | -0.0561 | 0.9408 | -0.4525 |
| Cu | **0.9919** | 0.8397 | -0.2806 | **0.9871** |
| Co | 0.1521 | -0.2899 | **-1.0000** | 0.1191 |
| Cr | -0.6766 | -0.2920 | 0.8332 | -0.6517 |
| Ni | 0.9291 | 0.6780 | -0.5108 | 0.9162 |
| Cd | -0.4668 | -0.8031 | -0.8004 | -0.4959 |
| Pb | -0.6714 | -0.2853 | 0.8371 | -0.6463 |

**Station R**

| | Salinity | DO | pH | Temp. |
|---|---|---|---|---|
| DIP | -0.7794 | -0.3518 | -0.8318 | -0.9053 |
| TDP | -0.6608 | -0.5066 | -0.9144 | -0.8193 |
| Ammonium | **-0.9794** | 0.1141 | -0.4869 | **-0.9994** |
| Nitrite | **0.9915** | -0.1859 | 0.4222 | **0.9942** |
| Nitrate | -0.0610 | **0.9673** | **0.9337** | 0.1764 |
| Urea | -0.7513 | -0.3922 | -0.8551 | -0.8859 |
| TDN | -0.2673 | **0.9989** | 0.8388 | -0.0322 |
| MCHO | 0.2025 | 0.8670 | **0.9949** | 0.4280 |
| T & L | 0.5991 | **-0.9478** | -0.5838 | 0.3931 |
| Fe | **-0.9991** | 0.2711 | -0.3413 | **-0.9810** |
| Mn | **-0.9981** | -0.1745 | -0.7161 | **-0.9677** |
| Zn | -0.3607 | -0.7733 | **-0.9980** | -0.5708 |
| Cu | **-0.9808** | 0.1210 | -0.4808 | **-0.9991** |
| Co | **0.9909** | -0.1815 | 0.4262 | **0.9947** |
| Cr | 0.6206 | 0.5510 | 0.9343 | 0.7882 |
| Ni | 0.6719 | -0.9134 | -0.5045 | 0.4781 |
| Cd | **0.9816** | -0.4881 | 0.1127 | **0.9087** |
| Pb | -0.4525 | -0.7058 | **-0.9865** | -0.6502 |

**Table C. 2: Correlation coefficients of dissolved components with hydrographical parameters.**

*Appendix C*

**Station 1**

| | Salinity | DO | pH | Temp. | % of sand | % of silt | % of clay |
|---|---|---|---|---|---|---|---|
| Ex.Ammo. | -0.4091 | **-0.9731** | 0.8085 | 0.1491 | -0.9313 | 0.9045 | **0.9545** |
| TN | **-0.9901** | -0.7139 | -0.0665 | -0.7569 | -0.8048 | 0.8432 | 0.7614 |
| TP | **0.9968** | 0.6696 | 0.1277 | 0.7956 | 0.7668 | -0.8086 | -0.7202 |
| TOC | 0.5858 | **0.9996** | -0.6722 | 0.0548 | **0.9859** | **-0.9722** | **-0.9952** |
| STCHO | 0.7471 | -0.0732 | 0.8045 | **0.9878** | 0.0670 | -0.1345 | 0.0028 |
| SP | 0.3448 | **0.9548** | -0.8474 | -0.2173 | 0.9038 | -0.8727 | -0.9315 |
| TSL | -0.3996 | **-0.9706** | 0.8146 | 0.1594 | -0.9275 | 0.9000 | **0.9513** |
| T & L | **0.9993** | 0.5786 | 0.2422 | 0.8607 | 0.6870 | -0.7347 | -0.6346 |
| Fe | -0.0147 | 0.7014 | **-0.9977** | -0.5528 | **-0.9783** | **0.9620** | **0.9904** |
| Mn | 0.5153 | **0.9720** | -0.8114 | -0.0297 | -0.7221 | 0.6736 | 0.7686 |
| Zn | -0.0424 | 0.6814 | **-0.9992** | -0.5757 | **-0.9844** | **0.9701** | **0.9943** |
| Cu | -0.0347 | 0.6870 | **-0.9988** | -0.5694 | **-0.9823** | **0.9673** | **0.9930** |
| Co | 0.2648 | 0.8724 | -0.9391 | -0.2985 | -0.8821 | 0.8481 | 0.9128 |
| Cr | 0.7680 | **0.9953** | -0.5747 | 0.2999 | -0.4545 | 0.3931 | 0.5156 |
| Ni | 0.4622 | **0.9559** | -0.8454 | -0.0904 | -0.7770 | 0.7325 | 0.8190 |
| Cd | **0.9456** | 0.8957 | -0.2459 | 0.6197 | -0.1078 | 0.0402 | 0.1769 |
| Pb | -0.2615 | 0.5033 | **-0.9835** | -0.7417 | **-0.9992** | **0.9996** | **0.9938** |

**Station 2**

| | Salinity | DO | pH | Temp. | % of sand | % of silt | % of clay |
|---|---|---|---|---|---|---|---|
| Ex.Ammo. | **0.9964** | 0.6650 | -0.8311 | 0.8561 | 0.5245 | -0.6701 | 0.2315 |
| TN | -0.5210 | **-0.9651** | -0.1266 | -0.8445 | **-0.9960** | **0.9633** | 0.7672 |
| TP | -0.2415 | 0.4917 | 0.7950 | 0.2121 | 0.6360 | -0.4857 | **-0.9954** |
| TOC | **-0.9995** | -0.7033 | 0.8008 | -0.8821 | -0.5685 | 0.7081 | -0.1801 |
| STCHO | 0.3874 | 0.9151 | 0.2737 | 0.7549 | **0.9714** | -0.9123 | -0.8546 |
| SP | **-0.9937** | -0.6448 | 0.8457 | -0.8420 | -0.5016 | 0.6500 | -0.2574 |
| TSL | 0.6931 | 0.0079 | **-0.9916** | 0.3033 | -0.1666 | -0.0147 | 0.8153 |
| T & L | -0.7708 | -0.1220 | **0.9999** | -0.4101 | 0.0530 | 0.1287 | -0.7439 |
| Fe | **-0.9970** | 0.4928 | -0.9296 | -0.9285 | -0.8506 | 0.9318 | 0.2293 |
| Mn | -0.2821 | -0.7491 | -0.5533 | 0.1708 | -0.4118 | 0.2399 | 0.9357 |
| Zn | -0.8479 | 0.8398 | -0.6531 | **-0.9949** | -0.8458 | 0.7351 | **0.9752** |
| Cu | -0.1627 | **0.9625** | 0.1364 | -0.5819 | 0.3076 | -0.1302 | -0.8905 |
| Co | -0.8903 | -0.0346 | **-0.9852** | -0.5976 | **-1.0000** | **0.9838** | 0.7055 |
| Cr | -0.0370 | 0.9206 | 0.2603 | -0.4747 | 0.4248 | -0.2537 | 0.9406 |
| Ni | -0.6470 | **0.9649** | -0.3925 | **-0.9173** | -0.2258 | 0.3985 | -0.5295 |
| Cd | **0.9805** | -0.5937 | 0.8786 | **0.9664** | 0.7811 | -0.8813 | -0.1105 |
| Pb | -0.9099 | 0.0104 | **-0.9919** | -0.6330 | **-0.9997** | **0.9875** | 0.6900 |

**Station 3**

| | Salinity | DO | pH | Temp. | % of sand | % of silt | % of clay |
|---|---|---|---|---|---|---|---|
| Ex.Ammo. | 0.6469 | 0.2540 | -0.8544 | 0.6212 | 0.6809 | -0.7359 | -0.6180 |
| TN | **-0.9788** | -0.7942 | 0.3555 | **-0.9714** | -0.0879 | 0.1653 | 0.0053 |
| TP | 0.8379 | 0.5199 | -0.6702 | 0.8193 | 0.4431 | -0.5116 | -0.3675 |
| TOC | -0.3087 | 0.1326 | **0.9878** | -0.2769 | **-0.9081** | **0.9380** | 0.8704 |
| STCHO | -0.3855 | 0.0510 | **0.9717** | -0.3546 | -0.8708 | 0.9064 | 0.8272 |
| SP | **-0.9955** | **-0.9389** | 0.0618 | **-0.9981** | 0.2120 | -0.1352 | -0.2920 |
| TSL | -0.1398 | 0.3018 | **0.9999** | -0.1067 | **-0.9668** | **0.9838** | 0.9423 |
| T & L | -0.6248 | -0.2261 | 0.8690 | -0.5984 | -0.7016 | 0.7550 | 0.6403 |
| Fe | 0.5547 | 0.7571 | 0.8423 | 0.5268 | -0.9063 | 0.8706 | 0.9381 |
| Mn | -0.5874 | 0.8757 | -0.2127 | -0.6140 | -0.7114 | 0.7640 | 0.6509 |
| Zn | -0.5356 | 0.9042 | -0.1512 | -0.5634 | -0.7538 | 0.8028 | 0.6970 |
| Cu | 0.1651 | **0.9583** | 0.5475 | 0.1322 | **-0.9999** | **0.9958** | **0.9976** |
| Co | 0.0844 | **0.9784** | 0.4777 | 0.0512 | **-0.9977** | **0.9999** | **0.9888** |
| Cr | 0.8932 | -0.5566 | 0.6372 | 0.9077 | 0.3100 | -0.3832 | -0.2304 |
| Ni | 0.3294 | 0.8963 | 0.6810 | 0.2978 | **-0.9832** | **0.9660** | **0.9949** |
| Cd | -0.4246 | **0.9509** | -0.0250 | -0.4545 | -0.8309 | 0.8718 | 0.7821 |
| Pb | -0.3890 | **0.9622** | 0.0140 | -0.4194 | -0.8521 | 0.8903 | 0.8060 |

