BIOGEOORGANICS AND TRACE METAL SPECIATION IN MANGROVES

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CERTIFICATE

This is to certify that the thesis titled "Biogeoorganics and Trace Metal Speciation in Mangroves" is an authentic record of the research work carried out by Sarika P.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 Ph.D degree of Cochin University of Science and Technology and no part of this has been presented before for any degree in any university.

Kochi – 16
June, 2005

Dr. N. Chandramohanakumar
(Supervising Guide)

DECLARATION

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

Sarika

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CONTENTS

Preface

Mangroves are one among the world's most productive ecosystem and form an important part of the coastal and estuarine environment. Living at the interface between land and sea, the mangrove plants have morphological and physiological adaptations to survive in harsh saline environment. Mangroves produce organic carbon well in excess of the ecosystem requirement and contribute significantly to global carbon cycle. They have enormous ecological value. They protect and stabilize coast lines, enrich coastal waters, yield commercial products and support coastal fisheries. The mangal may play a special role as nursery habitat for juveniles of fish and prawn. In Kerala, they have a major role in preserving the fishery resources of the state. Mangroves are one of the most threatened ecosystems as well. Over the past few years, mangroves are disappearing at an alarming rate. Diversion of fresh water for irrigation, conversion to aquaculture and other developmental activities destroyed large mangal areas in Kerala. Mangroves are seriously threatened by human activities. Due to the proximity to the centers of urbanization and industrialization, a huge amount of pollutants enter these coastal ecosystems.

Among the pollutants, metals deserve special attention due to its non degradable nature and environmental persistence. Though the total metal concentration in sediment is a valuable index of pollution, it did not give an indication of the available metal concentrations. The chemical forms of trace metals in sediment need to be determined in order to assess the bioavailability and long term environmental consequences of soil contamination. Though the chemical and physical environment of the mangal efficiently trap metals in non – bio available forms, disturbances associated with human activities can spoil the metal binding capacity resulting in the mobilization of metals. A number of reports are available on the productivity and management of mangroves. Biogeochemical role of the contaminants entering these coastal systems are never been addressed so far in its totality. The thesis is an attempt to study the distribution of metals in different compartments of mangroves and their speciation in different fractions of the sediment.

The thesis is divided into five chapters. The first chapter gives a brief introduction on the mangrove ecosystem and the role of metals in mangroves. The aim and scope of the work is discussed in this chapter.

The second chapter gives a description of the study area, along with the sampling protocols and the various analytical techniques used in the investigation. This chapter also describes the seasonal and spatial variation of hydrographical and sediment parameters.

The third chapter is about the distribution of trace metals in different compartments of mangroves – sediment, water and plant tissues. Seasonal variations of the metal concentrations in sediments are also assessed.

The fourth chapter summarises the results of the trace metal speciation studies in sediments. The conventional speciation scheme (modified Tessier's protocol) is compared with the one based on pH.

The principal component analysis is attempted at the fifth chapter to get an understanding of the various geochemical processes determining the fate of metals in sediments. A mass balance model is also attempted here.

The salient features of the present investigation are summarized at the end of the thesis. The references are given at the end of each chapter.

Chapter 1

INTRODUCTION

1.1 Mangrove ecosystem

1.2 Trace metals in the environment

1.3 Trace metals in mangroves

1.4 Speciation of trace metals in sediments

1.5 Aim and scope of the work

1.1 Mangrove ecosystem

The mangroves have been often referred to as the forest between land and sea. The term *mangrove* can be used to describe any vascular plant or community that occurs in areas subject to periodic fresh and salt water inundation. The common characteristic of all these plants is tolerance to salt and brackish waters. There are 70 known mangrove species (Field, 1998). Among coastal ecosystems, the mangrove ecosystem is as much a store house of biological diversity as the tropical rainforest (Swaminathan, 1991).

Mangrove forests are highly productive ecosystems with an average production of 2,500 mg cm^2 per day (Bunt, 1992).Plant litter, mainly leaves represents about one third of the production and up to half this quantity can be exported by mangrove creeks to adjacent waters. Due to their high primary productivity, turn over rates of organic matter and the permanent exchange with the terrestrial and marine ecosystems mangroves are of particular interest for the biogeochemical cycling of carbon and associated elements along tropical continental margins (Jennerjahn *et al.*, 2002). The export of this large amount of organic matter has a recognizable effect on the food webs in coastal waters (Clough, 1998). These system are important nurseries for early life stages of a number of fish and invertebrate including various species of shrimp in the genus *Penaeus*.The mangrove root system also provides shelter from predation by larger carnivorous fishes.

Mangroves are inundated twice daily by the tides. Tidal flushing facilitates the exchange of detritus, nutrients and pollutants with adjacent waters (Imelda and Chandra, 2000). Terrestrial run off acts as main source of dissolved nutrients to mangrove waters. They receive high inputs of biogenic and abiogenic materials from the land and the sea and are in permanent exchange with coastal waters. The amount and origin of organic carbon in mangrove sediments should be influenced by both physical (eg. tidal amplitude) and biological (eg. consumption, removal, degradation) factors and may in turn influence the quality and availability of food sources for benthic faunal communities.

Mangroves grow in conditions where no other plant species can survive (Hutchings and Saenger, 1987). The mangrove environment is primarily saline and the vegetation grows and flourishes by three different mechanisms which cope with excess salt. The roots of salt excluding species of *Ceriops*, *Exoecaria* and *Rhizophora* can absorb only fresh water from the saline water through the process of ultra filtration (Scholander, 1968). Species of *Avicennia* and *Sonnertia* can regulate the salt content of their tissues by glants in their leaves. *Xylocarpous sp.*, *Lumnitzera sp.*and *Sonnertia sp.* deposit salt in older leaves roots and barks (Joshi *et al.*, 1975).

The most extensive growth of mangroves can be seen in estuaries of rivers and protected lagoons and coastal lakes. Mangroves occur in areas of high humidity and their luxuriant growth is often associated with high rain fall. The mangrove plants prefer mostly the humid atmosphere (60 %– 90 %) with moderate to high annual rain fall between 1000 mm to 3000mm. Mangroves can not tolerate frost(Tomlinson,1986). Minimum air temperature and seasonal variations are important in the growth of mangroves. As cited by Chapman (1975; 1977), the best mangrove growth and development occurs where the seasonal temperature variation does not exceed 10°C and where the air temperature in the coldest month is higher than 10°C.

The community structure of mangroves is greatly influenced by biotic and abiotic factors. Since abiotic factors vary widely over geo-morphic regions, mangrove strands exhibit inter regional and local variations in structural characteristics. Mangroves are well adapted to the salt water environment and to anoxic and sulphide rich sediments. Pneumatophores (breathing roots which obtain oxygen directly from atmosphere when exposed to low tide), buttresses and prop roots for support, salt excretion from leaf pores, and floating seeds (viviparous propagules) are special features of mangroves. Mangroves flourish on fine alluvial muds composed predominantly of silt and clay particles. Mangrove vegetation exhibit morphological and physiological adaptations to survive in the harsh intertidal environment. The aerial roots, pnematophores and lenticles on the tree bark facilitate the exchange of gases to the inner tissue, this is essential for plants rooted in anaerobic soils. Salinity tolerance is the peculiarity of mangrove plants and is species dependent. Mangroves act as nutrient and toxicant trap. Mangroves act as natural filters between land and the sea. They trap and bind sediment, and prevents the nutrients, metals other toxicants from entering coastal waters (*Robertson et al.*, 1995).