**Station R**

| | Salinity | DO | pH | Temp. | % of sand | % of silt | % of clay |
|---|---|---|---|---|---|---|---|
| Ex.Ammo. | 0.8433 | -0.7740 | -0.2593 | 0.6925 | -0.9369 | -0.1591 | 0.9189 |
| TN | -0.0239 | -0.9422 | **-0.9607** | -0.2593 | -0.7838 | 0.7627 | 0.1375 |
| TP | 0.8362 | 0.2597 | 0.7743 | 0.9421 | -0.0657 | **-0.9656** | 0.7370 |
| TOC | **0.9972** | -0.3831 | 0.2277 | **0.9512** | -0.6606 | -0.6066 | **0.9963** |
| STCHO | **0.9469** | 0.0096 | 0.5911 | **0.9960** | -0.3135 | -0.8697 | 0.8828 |
| SP | **0.9599** | -0.5661 | 0.0210 | 0.8666 | -0.8018 | -0.4287 | **0.9925** |
| TSL | -0.1573 | -0.8890 | **-0.9892** | -0.3860 | -0.6938 | 0.8423 | 0.0038 |
| T & L | 0.8610 | -0.7521 | -0.2265 | 0.7165 | -0.9245 | -0.1924 | 0.9317 |
| Fe | 0.7802 | -0.1319 | -0.6854 | **0.9058** | -0.8836 | -0.2858 | **0.9623** |
| Mn | 0.2040 | -0.7324 | **-0.9920** | 0.4294 | **-0.9795** | 0.3897 | 0.5688 |
| Zn | 0.0395 | -0.8348 | **-0.9992** | 0.2744 | -0.9331 | 0.5357 | 0.4260 |
| Cu | 0.7464 | -0.1836 | -0.7225 | 0.8824 | -0.9069 | -0.2352 | **0.9467** |
| Co | 0.6715 | -0.2870 | -0.7919 | 0.8275 | **-0.9465** | -0.1306 | 0.9071 |
| Cr | **0.9829** | 0.3506 | -0.2616 | **0.9986** | -0.5589 | -0.7035 | **0.9770** |
| Ni | 0.8629 | 0.0138 | -0.5721 | **0.9579** | -0.8063 | -0.4219 | **0.9916** |
| Cd | -0.1813 | -0.1813 | **-0.9660** | 0.0560 | -0.8306 | 0.7090 | 0.2156 |
| Pb | -0.7704 | -0.9441 | -0.5746 | -0.5980 | -0.2800 | **0.9963** | -0.4609 |

**Table C. 3: Correlation coefficients of sedimentary components with hydrographical and sedimentary parameters.**

## *Appendix C*

### Station 1

| | Salinity | DO | pH | Temp |
|---|---|---|---|---|
| Fe | -0.0790 | 0.7432 | **-0.9917** | -0.6053 |
| Mn | 0.2583 | 0.9239 | -0.8920 | -0.3048 |
| Zn | 0.1092 | 0.8554 | **-0.9501** | -0.4454 |
| Cu | 0.3993 | **0.9706** | -0.8148 | -0.1596 |
| Co | 0.3458 | **0.9551** | -0.8468 | -0.2163 |
| Cr | 0.1320 | 0.8670 | -0.9427 | -0.4247 |
| Ni | 0.3876 | **0.9674** | -0.8221 | -0.1722 |
| Cd | 0.0917 | 0.8461 | **-0.9555** | -0.4611 |
| Pb | 0.1035 | 0.8524 | **-0.9519** | -0.4505 |

### Station 2

| | Salinity | DO | pH | Temp |
|---|---|---|---|---|
| Fe | -0.4690 | 0.2664 | 0.9181 | -0.0306 |
| Mn | -0.3424 | 0.3971 | 0.8545 | 0.1079 |
| Zn | -0.0832 | 0.6246 | 0.6877 | 0.3656 |
| Cu | -0.2852 | 0.4517 | 0.8216 | 0.1676 |
| Co | -0.4696 | 0.2659 | 0.9183 | -0.0312 |
| Cr | -0.4208 | 0.3180 | 0.8954 | 0.0233 |
| Ni | -0.2955 | 0.4421 | 0.8277 | 0.1570 |
| Cd | -0.4661 | 0.2697 | 0.9168 | -0.0272 |
| Pb | -0.4703 | 0.2651 | 0.9187 | -0.0320 |

### Station 3

| | Salinity | DO | pH | Temp |
|---|---|---|---|---|
| Fe | -0.2922 | -0.6767 | -0.8988 | -0.3239 |
| Mn | -0.2522 | -0.7467 | -0.9163 | -0.2842 |
| Zn | -0.3860 | -0.7467 | -0.8507 | -0.4165 |
| Cu | 0.1388 | -0.3027 | **-0.9998** | 0.1057 |
| Co | -0.4210 | -0.7716 | -0.8300 | -0.4509 |
| Cr | -0.4944 | -0.8214 | -0.7811 | -0.5231 |
| Ni | -0.0594 | -0.4849 | **-0.9766** | -0.0926 |
| Cd | -0.4487 | -0.7908 | -0.8124 | -0.4782 |
| Pb | -0.3817 | -0.7435 | -0.8532 | -0.4122 |

**Station R**

| | Salinity | DO | pH | Temp |
|---|---|---|---|---|
| Fe | -0.8504 | 0.7655 | 0.2464 | -0.7021 |
| Mn | -0.2755 | **0.9993** | 0.8342 | -0.0407 |
| Zn | **0.9894** | -0.4471 | 0.1587 | 0.9271 |
| Cu | -0.1326 | **0.9830** | 0.9056 | 0.1052 |
| Co | **-0.9526** | 0.5865 | 0.0040 | -0.8538 |
| Cr | -0.8936 | 0.7056 | 0.1598 | -0.7623 |
| Ni | -0.2908 | **0.9997** | 0.8252 | -0.0567 |
| Cd | -0.1882 | **0.9918** | 0.8802 | 0.0490 |
| Pb | -0.1717 | **0.9895** | 0.8881 | 0.0658 |

**Table C. 4: Correlation coefficients of particulate trace metals with hydrographical parameters**

**Station 1**

| | DIP | TDP | Ammonium | Nitrite | Nitrate | Urea | TDN |
|---|---|---|---|---|---|---|---|
| DIP | 1 | | | | | | |
| TDP | 0.6903 | 1 | | | | | |
| Ammonium | 0.9217 | 0.9169 | 1 | | | | |
| Nitrite | 0.7181 | **0.9992** | 0.9318 | 1 | | | |
| Nitrate | -0.8845 | **-0.9482** | **-0.9962** | **-0.9599** | 1 | | |
| Urea | **0.9894** | 0.7880 | **0.9682** | 0.8114 | -0.9428 | 1 | |
| TDN | 0.9177 | 0.9209 | **0.9999** | 0.9355 | **-0.9970** | **0.9661** | 1 |

**Station 2**

| | DIP | TDP | Ammonium | Nitrite | Nitrate | Urea | TDN |
|---|---|---|---|---|---|---|---|
| DIP | 1 | | | | | | |
| TDP | **0.9765** | 1 | | | | | |
| Ammonium | 0.6841 | 0.5108 | 1 | | | | |
| Nitrite | 0.7530 | 0.5935 | **0.9951** | 1 | | | |
| Nitrate | -0.4682 | -0.2667 | **-0.9648** | -0.9340 | 1 | | |
| Urea | 0.3270 | 0.1156 | 0.9130 | 0.8681 | **-0.9882** | 1 | |
| TDN | 0.7886 | 0.6375 | **0.9880** | **0.9984** | -0.9126 | 0.8390 | 1 |

**Station 3**

| | DIP | TDP | Ammonium | Nitrite | Nitrate | Urea | TDN |
|---|---|---|---|---|---|---|---|
| DIP | 1 | | | | | | |
| TDP | **1.0000** | 1 | | | | | |
| Ammonium | -0.0334 | -0.0334 | 1 | | | | |
| Nitrite | **0.9794** | **0.9795** | 0.1689 | 1 | | | |
| Nitrate | **0.9907** | **0.9907** | -0.1689 | **0.9429** | 1 | | |
| Urea | 0.8314 | 0.8314 | 0.5276 | 0.9264 | 0.7481 | 1 | |
| TDN | 0.3104 | 0.3104 | 0.9397 | 0.4958 | 0.1783 | 0.7863 | 1 |

**Station R**

| | DIP | TDP | Ammonium | Nitrite | Nitrate | Urea | TDN |
|---|---|---|---|---|---|---|---|
| DIP | 1 | | | | | | |
| TDP | **0.9853** | 1 | | | | | |
| Ammonium | 0.8899 | 0.7988 | 1 | | | | |
| Nitrite | -0.8544 | -0.7530 | **-0.9974** | 1 | | | |
| Nitrate | -0.5779 | -0.7089 | -0.1419 | 0.0696 | 1 | | |
| Urea | **0.9991** | **0.9918** | 0.8691 | -0.8310 | -0.6128 | 1 | |
| TDN | -0.3954 | -0.5467 | 0.0672 | -0.1394 | **0.9781** | -0.4351 | 1 |

**Table C. 5: Correlation coefficients of dissolved nutrients with each other**

**Station 1**

| | Ex.Ammo. | TN | TP | TOC |
|---|---|---|---|---|
| Ex.Ammo. | 1 | | | |
| TN | 0.5333 | 1 | | |
| TP | -0.4804 | **-0.9981** | 1 | |
| TOC | **-0.9792** | -0.6940 | 0.6485 | 1 |

**Station 2**

| | Ex.Ammo. | TN | TP | TOC |
|---|---|---|---|---|
| Ex.Ammo. | 1 | | | |
| TN | -0.4463 | 1 | | |
| TP | -0.3234 | -0.7024 | 1 | |
| TOC | **-0.9986** | 0.4927 | 0.2733 | 1 |

**Station 3**

| | Ex.Ammo. | TN | TP | TOC |
|---|---|---|---|---|
| Ex.Ammo. | 1 | | | |
| TN | -0.7894 | 1 | | |
| TP | **0.9583** | -0.9320 | 1 | |
| TOC | -0.9250 | 0.4970 | -0.7778 | 1 |

**Station R**

| | Ex.Ammo. | TN | TP | TOC |
|---|---|---|---|---|
| Ex.Ammo. | 1 | | | |
| TN | 0.5172 | 1 | | |
| TP | 0.4105 | -0.5682 | 1 | |
| TOC | 0.8814 | 0.0516 | 0.7925 | 1 |

**Table C. 6: Correlation coefficients of sedimentary nutrients with each other**

**Station 1**

| | TCHO | SP | SPL | T&L |
|---|---|---|---|---|
| TCHO | 1 | | | |
| SP | -0.3664 | 1 | | |
| SPL | 0.3109 | **-0.9983** | 1 | |
| T&L | 0.7711 | 0.3100 | -0.3655 | 1 |

**Station 2**

| | TCHO | SP | SPL | T&L |
|---|---|---|---|---|
| TCHO | 1 | | | |
| SP | -0.2818 | 1 | | |
| SPL | -0.3960 | -0.7694 | 1 | |
| T&L | 0.2887 | 0.8373 | **-0.9935** | 1 |

**Station 3**

| | TCHO | SP | SPL | T&L |
|---|---|---|---|---|
| TCHO | 1 | | | |
| SP | 0.2959 | 1 | | |
| SPL | **0.9675** | 0.0449 | 1 | |
| T&L | -0.3037 | 0.8202 | -0.5347 | 1 |

**Station R**

| | TCHO | SP | SPL | T&L |
|---|---|---|---|---|
| TCHO | 1 | | | |
| SP | 0.8188 | 1 | | |
| SPL | -0.4664 | 0.1258 | 1 | |
| T&L | 0.6517 | **0.9690** | 0.3669 | 1 |

**Table C.7:- Correlation coefficients of sedimentary bioorganics with each other**

**Station1**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | -0.0279 | 1 | | | | | | | |
| Zn | 0.8473 | -0.5546 | 1 | | | | | | |
| Cu | 0.5277 | 0.8344 | -0.0040 | 1 | | | | | |
| Co | 0.0886 | **0.9932** | -0.4539 | 0.8928 | 1 | | | | |
| Cr | -0.6838 | -0.7103 | -0.1918 | **-0.9807** | -0.7874 | 1 | | | |
| Ni | 0.2979 | **0.9459** | -0.2546 | **0.9681** | **0.9772** | -0.9003 | 1 | | |
| Cd | 0.9230 | -0.4104 | **0.9864** | 0.1603 | -0.3014 | -0.3504 | -0.0923 | 1 | |
| Pb | -0.4665 | -0.8712 | 0.0746 | **-0.9975** | -0.9224 | **0.9644** | **-0.9833** | -0.0902 | 1 |

**Station 2**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | -0.6835 | 1 | | | | | | | |
| Zn | 0.4734 | 0.3195 | 1 | | | | | | |
| Cu | **-0.9996** | 0.6630 | -0.4975 | 1 | | | | | |
| Co | **0.9988** | -0.7190 | 0.4289 | **-0.9970** | 1 | | | | |
| Cr | **-0.9962** | 0.7447 | -0.3945 | **0.9934** | **-0.9993** | 1 | | | |
| Ni | -0.6442 | **0.9986** | 0.3688 | 0.6228 | -0.6815 | 0.7086 | 1 | | |
| Cd | 0.5452 | 0.2393 | **0.9965** | -0.5682 | 0.5028 | -0.4698 | 0.2899 | 1 | |
| Pb | 0.5766 | **-0.9905** | -0.4468 | -0.5538 | 0.6165 | -0.6458 | **-0.9963** | -0.3706 | 1 |

**Station 3**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | **-0.9862** | 1 | | | | | | | |
| Zn | -0.8953 | **0.9568** | 1 | | | | | | |
| Cu | 0.8874 | -0.7987 | -0.5893 | 1 | | | | | |
| Co | 0.6882 | -0.7989 | -0.9393 | 0.2763 | 1 | | | | |
| Cr | **-0.9756** | **0.9985** | **0.9713** | -0.7646 | -0.8307 | 1 | | | |
| Ni | **0.9743** | -0.9234 | -0.7719 | **0.9685** | 0.5069 | -0.9010 | 1 | | |
| Cd | 0.1204 | -0.2833 | -0.5499 | -0.3507 | 0.8031 | -0.3354 | -0.1065 | 1 | |
| Pb | **-0.9740** | **0.9981** | **0.9729** | -0.7600 | -0.8346 | **1.0000** | -0.8979 | -0.3420 | 1 |

**Station R**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | **0.9005** | 1 | | | | | | | |
| Zn | 0.4006 | 0.7592 | 1 | | | | | | |
| Cu | **0.9883** | **0.9563** | 0.5358 | 1 | | | | | |
| Co | **-0.9958** | -0.9367 | -0.4832 | **-0.9981** | 1 | | | | |
| Cr | -0.6538 | -0.9178 | **-0.9552** | -0.7617 | 0.7206 | 1 | | | |
| Ni | -0.6394 | -0.2414 | 0.4484 | -0.5145 | 0.5660 | -0.1637 | 1 | | |
| Cd | **-0.9724** | -0.7742 | -0.1759 | -0.9254 | **0.9469** | 0.4594 | 0.8010 | 1 | |
| Pb | 0.4905 | 0.8207 | **0.9950** | 0.6178 | -0.5685 | **-0.9801** | 0.3565 | -0.2738 | 1 |

**Table C. 8: Correlation coefficients of dissolved trace metals with each other**

**Station 1**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | 0.9426 | 1 | | | | | | | |
| Zn | **0.9823** | **0.9885** | 1 | | | | | | |
| Cu | 0.8824 | **0.9889** | **0.9550** | 1 | | | | | |
| Co | 0.9081 | **0.9958** | **0.9705** | **0.9983** | 1 | | | | |
| Cr | **0.9777** | **0.9917** | **0.9997** | **0.9615** | **0.9757** | 1 | | | |
| Ni | 0.8883 | **0.9907** | **0.9587** | **0.9999** | **0.9990** | **0.9649** | 1 | | |
| Cd | **0.9854** | **0.9857** | **0.9998** | **0.9496** | **0.9661** | **0.9992** | **0.9535** | 1 | |
| Pb | **0.9833** | **0.9876** | **1.0000** | **0.9532** | **0.9691** | **0.9996** | **0.9570** | **0.9999** | 1 |

**Station 2**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | **0.9904** | 1 | | | | | | | |
| Zn | 0.9192 | **0.9648** | 1 | | | | | | |
| Cu | **0.9803** | **0.9982** | **0.9789** | 1 | | | | | |
| Co | **1.0000** | **0.9903** | 0.9189 | **0.9802** | 1 | | | | |
| Cr | **0.9985** | **0.9964** | 0.9390 | **0.9895** | **0.9985** | 1 | | | |
| Ni | **0.9823** | **0.9988** | **0.9766** | **0.9999** | **0.9822** | **0.9910** | 1 | | |
| Cd | **1.0000** | **0.9909** | 0.9205 | **0.9809** | **1.0000** | **0.9987** | **0.9830** | 1 | |
| Pb | **1.0000** | **0.9902** | 0.9186 | **0.9800** | **1.0000** | **0.9985** | **0.9821** | **1.0000** | 1 |