1.1.1 Global status

Geological history and evidences show that mangroves appeared between Eocene and Oligocene period (30 – 40 million years ago) Plant remains or fossils of major mangrove genera like *Rhizophora, Nypa* and others provide important clues in this matter(Subramanian, 2002).The World Conservation Union's report on global status of mangroves lists 61 species (IUCN, 1983). Major mangrove species belong to less than 15 families, but the most frequent occurring mangroves belong to the *Rhizophoraceae, Sonneratiaceae*, and *Avicenniacea.* At present, mangrove forests cover an area of 181,000 km^2, distributed in over 100 countries, but during the past 50 years, over 50% have been lost. Some direct activities are destroying mangroves or are degrading them, including substitution by other activities such as shrimp farming and agriculture, forestry, urban development, tourist development and infrastructure. Furthermore, other impacts include deviation of river water and contamination caused by heavy metals, oil spills, pesticides and other products. The establishment of shrimp farms has been the main cause of mangrove loss in many countries over the past 30 years (Elmer López Rodríguez, 2001).

1.1.2 Status of Indian Mangroves

The Indo – Malaysian area is considered as the cradle of evolution of mangrove ecosystems (Krishnamurthy, 1993). It is widely believed that the mangrove plants developed first in this area and then only spread to other regions of the tropics. In India studies on the botanical aspects of mangroves started as early as *Hortus Malabaricus.* According to the status report in the Government of India publication (Anon, 1987) the total area of mangroves in India was reckoned at about 6740 km ^{2}. This covered 7 % of the world's mangroves and 8 % of the Indian Coast (Untawale, 1987). The Sunderban's of India and Bangladesh put together forms the single largest block of mangroves of the world.

Mangroves are one of the most threatened ecosystems of the world. Over the past few years mangroves are disappearing at alarming rate. Changes are response to external influences, shore line development (eg. coastal urbanization, conversion to aquaculture); changes in the local hydrology are the biggest threats to mangroves. Many people think of mangroves as smelly places suitable for dumping trash and other unwanted material. The utilization and conversion of mangrove areas for acquaculture, human settlement, and industrial sites is now common. This unique ecosystem is in imminent danger of extinction as a consequence of indiscriminate and unplanned development and needs immediate protection and conservation (Subramanian, 2002).Urgent steps are to be taken to save this fragile ecosystem. The recognition of the environmental and economic importance has led many nations to new legislation for the protection of these ecosystems. The Supreme Court of India has categorized mangrove habitats under the coastal zone regulation – 1 (CRZ – 1)* area to ensure that they are sustainably utilized and conserved.

1.1.3 Mangroves of Kerala Coast

The mangrove formations of Kerala represented only a feeble fraction of the total mangroves in India (Blasco, 1975). There are clear evidences to show that mangrove vegetation existed along the coastal tracts of Kerala and once supported about 700 km^2 of mangroves along its coast and what exists now are only relics of the past. For urbanization, construction of harbors, ports, prawn farming, coconut plantation and rice – fish culture, vast mangal lands were cleared or reclaimed (Naskar and Mandal, 1999). In 1992, the mangrove area in Kerala is estimated to be about 17km^2. 36% of these are degraded or are in degrading condition (Basha, 1992). In Kerala coast more and more wet lands are being destroyed for developmental activities and human settlement.

Though the existing mangrove forests of Kerala are highly localized, the species diversity of these mangroves and its associates is comparatively rich. It is

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* **CRZ 1** : Areas that are ecologically sensitive and important such as national parks, Sanctuaries, reserve forests, wildlife habitats, mangroves, corals coral reef areas; areas close to breeding and spawning grounds of fish and other marine life, areas of outstanding beauty/areas rich in genetic diversity, areas likely to be inundated due to rising Sea level consequent upon global warming and such other areas, as may be declared by the Central and State Government at the State or Union territory level from time to time.

ii) Area between low Tide Line and the High Tide Line,

The relevant norms for regulation of activities are as follows:

For CRZ-I: No new Construction shall be permitted within 500 meters of the High tide Line. No construction activity except as listed under 2 (ix) will be permitted between the Low, Tide Line and the High Tide Line.

reported that 17 true mangrove species and 23 semi-mangrove species occur in the state. In Kerala mangroves are distributed in eight coastal districts of which Kannur (755 ha) has the largest area followed by Kozhikode (293 ha) Ernakulam (260 ha) Alappuzha (90 ha) and Kottayam (80 ha) (Subramanian, 2002)

1.2 Trace metals in the environment:

Heavy metals are naturally occurring. But, human activities have dramatically increased the back ground levels in the environment. Urbanisation and population growth have greatly increased non- point source pollution of coastal waters. A diversity of pollutants enter the coastal environment via rivers, diffuse run off and point sources (industry and urban). Among them metals are considered serious pollutants because or their environmental persistence and their ability to concentrate in aquatic organisms. Unlike organic pollutants, natural decomposition do not remove metals. Metals are found naturally in the environment. Metals are elemental and hence do not break down. A metal's chemical aspect may change but the element itself remains. Their toxicity even at low concentrations have been found to induce serious health hazards. Once they enter into the environment they persist for years. Cycling of metals plays an important role in modifying the spatial and temporal trends.

Trace metals have the ability to accumulate in different compartments of the ecosystem. As metals enter a coastal environment, they are transferred to the sediments by various processes such as adsorption onto particle surfaces and co precipitation with solid phases (Santschi *et al.*, 1990; Sharma *et al.*,1999).These sediments become an important reservoir of metals and provide input records of the metals in the ecosystem(Zwolsman *et al.*,1996; Sharma *et al.*,1999).The knowledge of the metal concentration in the sediment is of extreme importance in order to understand the bioavailability and the extent of toxicity.

An assessment of metal contamination in the environment requires a detailed understanding of the element's chemistry, production, uses and discharges. A detailed note on the metals studied in this thesis is given below.

Cadmium

In its compounds cadmium exhibits almost exclusively the +2 oxidation state. Cd has no essential biological function and is toxic to plants and animals. The estimated half-life of Cd in soils vary between 15 and 1100 years. The concentration of Cd in the earth's crust was estimated to be around 0.1 mg/kg. Cd is closely associated with Zn in its geochemistry. Both the elements have similar ionic structures and electro negativities. Cd has a higher affinity for S than Zn. Cd is a soft Lewis acid and will therefore react and complex readily with soft bases such as chloride and hydroxyl groups. Cd forms anionic complexes with humic acid and fulvic acid. These are less stable than those with Cu and Pb. The oxides and hydroxides of iron have a capacity to adsorb Cd at pH 6 and 7. Cd is also adsorbed onto clays and organic matter (Alloway, 1990).Cadmium has a tendency to form soluble chloro complexes. Cadmium can exist in a number of bisulphide complexes, Cd $(HS)^{2-n}$ (n = 1 to 4),which are typical for the reaction of class B metals (Stumm and Morgan, 1996).

Sources of soil contamination by Cd are mining and smelting of Zn, atmospheric pollution from metallurgical industries, disposal of wastes containing Cd such as incineration of plastic containers and batteries, sewage sludge application to land and the burning of fossil fuels. Cd contamination was also found to be occurring from a wide range of materials containing Cd as impurity. Phosphatic fertilizers are important example for this.

Chromium

Chromium is a relatively abundant element in the Earth's crust. It is widely dispersed in natural deposits, where it is always found in combination with other elements, especially oxygen. Chromite ($FeCr_2O_4$) is a commercially important mineral. The most common oxidation states of chromium are +6, +3, and +2. A few stable compounds of the +5, +4, and +1 states, however, are known. In the hexavalent state, the most important species formed by chromium are the chromate (VI), CrO_4^{2-}, and dichromate (VI), $Cr_2O_7^{2-}$ ions. These ions form the basis for a series of industrially important salts. Among them sodium chromate, $NaCrO_4$, and sodium dichromate, $Na_2Cr_2O_7$, are used in leather tanning, in metal surface treatment, and as catalysts in various industrial processes. Chromium forms several commercially valuable oxygen compounds, the most important of which is chromium (VI) oxide, commonly called chromium trioxide or chromic acid, CrO_3.