**Station 3**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | **0.9991** | 1 | | | | | | | |
| Zn | **0.9950** | **0.9900** | 1 | | | | | | |
| Cu | 0.9066 | 0.9233 | 0.8600 | 1 | | | | | |
| Co | **0.9905** | **0.9839** | **0.9993** | 0.8399 | 1 | | | | |
| Cr | **0.9758** | **0.9658** | **0.9927** | 0.7922 | **0.9966** | 1 | | | |
| Ni | **0.9720** | **0.9810** | 0.9438 | **0.9803** | 0.9305 | 0.8971 | 1 | | |
| Cd | **0.9858** | **0.9780** | **0.9976** | 0.8228 | **0.9995** | **0.9987** | 0.9188 | 1 | |
| Pb | **0.9955** | **0.9907** | **1.0000** | 0.8624 | **0.9991** | **0.9921** | 0.9453 | **0.9973** | 1 |

**Station R**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | 0.7401 | 1 | | | | | | | |
| Zn | -0.9178 | -0.4122 | 1 | | | | | | |
| Cu | 0.6343 | **0.9893** | -0.2752 | 1 | | | | | |
| Co | **0.9701** | 0.5548 | **-0.9867** | 0.4278 | 1 | | | | |
| Cr | **0.9961** | 0.6777 | **-0.9493** | 0.5635 | **0.9878** | 1 | | | |
| Ni | 0.7507 | **0.9999** | -0.4267 | **0.9869** | 0.5681 | 0.6894 | 1 | | |
| Cd | 0.6768 | **0.9960** | -0.3289 | **0.9984** | 0.4781 | 0.6091 | **0.9944** | 1 | |
| Pb | 0.6644 | **0.9943** | -0.3130 | **0.9992** | 0.4632 | 0.5957 | **0.9925** | **0.9999** | 1 |

**Table C. 9: Correlation coefficients of particulate trace metals with each other**

*Simple correlation coefficients*

**Station 1**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | 0.8493 | 1 | | | | | | | |
| Zn | **0.9996** | 0.8344 | 1 | | | | | | |
| Cu | **0.9998** | 0.8386 | **1.0000** | 1 | | | | | |
| Co | **0.9603** | **0.9629** | **0.9522** | **0.9546** | 1 | | | | |
| Cr | 0.6292 | 0.9446 | 0.6074 | 0.6135 | 0.8210 | 1 | | | |
| Ni | 0.8799 | **0.9982** | 0.8664 | 0.8702 | **0.9775** | 0.9230 | 1 | | |
| Cd | 0.3113 | 0.7661 | 0.2849 | 0.2923 | 0.5641 | 0.9345 | 0.7256 | 1 | |
| Pb | **0.9689** | 0.6924 | **0.9754** | **0.9737** | 0.8615 | 0.4174 | 0.7350 | 0.0667 | 1 |

**Station 2**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | 0.2073 | 1 | | | | | | | |
| Zn | 0.8862 | -0.2695 | 1 | | | | | | |
| Cu | 0.2383 | -0.9007 | 0.6611 | 1 | | | | | |
| Co | 0.8526 | 0.6880 | 0.5135 | -0.3044 | 1 | | | | |
| Cr | 0.1139 | **-0.9483** | 0.5612 | **0.9920** | -0.4221 | 1 | | | |
| Ni | 0.7039 | -0.5490 | **0.9529** | 0.8576 | 0.2289 | 0.7859 | 1 | | |
| Cd | **-0.9928** | -0.0883 | -0.9354 | -0.3533 | -0.7836 | -0.2324 | -0.7841 | 1 | |
| Pb | 0.8752 | 0.6546 | 0.5515 | -0.2612 | **0.9990** | -0.3809 | 0.2725 | -0.8108 | 1 |

**Station 3**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | 0.3475 | 1 | | | | | | | |
| Zn | 0.4055 | **0.9980** | 1 | | | | | | |
| Cu | 0.9122 | 0.7012 | 0.7444 | 1 | | | | | |
| Co | 0.8759 | 0.7569 | 0.7962 | **0.9967** | 1 | | | | |
| Cr | 0.1214 | -0.8886 | -0.8581 | -0.2960 | -0.3727 | 1 | | | |
| Ni | **0.9683** | 0.5707 | 0.6209 | **0.9856** | **0.9686** | -0.1304 | 1 | | |
| Cd | 0.5178 | **0.9821** | **0.9920** | 0.8229 | 0.8663 | -0.7864 | 0.7150 | 1 | |
| Pb | 0.5507 | **0.9741** | **0.9863** | 0.8444 | 0.8851 | -0.7617 | 0.7417 | **0.9992** | 1 |

**Station R**

| | Fe | Mn | Zn | Cu | Co | Cr | Ni | Cd | Pb |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | |
| Mn | 0.7716 | 1 | | | | | | | |
| Zn | 0.6559 | **0.9863** | 1 | | | | | | |
| Cu | **0.9986** | 0.8038 | 0.6945 | 1 | | | | | |
| Co | **0.9874** | 0.8624 | 0.7670 | **0.9943** | 1 | | | | |
| Cr | 0.8821 | 0.3810 | 0.2230 | 0.8563 | 0.7965 | 1 | | | |
| Ni | **0.9894** | 0.6708 | 0.5390 | **0.9804** | **0.9539** | 0.9413 | 1 | | |
| Cd | 0.4737 | 0.9257 | **0.9755** | 0.5191 | 0.6070 | 0.0030 | 0.3405 | 1 | |
| Pb | -0.2022 | 0.4670 | 0.6066 | -0.1507 | -0.0448 | -0.6397 | -0.3426 | 0.7667 | 1 |

**Table C. 10: Correlation coefficients of sediment trace metals with each other**

**Station 1**

| | IP | TDP | Ammonium | Nitrite | Nitrate | TDN |
|---|---|---|---|---|---|---|
| MCHO | -0.3246 | -0.5857 | -0.6661 | -0.8913 | 0.7285 | -0.3249 |
| T & L | 0.6680 | 0.4228 | 0.3271 | -0.0381 | -0.2436 | 0.6678 |
| Fe | **-0.9996** | -0.8523 | -0.9329 | -0.2990 | **0.9546** | -0.8218 |
| Mn | 0.0579 | -0.4990 | -0.3339 | **-0.9455** | -0.3244 | -0.5465 |
| Zn | -0.8628 | -0.4443 | -0.5992 | 0.2535 | **0.9670** | -0.3938 |
| Cu | -0.5020 | -0.8941 | -0.7982 | **-0.9684** | 0.2508 | -0.9176 |
| Co | -0.0587 | -0.5965 | -0.4414 | **-0.9770** | -0.2121 | -0.6403 |
| Cr | 0.6616 | **0.9644** | 0.9007 | **0.9008** | -0.4354 | **0.9777** |
| Ni | -0.2691 | -0.7532 | -0.6217 | **-1.0000** | 0.0000 | -0.7887 |
| Cd | -0.9341 | -0.5854 | -0.7225 | 0.0912 | **0.9957** | -0.5394 |
| Pb | 0.4397 | 0.8602 | 0.7537 | **0.9836** | -0.1818 | 0.8873 |

**Station 2**

| | IP | TDP | Ammonium | Nitrite | Nitrate | TDN |
|---|---|---|---|---|---|---|
| MCHO | -0.3597 | -0.1501 | -0.8644 | -0.8848 | **0.9929** | -0.3593 |
| T & L | -0.5180 | -0.6902 | 0.1311 | 0.1728 | -0.5130 | -0.5183 |
| Fe | **-0.9523** | -0.4836 | -0.4288 | -0.5909 | 0.9074 | 0.2565 |
| Mn | 0.4280 | -0.3085 | -0.3664 | -0.1851 | -0.3133 | -0.8809 |
| Zn | -0.7197 | **-0.9999** | **-0.9988** | **-0.9904** | 0.7998 | -0.7300 |
| Cu | **0.9603** | 0.5076 | 0.4536 | 0.6129 | -0.9186 | -0.2297 |
| Co | -0.9359 | -0.4394 | -0.3833 | -0.5500 | 0.8853 | 0.3043 |
| Cr | 0.9219 | 0.4052 | 0.3482 | 0.5181 | -0.8671 | -0.3401 |
| Ni | 0.3800 | -0.3579 | -0.4147 | -0.2364 | -0.2630 | -0.9045 |
| Cd | -0.7751 | **-0.9974** | **-0.9911** | **-0.9985** | 0.8471 | -0.6704 |
| Pb | -0.2997 | 0.4364 | 0.4909 | 0.3185 | 0.1797 | 0.9376 |

**Station 3**

| | IP | TDP | Ammonium | Nitrite | Nitrate | TDN |
|---|---|---|---|---|---|---|
| MCHO | -0.6064 | -0.6165 | 0.8150 | -0.4336 | -0.7092 | -0.6064 |
| T & L | **0.9831** | **0.9807** | 0.1499 | **0.9998** | **0.9490** | **0.9832** |
| Fe | 0.9151 | 0.6104 | -0.4335 | 0.7126 | 0.9258 | -0.5892 |
| Mn | -0.8357 | -0.4706 | 0.5769 | -0.5865 | **-0.9756** | 0.7150 |
| Zn | -0.6398 | -0.1937 | 0.7895 | -0.3256 | **-0.9973** | 0.8874 |
| Cu | **0.9979** | 0.9068 | 0.0307 | **0.9558** | 0.6473 | -0.1504 |
| Co | 0.3373 | -0.1546 | **-0.9521** | -0.0185 | 0.9114 | **-0.9917** |
| Cr | -0.8043 | -0.4216 | 0.6207 | -0.5413 | **-0.9862** | 0.7522 |
| Ni | **0.9825** | 0.7733 | -0.2192 | 0.8525 | 0.8167 | -0.3918 |
| Cd | -0.2900 | -0.7128 | **-0.9468** | -0.6106 | 0.4868 | -0.8731 |
| Pb | -0.8001 | -0.4152 | 0.6263 | -0.5353 | **-0.9873** | 0.7568 |

**Station R**

| | IP | TDP | Ammonium | Nitrite | Nitrate | TDN |
|---|---|---|---|---|---|---|
| MCHO | -0.7714 | -0.8688 | -0.3961 | 0.3284 | **0.9651** | -0.7699 |
| T & L | 0.0348 | 0.2051 | -0.4250 | 0.4896 | -0.8358 | 0.0325 |
| Fe | 0.8057 | -0.7417 | **0.9872** | 0.7252 | -0.0964 | 0.9133 |
| Mn | **0.9831** | -0.3761 | **0.9583** | **0.9525** | -0.5197 | **0.9995** |
| Zn | 0.8655 | 0.3175 | 0.5417 | 0.9214 | **-0.9506** | 0.7391 |
| Cu | 0.8867 | -0.6305 | **1.0000** | 0.8218 | -0.2473 | **0.9648** |
| Co | -0.8567 | 0.6768 | **-0.9977** | -0.7854 | 0.1875 | **-0.9469** |
| Cr | **-0.9750** | -0.0226 | -0.7662 | **-0.9951** | 0.8162 | -0.9054 |
| Ni | -0.0596 | **0.9900** | -0.5085 | 0.0657 | -0.7037 | -0.2707 |
| Cd | -0.6453 | 0.8776 | -0.9228 | -0.5447 | -0.1383 | -0.7931 |
| Pb | 0.9114 | 0.2208 | 0.6233 | **0.9557** | -0.9147 | 0.8030 |

**Table C. 11: Correlation coefficients of dissolved components with each other**

**Station 1**

| | Ex.Ammo. | TSN | TSP | TOC |
|---|---|---|---|---|
| STCHO | 0.3010 | -0.6461 | 0.6918 | -0.1011 |
| SP | **-0.9976** | -0.4734 | 0.4184 | **0.9627** |
| TSL | **0.9999** | 0.5245 | -0.4712 | **-0.9770** |
| T & L | -0.3751 | **-0.9842** | **0.9932** | 0.5555 |
| Fe | -0.6174 | **0.9865** | 0.6645 | -0.8272 |
| Mn | -0.1092 | 0.9243 | 0.1700 | -0.4060 |
| Zn | -0.6389 | **0.9816** | 0.6850 | -0.8425 |
| Cu | -0.6330 | **0.9831** | 0.6793 | -0.8383 |
| Co | -0.3735 | **0.9930** | 0.4297 | -0.6377 |
| Cr | 0.2230 | 0.7478 | -0.1627 | -0.0837 |
| Ni | -0.1694 | **0.9458** | 0.2296 | -0.4608 |
| Cd | 0.5553 | 0.4626 | -0.5032 | 0.2764 |
| Pb | -0.7928 | 0.9154 | 0.8287 | -0.9405 |

**Station 2**

| | Ex.Ammo. | TSN | TSP | TOC |
|---|---|---|---|---|
| STCHO | 0.3073 | **-0.9887** | 0.8011 | -0.3569 |
| SP | **-0.9996** | 0.4223 | 0.3486 | **0.9969** |
| TSL | 0.7521 | 0.2541 | -0.8669 | -0.7165 |
| T & L | -0.8224 | -0.1421 | 0.8043 | 0.7914 |
| Fe | -0.1361 | -0.8934 | 0.8007 | 0.9395 |
| Mn | **-0.9974** | 0.2542 | 0.7520 | -0.1403 |
| Zn | 0.3383 | **-0.9999** | 0.4321 | **0.9913** |
| Cu | 0.9297 | -0.6492 | -0.3909 | 0.5565 |
| Co | -0.6338 | -0.5270 | **0.9957** | 0.6220 |
| Cr | **0.9687** | -0.5480 | -0.5039 | 0.4473 |
| Ni | 0.6079 | **-0.9479** | 0.1381 | 0.9046 |
| Cd | 0.0161 | 0.9409 | -0.7230 | **-0.9739** |
| Pb | -0.5983 | -0.5647 | **0.9906** | 0.6566 |

**Station 3**

| | Ex.Ammo. | TSN | TSP | TOC |
|---|---|---|---|---|
| STCHO | **-0.9530** | 0.5664 | -0.8266 | **0.9966** |
| SP | -0.5714 | **0.9548** | -0.7822 | 0.2168 |
| TSL | -0.8455 | 0.3396 | -0.6575 | **0.9850** |
| T & L | **-0.9996** | 0.7715 | **-0.9497** | 0.9355 |
| Fe | -0.0225 | -0.3074 | -0.3414 | 0.6985 |
| Mn | **-0.9453** | **-0.9991** | 0.7627 | 0.9137 |
| Zn | -0.9230 | **-0.9945** | 0.7207 | 0.9374 |
| Cu | -0.4302 | -0.6703 | 0.0737 | 0.9304 |
| Co | -0.5022 | -0.7284 | 0.1545 | **0.9571** |
| Cr | **0.9896** | 0.9072 | **-0.9744** | -0.6255 |
| Ni | -0.2715 | -0.5353 | -0.0959 | 0.8551 |
| Cd | -0.8670 | **-0.9733** | 0.6273 | **0.9739** |
| Pb | -0.8469 | **-0.9636** | 0.5965 | **0.9820** |

**Station R**

| | Ex.Ammo. | TSN | TSP | TOC |
|---|---|---|---|---|
| STCHO | 0.6257 | -0.3440 | **0.9681** | 0.9200 |
| SP | **0.9601** | 0.2573 | 0.6490 | **0.9783** |
| TSL | 0.3981 | **0.9910** | -0.6731 | -0.0824 |
| T & L | **0.9994** | 0.4879 | 0.4411 | 0.8969 |
| Fe | **0.9787** | **0.9916** | 0.4019 | 0.9352 |
| Mn | 0.6247 | 0.8475 | 0.8926 | 0.4963 |
| Zn | 0.4871 | 0.7482 | **0.9548** | 0.3461 |
| Cu | **0.9667** | **0.9970** | 0.4492 | 0.9154 |
| Co | 0.9340 | **0.9996** | 0.5416 | 0.8675 |
| Cr | **0.9600** | 0.8136 | -0.0768 | **0.9918** |
| Ni | **0.9982** | **0.9621** | 0.2643 | **0.9768** |
| Cd | 0.2829 | 0.5838 | **0.9968** | 0.1311 |
| Pb | -0.3988 | -0.0736 | 0.8155 | -0.5359 |

**Table C. 12:- Correlation coefficients of sedimentary components with each other**

# *Appendix D*

## Canonical regression coefficients

| **Fe** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Canonical R | $Chi^2$ (4) | p | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
| | | | Left set | Right set | | | | |
| 0.55925 | 3.0006 | 0.55773 | 4 | 1 | 22.12 | 100 | 6.92 | 31.28 |
| **Mn** | | | | | | | | |
| 0.60029 | 3.5746 | 0.46664 | 4 | 1 | 30.26 | 100 | 10.90 | 36.03 |
| **Zn** | | | | | | | | |
| 0.72324 | 5.9231 | 0.20499 | 4 | 1 | 19.58 | 100 | 10.24 | 52.31 |
| **Cu** | | | | | | | | |
| 0.57065 | 3.1520 | 0.53273 | 4 | 1 | 34.24 | 100 | 11.15 | 32.57 |
| **Co** | | | | | | | | |
| 0.73446 | 6.2024 | 0.1857 | 4 | 1 | 23.03 | 100 | 12.42 | 53.94 |
| **Cr** | | | | | | | | |
| 0.54685 | 2.8425 | 0.58452 | 4 | 1 | 24.23 | 100 | 7.24 | 29.91 |
| **Ni** | | | | | | | | |
| 0.72489 | 5.9634 | 0.20193 | 4 | 1 | 29.36 | 100 | 15.43 | 52.55 |
| **Cd** | | | | | | | | |
| 0.80568 | 8.3784 | 0.07869 | 4 | 1 | 18.98 | 100 | 12.32 | 64.91 |
| **Pb** | | | | | | | | |
| 0.76983 | 7.1846 | 0.12648 | 4 | 1 | 28.10 | 100 | 16.65 | 59.26 |