Cobalt

Cobalt, though widely dispersed, makes up only 0.001 percent of the Earth's crust. It is found in small quantities in terrestrial and meteoritic native nickel-iron, in the Sun and stellar atmospheres, and combined with other elements in natural waters, in nodules beneath the oceans, in soils, in plants and animals, and in such minerals as cobaltite, linnaeite, skutterudite, smaltite, heterogenite, and erythrite. Traces of cobalt are present in many ores of iron, nickel, copper, silver, manganese, zinc, and arsenic, from which it is often recovered as a by-product. Cobalt is a trace element essential in the nutrition of ruminants (cattle, sheep) and in the maturation of human red blood cells in the form of vitamin B_{12}, the only vitamin known to contain such a heavy element. In its compounds cobalt nearly always exhibits a +2 or +3 oxidation state, although states of +4, +1, 0, and -1 are known. Co^{2+} is the stable ion in water.

Copper

Copper occurs combined with many minerals, such as chalcocite, chalcopyrite, bornite, cuprite, malachite, and azurite. It is present in the ashes of seaweeds, in many sea corals, in the human liver, and in many mollusks and arthropods. Copper plays the same role of oxygen transport in the hemocyanin of blue-blooded mollusks and crustaceans as iron does in the hemoglobin of red-blooded animals. The copper present in humans as a trace element helps to catalyze hemoglobin formation. Copper forms compounds in the oxidation states +1 and +2 in its normal chemistry.

Iron

Iron is the fourth most abundant element in the Earth's crust. Iron is a trace element required by both animals and plants. Atmospheric rain out, river transport and natural emissions are the major sources of iron to the atmosphere. The primary oxidation states of iron are Fe^{2+} (ferrous) and Fe^{3+} (ferric). The redox chemistry of iron plays an important role in controlling the fate of iron in natural waters.

In unpolluted oceanic seawater, concentrations of iron between 2.8 - 29 ng l^{-1} and 224 - 1,228 ng l^{-1} have been reported, although higher concentrations may be found in estuarine waters. Iron concentrations in salt marsh sediments are frequently much higher than those occurring in the overlying waters. Mean concentrations as high as 20,800 mg kg^{-1} appears to be tolerated in coastal salt marshes, which are designated as 'healthy'.

Although it is of less toxicological significance it often controls the concentration of other metals. Iron forms complexes with sulphates to form sulphides. Diagenetic sulphides were an important sink for trace metals in reduced sulphidic sediments. Iron often causes a reduction in the toxicity of other heavy metals like Cu, Pb and Zn. This is probably the result of the competition between iron and other metals for binding sites and / or partial sequestration of metals by iron colloids (Moore, 1991).

Iron, which is the chief constituent of the Earth's core, is the most abundant element in the Earth as a whole (about 35 percent). Iron makes up 5 percent of the Earth's crust and is second in abundance to aluminum among the metals and fourth in abundance behind oxygen, silicon, and aluminum among the elements. The average quantity of iron in the human body is about 4.5 g (about 0.004 percent), of which approximately 65 percent is in the form of hemoglobin, which transports molecular oxygen from the lungs throughout the body; 1 percent in the various enzymes that control intracellular oxidation; and most of the rest stored in the body (liver, spleen, bone marrow) for future conversion to hemoglobin.

Lead

Lead is the 36th most abundant element in the earth's crust with the average concentration of 15 mg/kg. The input of anthropogenically derived Pb in the environment now out weighs all natural sources. Lead continues to be used in large amounts in storage batteries, metal products, pigments and chemicals. Approx. 96 % of all Pb emissions originate from anthropogenic forces (Nriagu, 1979).

Nickel can achieve oxidation states from – 1 to + 4 ; compounds of +2 state are most common.Rarely found free in nature, lead is present in several minerals, but all are of minor significance except the sulfide, PbS (galena, or lead glance), which is the major source of lead production throughout the world. Lead shows valences of +2 and +4 in its compounds. The important lead compounds are the oxides: PbO, PbO_2, and Pb_3O_4.

Lead has a special affinity for clay mineral structures due to its ionic radius, which is very similar to that of potassium. Lead is also capable of replacing potassium in the montmorillonite lattice (Forstner and Whitmann, 1981). Though lead is highly toxic to the biota, studies showed that bio availability of the metal in estuarine and marine environments are reduced through the geochemical immobilization of the element in these environments.

Manganese

Manganese combined with other elements is widely distributed in the Earth's crust. Manganese is essential to plant growth and is involved in the reduction of nitrates in green plants and algae. It is an essential trace element in higher animals, in which it participates in the action of many enzymes. An excess of this element in plants and animals is toxic. Of the wide variety of compounds formed by manganese, the most stable oxidation states are +2, +6, and +7.

Nickel

Nickel (atomic number 28) resembles iron (atomic number 26) in strength and toughness but is more like copper (atomic number 29) in resistance to oxidation and corrosion, a combination accounting for many of its applications. More than half the nickel produced is used in alloys with iron (particularly in stainless steels), and most of the rest is used in corrosion-resistant alloys with copper (including Monel metal) and in heat-resistant alloys with chromium. Nickel is also used in electrically resistive, magnetic, and many other kinds of alloys, such as nickel silver (with copper and zinc). The unalloyed metal is utilized to form protective coatings on other metals, especially by electroplating.

In its compounds nickel exhibits oxidation states of -1, 0, +1, +2, +3, and +4, though nickel (II) is by far the most common. Divalent nickel forms a large number of complexes, encompassing coordination numbers 4, 5, and 6 and all of the main structural types, - eg; octahedral, trigonal bipyramidal, tetrahedral, and square. Ni (+2) forms stable complexes with organic ligands. Inorganic complexes includes halides, sulphates, carbonates and carbonyls. Humic and fulvic acids form strong complexes with nickel. In the aquatic systems, a large fraction of nickel is removed by the scavenging action of Fe and Mn oxides and hydroxides.

Ni is not a significant and wide spread contaminant in marine sediments. In industrialized parts of the world concentrations seldom exceed 50 – 100 mg/kg. Ni is less toxic than Cd, Cu, Cr, Pb and Zn.

Zinc

Zinc is relatively rare in nature. This is classified as a border line element according to HSAB (Hard and soft acids and bases) concept, it is intermediate between hard and soft acceptors. Zinc forms complexes with hard and soft bases. This is reflected in the occurrence of Zn in nature both as sulphide and carbonate ores. It forms bonds with oxygen as well as with nitrogen and sulphur donor atoms.

Zinc is an essential trace element in the human body. It is found in high concentration in the red blood cells as an essential part of the enzyme carbonic anhydrase, which promotes many reactions relating to carbon dioxide metabolism. The zinc present in the pancreas may aid in the storage of insulin. Zinc is a component of some enzymes that digest protein in the gastrointestinal tract.

The major uses of zinc metal are in galvanizing iron and steel and in making brass and alloys for die-casting. The negative electrode (outside can) in one common type of electric dry cell is composed of zinc. In chemical compounds, zinc exhibits almost exclusively a +2 oxidation state. A few zinc (I) compounds have been reported, but never any compounds of zinc (III) or higher.

In unpolluted fresh waters, dissolved zinc concentrations generally range from 0.5 to 15 μg/l and much higher concentrations have been reported for industrial areas. Large quantities of zinc are reported in the environment by precipitation. For sediments from uncontaminated areas concentrations are < 50 mg/kg. Similar ranges of values have been reported for estuarine and coastal sediments (Moore and Ramamoorthy, 1984).