**Table D. 1:- Canonical regression coefficients of dissolved trace metals with hydrographical parameters at station 1**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Fe** | | | | | | | | |
| Canonical R | Chi$^2$ (4) | p | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
| | | | Left set | Right set | | | | |
| 0.80348 | 8.2980 | 0.08128 | 4 | 1 | 22.36 | 100 | 14.43 | 64.56 |
| **Mn** | | | | | | | | |
| 0.55341 | 2.9253 | 0.57041 | 4 | 1 | 16.83 | 100 | 5.16 | 30.63 |
| **Zn** | | | | | | | | |
| 0.42697 | 1.60101 | 0.80697 | 4 | 1 | 25.22 | 100 | 4.60 | 18.23 |
| **Cu** | | | | | | | | |
| 0.83186 | 9.4210 | 0.05142 | 4 | 1 | 31.04 | 100 | 21.48 | 69.20 |
| **Co** | | | | | | | | |
| 0.63665 | 4.1579 | 0.38508 | 4 | 1 | 29.45 | 100 | 11.94 | 40.53 |
| **Cr** | | | | | | | | |
| 0.77736 | 7.41164 | 0.11548 | 4 | 1 | 27.82 | 100 | 16.81 | 60.43 |
| **Ni** | | | | | | | | |
| 0.63393 | 4.1115 | 0.39115 | 4 | 1 | 30.48 | 100 | 12.25 | 40.19 |
| **Cd** | | | | | | | | |
| 0.39913 | 1.3882 | 0.84624 | 4 | 1 | 31.93 | 100 | 5.09 | 15.93 |
| **Pb** | | | | | | | | |
| 0.52856 | 2.6211 | 0.62310 | 4 | 1 | 17.13 | 100 | 4.78 | 27.94 |

**Table D. 2:- Canonical regression coefficients of dissolved trace metals with hydrographical parameters at station 2**

| **Fe** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Canoni-cal R | Chi$^2$ (4) | p | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
| | | | Left set | Right set | | | | |
| 0.61865 | 3.8596 | 0.42535 | 4 | 1 | 20.84 | 100 | 7.98 | 38.27 |
| **Mn** | | | | | | | | |
| 0.58891 | 3.4072 | 0.49214 | 4 | 1 | 21.80 | 100 | 7.56 | 34.68 |
| **Zn** | | | | | | | | |
| 0.41711 | 1.5291 | 0.82147 | 4 | 1 | 22.69 | 100 | 3.95 | 17.40 |
| **Cu** | | | | | | | | |
| 0.58166 | 3.3039 | 0.50832 | 4 | 1 | 26.88 | 100 | 9.0 | 33.83 |
| **Co** | | | | | | | | |
| 0.73042 | 6.1002 | 0.19182 | 4 | 1 | 23.48 | 100 | 12.52 | 53.35 |
| **Cr** | | | | | | | | |
| 0.57975 | 3.2771 | 0.51258 | 4 | 1 | 16.19 | 100 | 5.44 | 33.61 |
| **Ni** | | | | | | | | |
| 0.73309 | 6.1675 | 0.18701 | 4 | 1 | 28.25 | 100 | 15.18 | 53.54 |
| **Cd** | | | | | | | | |
| 0.42927 | 1.6294 | 0.80350 | 4 | 1 | 27.32 | 100 | 5.04 | 18.43 |
| **Pb** | | | | | | | | |
| 0.52967 | 2.6341 | 0.62079 | 4 | 1 | 32.63 | 100 | 9.15 | 28.06 |

**Table D. 3:- Canonical regression coefficients of dissolved trace metals with hydrographical parameters at station 3**

| Canonical R | Chi$^2$ (4) | p | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
|---|---|---|---|---|---|---|---|---|
| | | | Left set | Right set | | | | |
| **Fe** | | | | | | | | |
| 0.98238 | 26.837 | 0.00002 | 4 | 1 | 26.17 | 100 | 25.26 | 96.51 |
| **Mn** | | | | | | | | |
| 0.30135 | 0.7616 | 0.94352 | 4 | 1 | 26.20 | 100 | 2.38 | 9.08 |
| **Zn** | | | | | | | | |
| 0.86349 | 10.951 | 0.02713 | 4 | 1 | 31.15 | 100 | 23.23 | 74.56 |
| **Cu** | | | | | | | | |
| 0.48095 | 2.1046 | 0.71653 | 4 | 1 | 25.15 | 100 | 5.82 | 23.13 |
| **Co** | | | | | | | | |
| 0.82870 | 9.2858 | 0.05436 | 4 | 1 | 33.46 | 100 | 22.98 | 68.67 |
| **Cr** | | | | | | | | |
| 0.69265 | 5.2278 | 0.26474 | 4 | 1 | 32.94 | 100 | 15.80 | 47.98 |
| **Ni** | | | | | | | | |
| 0.44824 | 1.7943 | 0.77352 | 4 | 1 | 31.30 | 100 | 6.29 | 20.09 |
| **Cd** | | | | | | | | |
| 0.62550 | 3.9707 | 0.41000 | 4 | 1 | 22.06 | 100 | 8.63 | 39.12 |
| **Pb** | | | | | | | | |
| 0.78915 | 7.7990 | 0.09925 | 4 | 1 | 23.91 | 100 | 14.89 | 62.27 |

**Table D. 4:- Canonical regression coefficients of dissolved trace metals with hydrographical parameters at station R**

| **Fe** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Canonical R | Chi$^2$ (4) | p | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
| | | | Left set | Right set | | | | |
| 0.72517 | 5.9702 | 0.20141 | 4 | 1 | 21.18 | 100 | 11.14 | 52.59 |
| **Mn** | | | | | | | | |
| 0.50812 | 2.3892 | 0.66458 | 4 | 1 | 21.41 | 100 | 5.53 | 25.82 |
| **Zn** | | | | | | | | |
| 0.84402 | 9.9685 | 0.04098 | 4 | 1 | 22.47 | 100 | 16.00 | 71.24 |
| **Cu** | | | | | | | | |
| 0.65520 | 4.4869 | 0.34413 | 4 | 1 | 16.96 | 100 | 7.28 | 42.93 |
| **Co** | | | | | | | | |
| 0.71830 | 5.8049 | 0.21424 | 4 | 1 | 18.77 | 100 | 9.68 | 51.60 |
| **Cr** | | | | | | | | |
| 0.68463 | 5.0638 | 0.28084 | 4 | 1 | 21.96 | 100 | 10.30 | 46.90 |
| **Ni** | | | | | | | | |
| 0.67638 | 4.8923 | 0.29855 | 4 | 1 | 21.42 | 100 | 9.80 | 45.75 |
| **Cd** | | | | | | | | |
| 0.72400 | 5.9416 | 0.20358 | 4 | 1 | 21.28 | 100 | 11.54 | 52.42 |
| **Pb** | | | | | | | | |
| 0.86849 | 11.229 | 0.02413 | 4 | 1 | 22.31 | 100 | 16.83 | 75.43 |

**Table D. 5:- Canonical regression coefficients of particulate trace metals with hydrographical parameters at station 1**

| Canonical R | Chi$^2$ (4) | P | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
|---|---|---|---|---|---|---|---|---|
| | | | Left set | Right set | | | | |
| **Fe** | | | | | | | | |
| 0.56579 | 3.0866 | 0.54344 | 4 | 1 | 23.83 | 100 | 7.63 | 32.01 |
| **Mn** | | | | | | | | |
| 0.78750 | 7.7439 | 0.10145 | 4 | 1 | 27.91 | 100 | 17.31 | 62.02 |
| **Zn** | | | | | | | | |
| 0.69359 | 5.2478 | 0.26283 | 4 | 1 | 16.26 | 100 | 7.82 | 48.11 |
| **Cu** | | | | | | | | |
| 0.73292 | 6.1632 | 0.18731 | 4 | 1 | 22.76 | 100 | 12.23 | 53.72 |
| **Co** | | | | | | | | |
| 0.81765 | 8.8343 | 0.06540 | 4 | 1 | 27.70 | 100 | 18.52 | 66.86 |
| **Cr** | | | | | | | | |
| 0.63430 | 4.1178 | 0.39032 | 4 | 1 | 22.33 | 100 | 9.98 | 40.23 |
| **Ni** | | | | | | | | |
| 0.76272 | 6.9733 | 0.13733 | 4 | 1 | 21.65 | 100 | 12.60 | 58.17 |
| **Cd** | | | | | | | | |
| 0.80293 | 8.2784 | 0.08192 | 4 | 1 | 21.53 | 100 | 13.88 | 64.47 |
| **Pb** | | | | | | | | |
| 0.80529 | 8.3643 | 0.07914 | 4 | 1 | 24.93 | 100 | 16.17 | 64.85 |