Important species of metals in aquatic systems:

A portion of the metals is bound to the sediments by ion exchange and adsorption. In surface water and pore water solutions of sediments, the predominant forms are chloride, sulphate and anionic species derived from H_2S.Complexation with sulphate is specific and corresponds to electrostatic interactions. Chlorides, bicarbonates and carbonates are important ligands for trace metal complexation. Precipitation of hydroxides, sulphides and carbonates occurs within the water body, when the corresponding solubility product is exceeded. Sulphides become important under anoxic conditions. Iron suphide formation and consequent sorption onto iron sulphides are important in reduced sediments. Sulphide formation depends on sediment composition, which is influenced by the concentration of the sulphide ion and organic matter. Metal oxides were found to have a greater ability to bind and retain metals. Hydroxides often possess greater affinity to Fe^{3+} than other organic/inorganic bases. Metal hydroxides exists in different forms in different aquatic environments with respect to the effects of co - precipitation and later redissolution. Among these,hydroxides and oxides of Fe/ Mn have strong affinities for trace metals. These affinities involve mechanisms of adsorption and co precipitation. Fe / Mn hydroxide complexes are potential carrier phases because of their appropriate sorption behaviour for other metals. Mineralogical constituents of sediments, considered to be important in controlling metal concentrations in sediment are hydrous oxides of iron and manganese, organic matter and clays. Sorption onto clay minerals (grain size effect), complexing with organic matter and scavenging by Fe/ Mn hydroxides has strong control on trace metal speciation in sediments.

A number of sediment forming minerals with a large surface area – particularly clay minerals- freshly precipitated iron hydroxides, amorphous silicic acids as well as organic substances are capable of sorbing cations from solution and releasing equivalent amount of other cations into the solution by cation exchange. The mechanism, which results in cation exchange, is based on the sorptive properties of negatively charged anionic sites, – SiOH, - $AlOH_2$, and - AlOH groups in clay minerals, Fe – OH groups in iron hydroxides, carboxyl and phenolic - OH groups in organic substances, towards positively charged cations. The balancing of negative charges of the lattice is a selective process which accounts for preferential adsorption of specific cations and release of equivalent charges associated with other species. All fine-grained materials with large surface area are capable of accumulating heavy metal ions at the solid – liquid interface as a result of intermolecular forces (adsorption). The pH values may dominate the adsorption processes of heavy metal cations. The heavy metals are completely released under extremely acidic conditions (Forstner and Whittmann, 1981).

Marine sediments are largely composed of biogenic macromolecules – proteins, carbohydrates, lipids (including hydrocarbons) and lignins. The affinity of trace metals for organic substances and their decomposition products is of great importance for the behaviour of trace metals in aquatic systems. In the marine environment organic complexes form stable complexes or even chelates with trace metals. They are formed by microbial and chemical reactions. Complexation reduces their free ion concentrations to lower values. The adsorption of cations on organic substances is due to the negative charge of the colloids. Complexation with organic acids (hydrophilic colloids) and humic substances (hydrophobic colloids) occur in aquatic systems. In humic substances chelation by neighbouring carboxyl and phenolic groups is the major mechanism of complexation. Even oxidation cannot release metals occluded in humic materials. Biogenic ligands synthesized by bacteria and phytoplankton assists in buffering intra cellular trace metal activity to desirable and tolerable concentrations. Sideropohores, metallothioneins and polychelatins are some examples of biogenic ligands. These ligands are membrane bound and are specific. Some of these may be released to water to reduce metal toxicity; others may function as transport ligands to assist microorganisms to acquire essential trace metals (Stumm and Morgan, 1996).

The free metal ions are the most mobile and the most bioavailable forms (Prokop *et al.*, 2003). The concentration of the free metal ions varies significantly with pH and organic substances. Ion- pairs, complex ions, polymers and micro particiulates as well as sorption on solid surfaces and biological surfaces reduce the activity of the free ionic form of the metals.

1.3 Trace metals in mangroves:

Mangrove forests play an important role in the biogeochemistry of trace metal contaminants in tropical coastal areas. They are potential sinks for anthropogenic metal contaminants (Dubinski *et al.*, 1986; Clark *et al.*, 1997; Haribson, 1986; Lacerda *et al.*, 1993; Ramanathan, 1997; Silva *et al.*, 1990; Tam and Wong, 1994; Tam and Wong, 1995; Tam and Wong, 1996; Tam *et al.*, 1998). Tidal activities, land – run – off and rainfall are the major sources of trace metals into the mangroves. Mangrove ecosystems were affected by solid wastes and wastewaters, which are important sources of trace metals (Nriagu and Pacyna, 1988). Besides the inputs from natural and anthropogenic sources heavy metal distribution in sediments can be affected by factors such as sediment chemical composition and diagenesis (Salmons and Forstner, 1989). Elements show different behaviour during diagenesis. Clark et al. (1998) presented a model that recognized the development of oxidation and reduction horizons, water table fluctuations and bioturbation as major factors controlling the metal behaviour within the mangrove sediments.

Mangroves act as natural sinks and filtration systems (Banus *et al.,* 1975; Simposon *et al.,* 1983; Dubinski *et al.,* 1986; Orson *et al.,* 1992; Saifullah *et al.,* 2002). Fine particulates, high organic matter content, reduced conditions, sulphide production (Clark *et al.,* 1997; Hutchings and Saenger, 1987; Saifullah *et al.,* 2002; Tam and Wong, 1996) and other geochemical conditions favour the accumulation of trace metals and prevent remobilization and biotic uptake (Haribson, 1986; Silva *et al.,* 1990; Lacerda *et al.,* 1993; Clark, 1998; Tam and Wong, 1996). Thus the mangroves reduce the potentially deleterious effects of metal contamination. The mangrove eco system, not only provides a physical trap for fine particulates and their transported load of trace metals, but also a chemical trap for precipitation of metals from solution (Haribson, 1986).

Mangrove ecosystems are under serious human contamination, since many are close to areas of urbanization and industrialization Studies on the distribution of trace metals are of great importance in the context of environmental pollution.

Sediments conserve important environmental information and are increasingly recognized both as a carrier and a possible source of contaminants in aquatic systems. The geochemical features of the study area as well as human interventions influence trace metal distribution. In mangroves only the oxidized surface layer of the sediment interacts with the overlying water and hence the metal concentrations in the surface sediment is only relevant to the benthic fauna (Luoma and Bryan, 1981; Harrison, 1986).They are potential sinks for anthropogenic metal contaminants (Haribson, 1986; Lacerda *et al.,* 1993; Silva *et al.,* 1990 Tam and Wong, 1994; Robertson and Philips, 1995; Tam and Wong; 1995;Wong *et al.,* 1995; Tam and Wong; 1996; Clark *et al.,* 1997; Ramanthan, 1997; Tam, 1998;).

The heavy metals being biologically non- degradable would be transferred and concentrated into plant tissues from soils and pose long term damaging effects on plants. In mangroves, metals are generally not available for uptake by mangrove plants (Harribson, 1986; Silva *et al.*, 1990; Lacerda *et al.*, 1993) and probably by other organisms. Mangrove sediments, acting as a sink for the heavy metals, may pose a threat in the future. There is a chance of these sediments becoming a secondary source of pollution. Metals are accumulated only temporarily and will be remobilized and suspended back to the water column with varying environmental conditions. The destruction of mangrove forests can promote the remobilization of sediment – trapped metals and facilitate the transport to adjacent areas (Peters *et al.*, 1997; Lacerda, 1998). Mobility of trace metals from mangrove soils also occurs when the retention capacity of the surface soil mass is saturated (Tam and Wong, 1993). Heavy metals accumulated in soils not only exert deleterious effects on plant growth, but also affect soil microbial communities and soil fertility (Yim and Tam 1999).

Increased levels of heavy metals in the environment may result in higher concentrations in biota. In mangrove plants, excess metals were translocated from roots to stem, then to leaf; the upward movement depending on the mobility of heavy metals. Different plants react differently to increased load of trace metals; some are more resistant than others (Wong *et al.*, 1995; Tam and Yao, 1998). Mangrove plants render metals inactive by binding and thereby delaying their reentry into system and slowing down their cycling. Small metal export in mangrove forests occurs through mangrove detritus (Lacerda *et al.*,1988 ; Silva *et al.*,1998). Removal of metals by plant uptake was less than 2% (Tam and Wong, 1997). Even if the plant material is poor in trace metals, substantial amounts of mangrove detritus can be exported from forests to the surrounding communities, counter balancing the low metal concentrations (Peters *et al.*, 1997). Certain processes may cause differences between this trend and that of leaf detritus transported out of the forests.

Mangrove plants exude oxygen through their roots to cope with the anaerobic condition of the sediments. Thus they create oxidized rhizospheres capable of fixing heavy metals under non bio available forms. In mangroves much larger metal concentrations are retained around the rhizosphere layer within the sediment preventing their migration. Root induced formation of oxy hydroxides may retain metals within the sediment through strong bonds and decrease metal uptake by plants and transfer via detritus. Iron plague formation is also important in trace metal immobilization (Machado *et al.*, 2004). In mangrove sediments, the heavy metals are present in the rhizosphere sediments under very refractory chemical forms, unable to be absorbed by plants. The reduced state of the bulk soil favours the immobilisation of heavy metals due to the formation of metal sulphides; but the oxidation processes in the rhizosphere may mobilize metals (Ong Che, 1999)

1.4 Speciation of trace metals in sediments

In order to assess the environmental impact of metals, it is important to examine the total metal concentration and also the different chemical forms of metals. The environmental behaviour and toxicity of an element can be understood only in terms of its actual molecular form. Heavy metals are associated with various compartments in the sediments and these associations can be different for natural and anthropogenic materials. The tendency and rate by which a metal participates in a geochemical or biological process depends on the physiochemical forms in which it exists. Each different form of an element can exhibit different bioaccumulation trends.

Sediments usually act as a sink but may also become a source under certain conditions, especially in heavily contaminated areas or in drastically changing environments. Sediments have a marked ability for converting inputs of metals from various sources into sparingly soluble forms either through precipitation as oxides or carbonates, or through formation of soil solutions with other minerals (Salmons and Forstner, 1984). The uptake of heavy metals by organisms occur chiefly in the dissolved state. Due to various diagenetic processes, the sediment – bound metals and other pollutants- may remobilize and be released back to overlying waters, and in turn pose adverse effects on aquatic organisms. For studying the concentrations and availability of such trace substances, interactions with solid phases along with mechanical and chemical processes as bioturbation, sorption, desorption, diffusion and mobilization should be considered (Calmano and Forstner, 1984). Speciation is not only useful in determining the degree of associations of trace metals in sediments and the extent of remobilization into the environment, but helps to distinguish metals with a lithogenic origin.

According to Rubio *et al.*, 1991, metals with an anthropogenic origin are mainly obtained in the first fractions; the residual component represents the fraction strongly bonded to lithogenic minerals of sediments. This fraction also includes metals occluded in humic materials. Residual fractions are of little importance in the studies of natural environments. The metals associated with this fraction corresponds to the metal with a natural origin and will not be remobilized into the aquatic medium under natural conditions (Rubio *et al.*, 1991). Levels of residual fraction should be considered as the background value of the elements in the sediment (Tessier *et al.*, 1997). Metals bound within the silicate mineral lattices probably accounts for bulk of the metals in this phase and concentrations are governed by catchment geology (Carral *et al.*, 1995). The metals bound in the residual phase are unlikely to be reactive during sedimentation and diagenesis and pose little environmental nuisance (Jones and Turkey, 1997). Non lithogenous fractions are susceptible to remobilization and hence contribute to bioavailability.

Multiple step sequential extraction schemes provide detailed information of possible chemical forms in soil (Tessier *et al.*, 1979; Pickering, 1986). The determination of different forms of contaminants helps to assess the bioavilability and long-term consequences of contamination (Li *et al.*, 1995). Sequential extraction processes appear to be of greater value than a single extractant, providing more detailed information of possible metal chemical forms in the soil (Tesssier, 1979; Pickering, 1986). The reagents used for sequential extraction have been chosen on the basis of their supposed selectivity and specificity towards particular physico – chemical forms. The amount of any given element extracted from a particular phase is dependent on the reagent concentration, type, extraction sequence and solid solution ratio (Miller *et al.*, 1986). The solid solution ratio is important only while considering metals adsorbed in solid lattices. The effectiveness of extractions depend on the affinity and specificity of the extracting chemicals for the target phase.

pH changes can significantly affect metal speciation and hence bioavailabilty. The metals associated with exchangeable ions and carbonates can be easily remobilized by changes in environmental conditions such as pH, salinity etc.

(Perzez *et al.*, 1991; Izquierdo *et al.*, 1997). Metal removal by ion exchange occurs even at neutral pH. The release of metals in the exchangeable fraction is promoted by ion exchange by cations such as Ca^{2+}, Mg^{2+} (or NH^{4+}). Ammonium acetate at pH 7 is the preferred reagent because of the relatively high metal complexing power of acetate ions. Carbonate phases are highly sensitive to pH changes (Izquierdo *et al.*, 1997). This fraction becomes easily mobile and available under conditions of lower pH. (Li *et al.*, 1995). The reducible metal oxides are classified into two; easily reducible fractions (Mn oxides and partly amorphous iron hydroxides and carbonates) and moderately reducible fractions (amorphous and poorly crystallized iron oxyhydrates). Easily reducible metals are leached with acidified hydroxylamine hydrochloride. Hydroxylamine hydrochloride being a weak reducing agent cannot release trace metals bound to oxides. They remain intact during the complete extraction procedure and the metals associated with them contribute to the residual fraction (Adamo *et al.*, 1996). Application of Schewertmann oxalate buffer reagent (0.2M ammonium oxalate + 0.2 M oxalic acid) leaches out moderately reducible fraction. Organically complexed metals are removed by oxidation with 30 % H_2O_2 adjusted to pH 3 and subsequent extraction with ammonium acetate; ammonium acetate prevents metal ion readsorption and precipitation.

Chemical speciation is one of the most important parameters that can enable us to understand the mechanisms by which the pollutants act in the environment. Fractionation studies also provide insight into the diagenetic processes occurring after deposition in sediments.

1.5 Aim and Scope of the work

Mangroves have multi fold roles in socio- economic- ecological life. The mangroves are ecologically important as they function as nutrient filters and recyclers in flood water mitigation, and help protect coastal areas from sea water intrusion. These habitats are of commercial benefits as they provide breeding grounds for important fishery species. The economy of our state largely depends on its fishery resources. Mangroves are highly productive ecosystems. The continuous flow of detrital food and particulate organic matter from the mangrove system into coastal waters enriches the productivity of these waters. In recent years the pressures of growing population, industrialization and urban development have caused a reduction in the world's mangrove resources. Mangrove ecosystems are highly dynamic and their growth and decline often reflect the changing conditions of the coastal environment. Sea level changes, frost, lightening, hurricanes and anthropogenic disturbances can all alter the mangrove growth. Only a better understanding of the system can save these fragile systems.

With the continuing degradation and destruction of mangroves, there is a critical need to understand them better. A number of reports are available on the biology, ecology and management of mangroves. The geochemical role of these ecosystems still remains poorly understood. Mangrove ecosystems acting as a sink for pollutants and can also become a source. Studies on the sediment chemistry and fate of metals thus become important. Detailed investigation of the metal concentrations in different compartments and speciation can better predict the role of mangroves in retaining metals. In this study, an attempt is made to understand the geochemical cycling of metals in mangroves with special emphasis to sediments.

The objectives of the present study are:

1) To find out the geochemical variability and seasonal trends in the distribution of trace metals in the sediments from mangroves
2) To find out the relation if any existing between the metal content in the different compartments in the system - sediments, plants and water.
3) To estimate the distribution pattern of trace metals in various chemical phases of the sediments in order to assess the mobility and bioavailability of trace metals.
4) To compare the conventional speciation procedure (modified Tesssier's procedure) with the one based on pH
5) To understand the various geochemical processes determining the fate and cycling of metals through multi variant factor analysis.