**Table D. 6:- Canonical regression coefficients of particulate trace metals with hydrographical parameters at station 2**

| **Fe** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Canonical R | Chi$^2$ (4) | P | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
| | | | Left set | Right set | | | | |
| 0.87196 | 11.428 | 0.02217 | 4 | 1 | 22.13 | 100 | 16.06 | 76.03 |
| **Mn** | | | | | | | | |
| 0.76199 | 6.9519 | 0.13848 | 4 | 1 | 20.54 | 100 | 11.93 | 58.06 |
| **Zn** | | | | | | | | |
| 0.71163 | 5.6484 | 0.02217 | 4 | 1 | 26.44 | 100 | 13.39 | 50.64 |
| **Cu** | | | | | | | | |
| 0.54347 | 2.80006 | 0.59174 | 4 | 1 | 22.91 | 100 | 6.77 | 29.54 |
| **Co** | | | | | | | | |
| 0.79378 | 7.59560 | 0.09323 | 4 | 1 | 24.84 | 100 | 15.65 | 63.00 |
| **Cr** | | | | | | | | |
| 0.61064 | 3.7329 | 0.44338 | 4 | 1 | 25.50 | 100 | 9.51 | 37.29 |
| **Ni** | | | | | | | | |
| 0.62614 | 3.9813 | 0.40857 | 4 | 1 | 18.25 | 100 | 7.15 | 39.20 |
| **Cd** | | | | | | | | |
| 0.76904 | 7.1606 | 0.12767 | 4 | 1 | 21.42 | 100 | 12.67 | 59.14 |
| **Pb** | | | | | | | | |
| 0.69442 | 5.2656 | 0.26114 | 4 | 1 | 24.33 | 100 | 17.73 | 48.22 |

**Table D. 7:- Canonical regression coefficients of particulate trace metals with hydrographical parameters at station 3**

| **Fe** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Canonical R | Chi$^2$ (4) | P | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | | |
| | | | Left set | Right set | | | | | |
| 0.64359 | 4.2782 | 0.36968 | 4 | 1 | 19.96 | 100 | 8.27 | 41.42 | |
| **Mn** | | | | | | | | | |
| 0.66635 | 4.6963 | 0.31998 | 4 | 1 | 23.13 | 100 | 10.27 | 44.40 | |
| **Zn** | | | | | | | | | |
| 0.51180 | 2.4298 | 0.65725 | 4 | 1 | 33.02 | 100 | 8.65 | 26.93 | |
| **Cu** | | | | | | | | | |
| 0.51484 | 2.4637 | 0.65115 | 4 | 1 | 34.96 | 100 | 9.26 | 26.51 | |
| **Co** | | | | | | | | | |
| 0.57430 | 3.2016 | 0.52498 | 4 | 1 | 34.45 | 100 | 11.36 | 32.98 | |
| **Cr** | | | | | | | | | |
| 0.69174 | 5.2085 | 0.26659 | 4 | 1 | 30.75 | 100 | 14.71 | 47.85 | |
| **Ni** | | | | | | | | | |
| 0.55178 | 2.9737 | 0.56224 | 4 | 1 | 20.82 | 100 | 6.46 | 31.05 | |
| **Cd** | | | | | | | | | |
| 0.74760 | 6.5480 | 0.16182 | 4 | 1 | 21.30 | 100 | 11.90 | 55.89 | |
| **Pb** | | | | | | | | | |
| 80074 | 8.1996 | 0.18456 | 4 | 1 | 26.53 | 100 | 17.00 | 64.12 | |

**Table D. 8:- Canonical regression coefficients of particulate trace metals with hydrographical parameters at station R**

| **Fe** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Canonical R | Chi$^2$ (4) | P | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
| | | | Left set | Right set | | | | |
| 0.34333 | 1.0034 | 0.90928 | 4 | 1 | 14.10 | 100 | 1.66 | 11.79 |
| **Mn** | | | | | | | | |
| 0.31690 | 0.8467 | 0.93208 | 4 | 1 | 26.59 | 100 | 2.67 | 10.04 |
| **Zn** | | | | | | | | |
| 0.38723 | 1.2996 | 0.86144 | 4 | 1 | 20.60 | 100 | 3.09 | 14.99 |
| **Cu** | | | | | | | | |
| 0.35978 | 1.1089 | 0.89285 | 4 | 1 | 22.66 | 100 | 2.99 | 12.94 |
| **Co** | | | | | | | | |
| 0.3152 | 0.8378 | 0.93331 | 4 | 1 | 27.34 | 100 | 2.71 | 9.94 |
| **Cr** | | | | | | | | |
| 0. 6707 | 4.7803 | 0.31062 | 4 | 1 | 32.34 | 100 | 14.55 | 44.98 |
| **Ni** | | | | | | | | |
| 0.43498 | 1.6780 | 0.79471 | 4 | 1 | 27.80 | 100 | 5.26 | 18.92 |
| **Cd** | | | | | | | | |
| 0.32255 | 0.8789 | 0.92757 | 4 | 1 | 30.73 | 100 | 3.20 | 10.43 |
| **Pb** | | | | | | | | |
| 0.31987 | 0.8635 | 0.92974 | 4 | 1 | 23.74 | 100 | 2.43 | 10.23 |

**Table D. 9:- Canonical regression coefficients of sedimentary trace metals with hydrographical parameters at station 1**

| **Fe** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Canonical R | Chi$^2$ (4) | P | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
| | | | Left set | Right set | | | | |
| 0.31232 | 0.82106 | 0.93560 | 4 | 1 | 11.70 | 100 | 1.14 | 9.75 |
| **Mn** | | | | | | | | |
| 0.52952 | 2.6324 | 0.62110 | 4 | 1 | 13.69 | 100 | 3.84 | 28.04 |
| **Zn** | | | | | | | | |
| 0.42871 | 1.6247 | 0.80434 | 4 | 1 | 34.20 | 100 | 6.29 | 18.38 |
| **Cu** | | | | | | | | |
| 0.41536 | 1.5150 | 0.82398 | 4 | 1 | 28.42 | 100 | 4.90 | 17.25 |
| **Co** | | | | | | | | |
| 0.33419 | 0.94742 | 0.91766 | 4 | 1 | 26.99 | 100 | 3.01 | 11.17 |
| **Cr** | | | | | | | | |
| 0.72491 | 5.9639 | 0.20189 | 4 | 1 | 33.31 | 100 | 17.51 | 52.55 |
| **Ni** | | | | | | | | |
| 0.38234 | 1.2643 | 0.86740 | 4 | 1 | 38.66 | 100 | 5.65 | 14.62 |
| **Cd** | | | | | | | | |
| 0.55305 | 2.9208 | 0.57118 | 4 | 1 | 43.22 | 100 | 13.22 | 30.59 |
| **Pb** | | | | | | | | |
| 0.50343 | 2.3383 | 0.67381 | 4 | 1 | 18.77 | 100 | 4.76 | 25.34 |

**Table D. 10:- Canonical regression coefficients of sedimentary trace metals with hydrographical parameters at station 2**

| Canoni-cal R | $Chi^2$ (4) | P | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
|---|---|---|---|---|---|---|---|---|
| | | | Left set | Right set | | | | |
| **Fe** | | | | | | | | |
| 0.49437 | 2.2419 | 0.69136 | 4 | 1 | 21.88 | 100 | 5.35 | 24.44 |
| **Mn** | | | | | | | | |
| 0.42744 | 1.6140 | 0.80627 | 4 | 1 | 10.52 | 100 | 1.92 | 18.27 |
| **Zn** | | | | | | | | |
| 0.11757 | 0.1113 | 0.99851 | 4 | 1 | 15.75 | 100 | 0.22 | 1.38 |
| **Cu** | | | | | | | | |
| 0.35657 | 1.0879 | 0.89619 | 4 | 1 | 21.29 | 100 | 2.70 | 12.71 |
| **Co** | | | | | | | | |
| 0.37313 | 1.1994 | 0.87819 | 4 | 1 | 39.80 | 100 | 5.54 | 0.88 |
| **Cr** | | | | | | | | |
| 0.34653 | 1.0234 | 0.90623 | 4 | 1 | 40.88 | 100 | 4.91 | 0.91 |
| **Ni** | | | | | | | | |
| 0.42850 | 1.6229 | 0.80467 | 4 | 1 | 27.45 | 100 | 5.04 | 0.80 |
| **Cd** | | | | | | | | |
| 0.34018 | 0.9839 | 0.91223 | 4 | 1 | 25.85 | 100 | 2.99 | 0.91 |
| **Pb** | | | | | | | | |
| 0.26160 | 0.5672 | 0.96664 | 4 | 1 | 31.66 | 100 | 2.17 | 0.97 |