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Chapter 2

MATERIALS AND METHODS

A brief description of the study area and the analytical techniques employed in the present study are presented in this chapter.

2.1 Description of the study area

The length of the Kerala coast is about 560 km, extending from north to south parallel to the 'Western Ghat'. The stations selected for the present study are 1) Chettuva 2) Vypin 3) Mangalavanam 4) Nettoor 5) Ayiramthengu and 6) Asramam. Among these three are in Cochin backwaters- Vypin, Mangangalavanam and Nettoor.

Station 1 – Chettuva: Chettuva situated in the latitude 10°32' N and longitude 76°02' E between Cochin and Calicut is a significant mangrove zone in Kerala. In this zone, Chetwaipuzha and Karanjirapuzha together join and form a small estuary. These private zones are reclaimed but about 5 ha mangrove zones are present here. Coastal tourism is one of the major threats to this area, a lot mangroves have been cleared for the construction of health resort and hotel.

Station 2 – Vypin: Vypin Island, situated at 9°58' N latitude and 79°17' E longitude, is the largest single stretch of mangroves found in Kerala. It covers an area of 101 hectares. It is a semi-closed system, which is lying closer to the Arabian Sea than the other stations. Vypin island is well known for its Pokkali fields. Mixed silvi – agri- aquacultural farming is practiced here. Here, large areas of mangroves have been destroyed for prawn and fish culture. The pressure of the growing population is also a threat to these mangroves. The dominant plant species found here are *Avicennia officinalis, Acanthus ilicifolious and Rhizophora Mucronata* sp.

Station 3 – Mangalavanam: Mangalavanam, considered as the 'green lung' of the city, (9°59' N latitude and 76°11' E longitude), is under the control of Forest and Wild life department of Govt. of Kerala. It occupies an area of 3.44 ha. The northern and eastern portion of the area is bordered by Bharath Petroleum Company, south by Ernakulam Railway goods station, west by Salim Ali Road and Central Marine Fisheries Research Institute. It is almost a closed system. It is connected to the Cochin backwaters by a canal. Mangalavanam gained importance

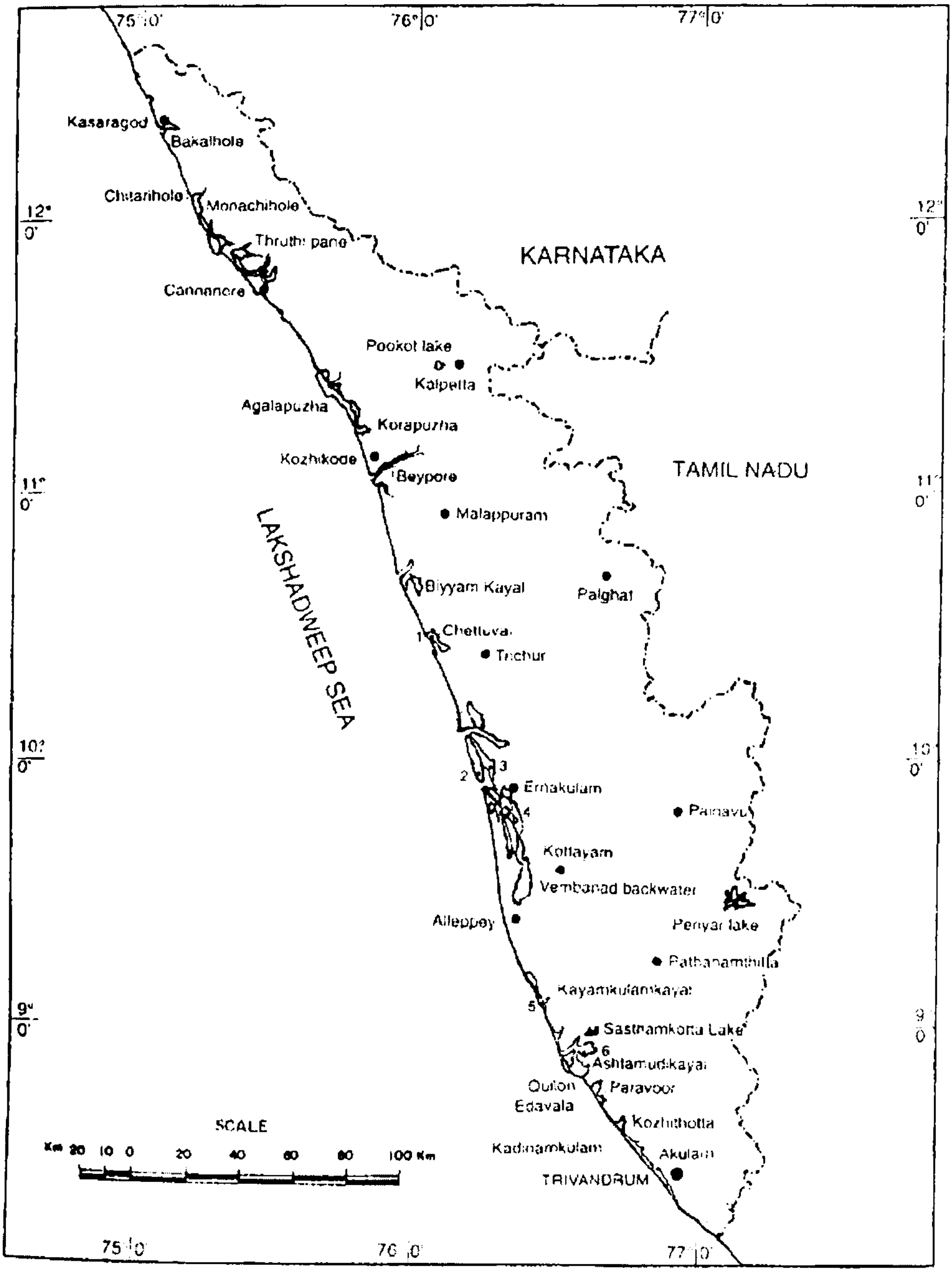

Fig. 2.1 Location Map

because of the vegetation and also due to the congregation of breeding birds. The dominant mangrove flora found here are *Avicennia officinalis, Acanthus ilicifolius* and *Rhizophora mucronata* sp. The most common bird species found here are little cormorant(*Phalacrocroax niger*) and night heron(*Nychcorax nychcorax*).Forty one species of birds were recorded from Mangalavanam representing 12 orders and 24 families(Jayson, 2002). Oil pollution is a serious threat faced by this mangrove ecosystem. Studies showed that the number of migratory birds visiting this mangrove area decreased over the past years.

Station 4 – Nettor: Nettoor can be considered as a vanishing mangrove ecosystem, which is largely affected by various developmental activities. This is an open system with maximum human intervention (Geetha, 2002). Here, majority of mangrove areas were converted to prawn farms. Increasing prawn culture in mangroves of Cochin back waters should be considered seriously as many studies from different parts of the world pointed out increased aquaculture practices as one of the major threats to these fragile ecosystems. Urbanization programmes in this area includes recently constructed Ernakulam - Kumbalam railway line, a part of coastal railway line to Alappuzha destroyed many patches of mangroves in this area.

Station 5 - Ayiramthengu is one of the most undisturbed mangrove potential of Kerala. It is located 3 km away from Ochira along the Arabian Sea and supports mangroves in few localities. Ayiramthengu area is rich in floral composition. Out of the 17 tree mangroves and 23 semi mangroves in Karalla 9 tree mangroves and 11 semi mangroves are available in this area (Murugan and Mohan Kumar, 2000).

Station 6 - Asramam: Ashtamudi, the second largest estuary in Kerala is having a few patches of mangroves. Asramam mangroves are in the river mouth of Kallada river.Waste disposal from Kollam Municipality is a threat to this site.

2.2 Sampling and Storage

All the glass wares and plastic bottles used for collecting the samples were thoroughly cleaned with a detergent and soaked in 6 N HNO_3 for 48 hrs. It is then washed with deionised water and rinsed several times with Milli – Q water for minimizing metal contamination. All the chemicals used were of analytical grade and the reagents were prepared in Milli- Q water.

Surface water and sediment samples were collected on a monthly basis from all the six stations for a period of 12 months from February 2001 to January 2002.Due to some inconveniences, samples were not collected during the months of August and December. As an extension of the study, surface sediment and water samples were collected during April '03 and September '03. Plant parts were also collected from all the six stations. Surface water samples were collected using clean plastic buckets and the sediment samples were taken using clean plastic spoons. The water samples were stored in previously washed plastic bottles, which were rinsed with the sample at the collection site. Sediment samples were collected in plastic bags. On returning to the laboratory a portion of the sediment is air dried and stored in dessicator. The remaining sediment is stored frozen at –5°C. List of plant species collected for the present study are given in Table **2.1**. Plant parts were collected, washed with de-ionised water to remove the adhering particles and dried at room temperature. Dried plant parts and sediments were stored in desiccators until analysis.

Table 2.1 List of plant species selected for the present study

No	Scientific names of species	Family
1	*Acanthus ilicifolious*	Acanthaceae
2	*Avicennia officinalis*	Avicenniaceae
3	*Rhizophora mucronata*	Rhizophoraceae
4	*Bruiguiera cylindrica*	Rhizophoraceae
5	*Exocoearia agallocha*	Euphoraceae
6	*Bruiguiera gymnrorphiza*	Rhizophoraceae
7	*Clerodendrum inermi*	Verbinaceae
8	*Aegiceras corniculatum*	Myrsinaceae

Water samples were filtered immediately after collection through previously weighed acid washed 0. 45 μm Whatmann membrane filters. The filtrate was acidified with 0.1N HCl and used for the determination of dissolved trace metals. The filter papers containing the suspended particulate material was stored in plastic petri dishes in a deep freezer until analysis. These filter papers were digested to determine the particulate metal concentrations.

2.3 Analytical Techniques

2.3.1 General Hydrographical Parameters and Sediment characteristics

The temperature of the water samples were measured using 1/ 10 ^{0} C mercury in glass thermometer and the pH was measured using a digital pH meter. Salinity was determined argentometrically by the modified Mohr-Knudsen method (Grasshoff *et al.*, 1999). Alkalinity was determined titrimetrically using the method by Koroleff (Grasshoff *et al.*, 1999).

Sedimentary Organic Carbon (SOC)

Sediment organic carbon was estimated on dried sediments by the procedure of El Wakeel and Riley modified by Gaudette et al. (1974).

Grain size analysis

Textural analysis of the sediment was done based on Stoke's law using the method of Krumbein and Pettijohn (1938). Sediment Grain size analysis was done on sediments from which the organic matter was removed by treatment of wet sediment with H_2O_2. The sediment was dispersed in sodium hexametaphoshate overnight and then wet sieved through a 63 µm sieve to collect the sand fraction. The mud fraction was divided into silt and clay fractions by timed gravimetric extraction of dispersed sediments (Folk, 1974).

2.3.2 Analysis of trace metals

Both the dissolved and particulate trace metals were determined in the water samples.

Dissolved trace metals:

Most environmental water samples have low metal concentrations. A pre concentration step is done before analysis. Dissolved metal concentrations were determined by the method of Danielsson et al. (1978; 1982). The filtered water samples were preconcentrated using APDC/ DDC/ $CHCl_3$ mixture after adjusting the pH of the acidified water sample to pH 4.5 by adding NH_4OH. The metals were extracted as dithiocarbamate complexes into chloroform an then back extracted into an acidic aqueous solution prior to determination by a graphite furnace AAS (Danielsson *et al.*, 1978, 1982). Then the extract was acidified with con. HNO_3 and brought into the aqueous phase by equilibration with a definite volume of water and analysed using AAS coupled with graphite furnace (Perkin Elmer model 3110, with HGA 600).

Particulate Trace metals:

Residue in the filter paper was leached with an acid mixture of $HClO_4$, HNO_3 and HCl in the ratio of 1:1:3 at 90 ^{o}C for 6 hrs (APHA, 1985). The resultant solution was centrifuged, made upto 25 ml with dil. HCl (0.1 M) and analysed using AAS (Perkin Elmer, 3110).Blank corrections for filters and reagents were applied.

Trace metals in sediments:

About 0.5 g of the finely powdered air dried sediment samples were weighed into beakers. Each sample was carefully digested with 10 ml of an acid solution ($HClO_4$, HNO_3 and HCl in the ratio 1:1:3) at 90°C until complete digestion and the mixture is evaporated to dryness. The residue was warmed with 0.1 N HCl. The resultant solution is centrifuged at 4000 rpm and made upto 25 ml. Analytical blanks were also prepared. The metal concentrations in the solution were determined by atomic absorption spectrophotometry (Perkin-Elmer 3110 AAS). Estimation of the accuracy and precision of the analysis was performed using standard addition techniques and replicate analyses.

Trace metals in plant tissues

One gram of the powdered plant parts were digested with 10 ml of HNO_3 and 3 ml of $HClO_4$ and heated on a hot plate until frothing ceases. After complete digestion, 10ml of (1+1) HCl is added and transferred quantitatively to a 50ml volumetric flask. Analysis of the extract was done using AAS (AOAC, 1995).

2.3.3 Speciation of trace metals in sediments:

Speciation studies on sediments are conducted using the modified Tessier's procedure and by using a pH based extraction scheme.

Speciation based on modified Tessier's scheme

Speciation analysis was performed using the speciation scheme of Tessier et al. (1979) modified by Calmano and Forstner (1983). The speciation scheme (Fig. **2.2**) summarizes the different steps involved. All the extracts were kept in acid washed polythene containers until analysis. The different metal species obtained were operationally defined as:

Fraction 1	Exchangeable fraction
Fraction 2	Easily reducible Fraction (Mn oxides, partly amorphous Fe- oxyhydrates and carbonate phases)
Fraction 3	Moderately reducible fraction (amorphous and poorly crystallized Fe oxyhydrates.
Fraction 4	Organic fraction including sulphides (oxidizable)
Fraction 5	Residual fraction.

Eight to ten grams of the wet sediment samples were weighed out into 250 ml Erlenmeyer flasks and allowed to equilibrate with 50 ml of the extractant by continuous agitation. The phases were separated by centrifugation. The supernatant liquid separated was analysed for trace metals by AAS. The residue was carefully washed back into the flask with the next extractant of the sequence and the operation repeated. Washings in between extractions were not done to avoid excessive solubilisation of solid phases. Analysis was done in duplicate.

Chemical fractionation based on a pH based scheme:

The steps involved in a pH based fractionation scheme are given in Table **2.2.** The extracts of different step is stored in acid washed plastic bottles in a refrigerator and analysed as immediately as possible.