**Table D. 11:- Canonical regression coefficients of sedimentary trace metals with hydrographical parameters at station 3**

| Canonical R | Chi$^2$ (4) | P | No. of variables | | Variance Extracted (%) | | Total Redundancy (%) | |
|---|---|---|---|---|---|---|---|---|
| | | | Left set | Right set | | | | |
| **Fe** | | | | | | | | |
| 0.89950 | 13.348 | 0.01013 | 4 | 1 | 32.51 | 100 | 26.31 | 80.91 |
| **Mn** | | | | | | | | |
| 0.78051 | 7.5164 | 0.11102 | 4 | 1 | 34.24 | 100 | 20.86 | 60.92 |
| **Zn** | | | | | | | | |
| 0.61939 | 3.8714 | 0.42371 | 4 | 1 | 12.72 | 100 | 4.88 | 38.36 |
| **Cu** | | | | | | | | |
| 0.93166 | 16.199 | 0.00277 | 4 | 1 | 29.32 | 100 | 25.46 | 86.80 |
| **Co** | | | | | | | | |
| 0.81622 | 8.7780 | 0.06692 | 4 | 1 | 30.43 | 100 | 20.27 | 66.62 |
| **Cr** | | | | | | | | |
| 0.72043 | 5.8553 | 0.21024 | 4 | 1 | 13.35 | 100 | 6.93 | 51.90 |
| **Ni** | | | | | | | | |
| 0.89362 | 12.818 | 0.01221 | 4 | 1 | 28.03 | 100 | 22.38 | 79.86 |
| **Cd** | | | | | | | | |
| 0.32501 | 0.8931 | 0.92555 | 4 | 1 | 17.57 | 100 | 1.86 | 10.56 |
| **Pb** | | | | | | | | |
| 0.23174 | 0.4416 | 0.97893 | 4 | 1 | 12.20 | 100 | 0.65 | 5.37 |

**Table D. 12:- Canonical regression coefficients of sedimentary trace metals with hydrographical parameters at station R**

# *Appendix E*

## PRINCIPAL COMPONENT SCORE PLOTS

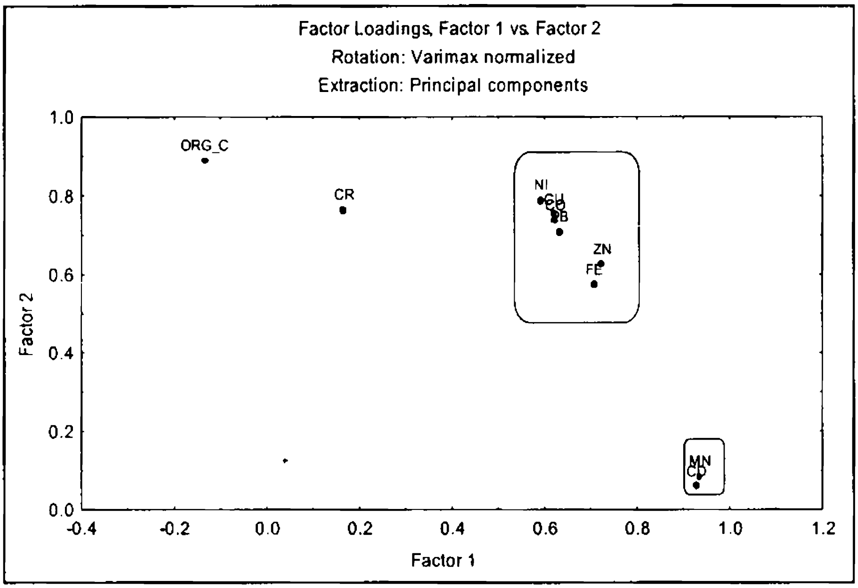

Figure E.1:- Factor analysis score plot of sedimentary trace metals at Station 1

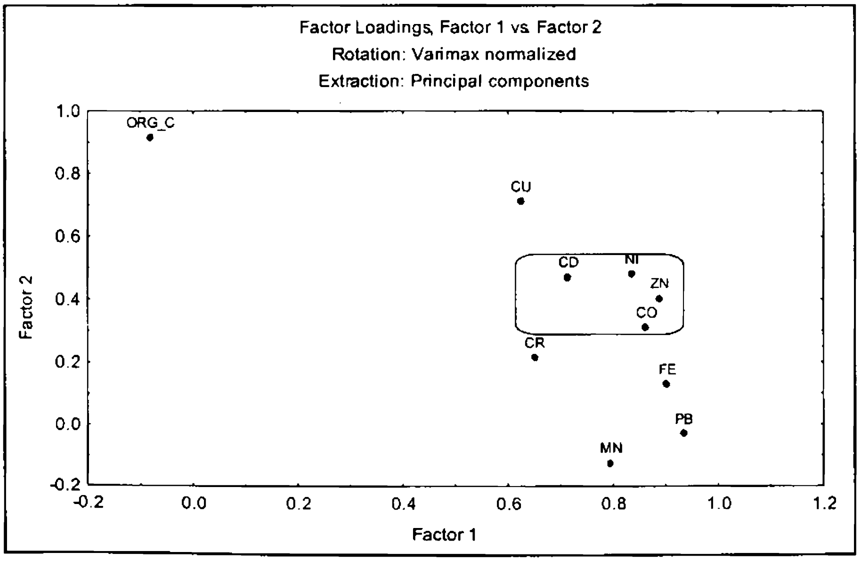

Figure E.2:- Factor analysis score plot of sedimentary trace metals at Station 2

***Appendix E***

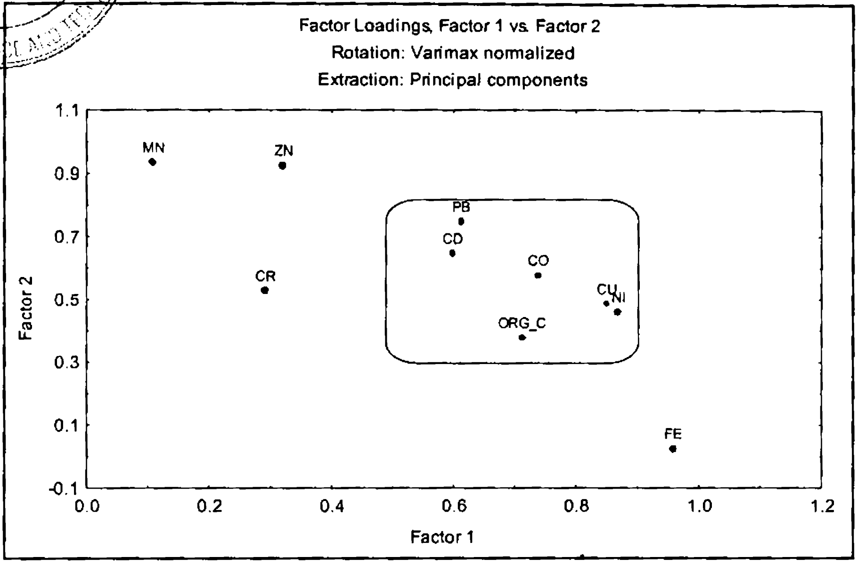

Figure E.3:- Factor analysis score plot of sedimentary trace metals at Station

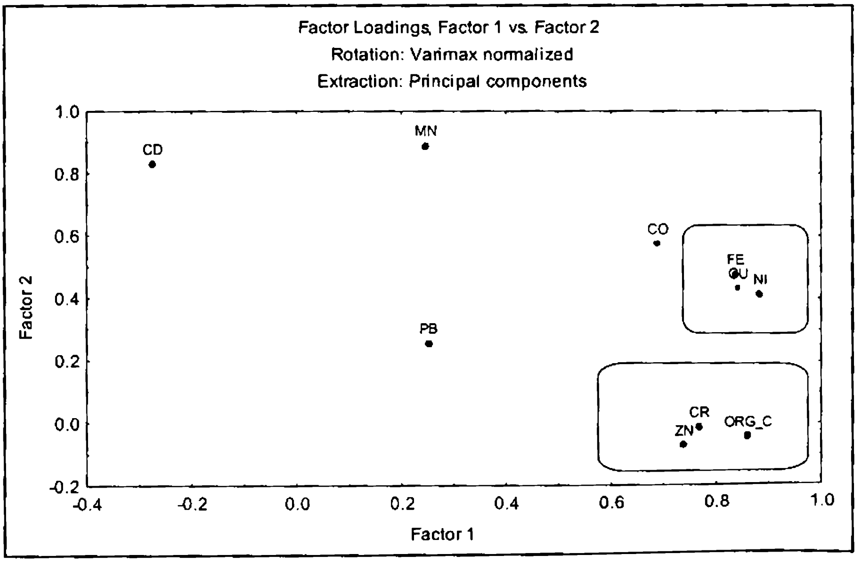

Figure E.4:- Factor analysis score plot of sedimentary trace metals at Station