Table 2.2 pH based fractionation scheme

Step	pH	Extractant	Conditions
1	8	0.05M sodium tetraborate +0.1M HCl	Shaken at room temperature for 6hrs
2	7	1 M Ammonium Acetate	Shaken at room temperature for 3hrs
3	6	0.1 M sodium citrate + 0.1N NaOH	Shaken at room temperature for 3hrs
4	5	0.1 M sodium citrate + 0.1N NaOH	Shaken at room temperature for 3hrs
5	4	0.1 M sodium citrate + 0.1N HCl	Shaken at room temperature for 3hrs
6	3	0.1 M sodium citrate + 0.1N HCl	Shaken at room temperature for 3hrs
7	2	0.1 M sodium citrate + 0.1N HCl	Shaken at room temperature for 3hrs

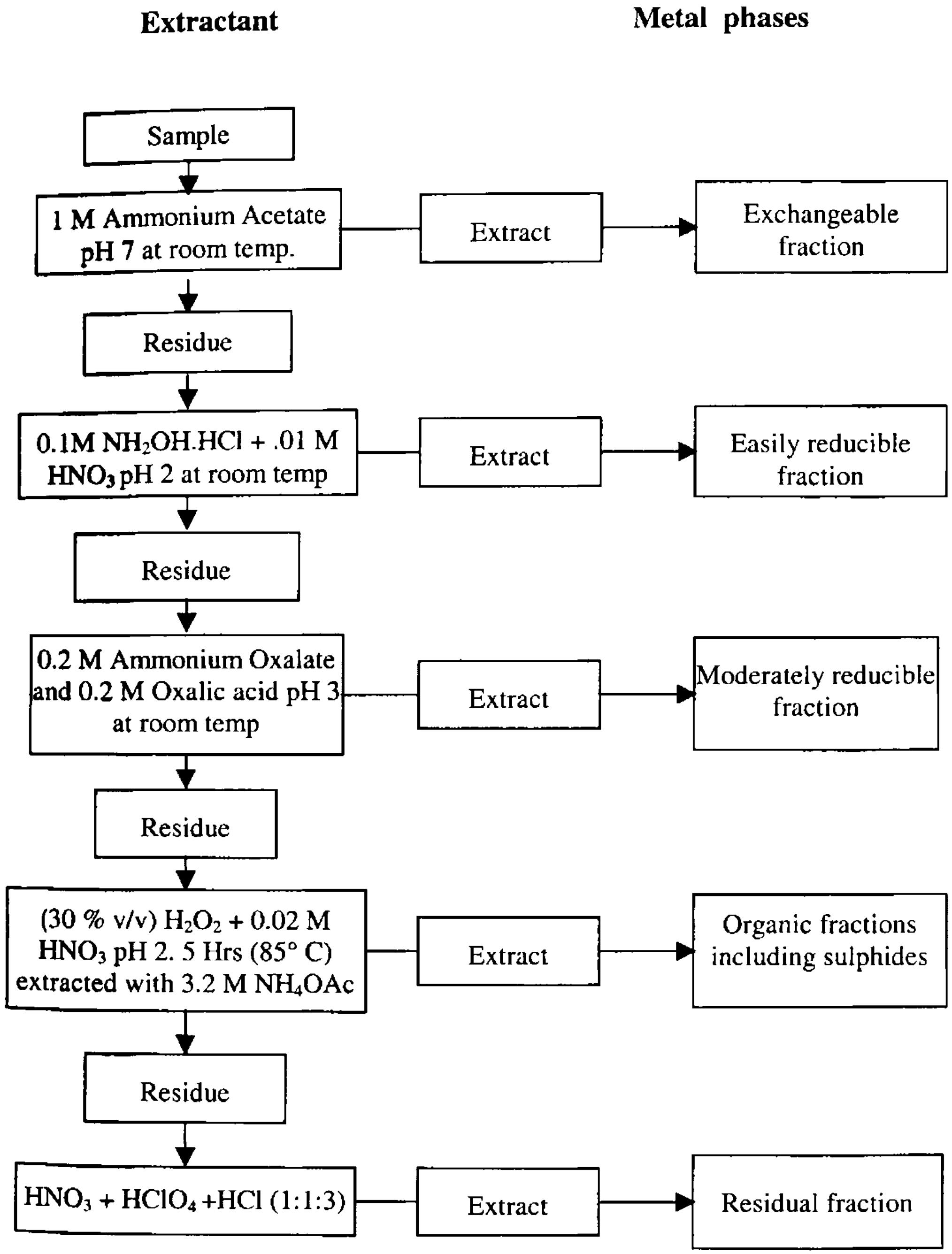

Fig. 2.2 Flow chart of the sequential extraction procedure

2.2 Data Analysis:

All data were subjected to statistical analysis wherever necessary. The annual mean, standard deviation and percentage coefficient of variation for all the parameters recorded were computed along with minimum and maximum values to get an idea of the spread of the data. Pearson correlations were determined to find out the inter relations between different parameters. Statistical significance of the observed spatial and monthly variations in sediments is checked using Two way ANNOVA (stations X months). For plant tissues, one way ANOVA was done separately between stations and species. Student's *t* - Test was done for the trace metals in water. Principal component analysis was done to find out the factors contributing to different processes occurring in mangrove sediments.

In the present study, seasonal cycle starting from pre monsoon (Feb- May) and moving through monsoon (June-Sept) to post monsoon (Oct – Jan) was considered. Speciation analysis was done only on a seasonal basis. The monthly variations of hydrographical and sediment characteristics and the seasonal variations of these parameters are given in Appendix I. Observed metal concentrations in sediments, plant tissues and water samples are presented in Appendix II. The results of the speciation studies on sediments are given in Appendix III.

2.5 Results of hydrographical parameters and sediment characteristics

2.5.1 Hydrographical parameters:

The study of hydrographical and environmental characteristics is a pre requisite for characterizing the ecosystem. Hydrography of the overlying water column has a major influence on the sedimental characteristics. Major influences on the hydrography of these systems are land run – off, rain fall, tidal action and temperature (Vasudevan, Nair, 1992).The hydrographical parameters are likely to influence the concentration and distribution of different trace metal species in aquatic systems. The station wise summary statistics of hydrographical parameters are given in table. Observed values are given in Appendix I.

Table 2.3 Station wise summary statistics of hydrographical parameters

Parameters	Stations	Min	Max	Mean	SD	CV %
pH	1	6.91	7.64	7.37	0.23	3.11
	2	7.01	7.9	7.64	0.29	3.82
	3	7.39	7.95	7.66	0.23	2.95
	4	7.43	8.07	7.65	0.19	2.44
	5	7.07	8.12	7.68	0.35	4.52
	6	7.46	8.61	8.03	0.45	5.58
Temperature(0C)	1	24	31	28.77	2.06	7.16
	2	23.8	30.8	29.05	2.08	7.15
	3	24.3	30.5	28.61	2.04	7.12
	4	23.5	32.5	28.43	2.95	10.39
	5	23.5	32	29.24	2.51	8.58
	6	26	32.1	30.03	1.76	5.85
Salinity(ppt)	1	0.32	24.65	12.04	8.52	70.76
	2	2.1	22.7	12.5	8.3	66.44
	3	2.3	25.67	11.68	8.42	72.08
	4	1.29	28.3	11.77	9.34	79.4
	5	4.99	22.7	15.12	6.95	45.97
	6	3.3	27.8	14.61	10.28	70.38
Alkalinity(mmol/l)	1	1.88	3.96	3.15	0.71	22.72
	2	0.2	3.64	1.83	0.88	48.37
	3	0.88	3.74	2.18	0.96	44.32
	4	1.48	4.4	3.4	0.84	24.65
	5	1.16	3.36	2.69	0.69	25.73
	6	0.48	2.76	1.79	0.65	36.61

pH

Many of the life processes are dependent on and are sensitive to the pH of the surrounding medium. The pH also influences to a large extent the speciation (abundance of the fraction) of the metal in the aquatic environment as well as their interphasial partitioning. Salinity intrusion and photosynthesis influences pH.

The pH of coastal waters responds to changes in: (i) dissolved carbon dioxide concentrations; (ii) alkalinity; (iii) hydrogen ion concentrations; and (iv) in a small way to temperature. Most aquatic organisms and some bacterial processes require that pH be in a specified range. It strongly influences the adsorption or desorption of cations and the toxicity of metals (Forstner and Whittmann, 1981).

In the present study, pH variations were found to be negligible. The observed pH values varied from 6.91(station 1) - 8.61(station 6).The station wise annual mean pH values were between 7.37 (station 1) to 8.03 (station 4). Here also the highest and the lowest values are for stations 6 and 1 respectively. Seasonal average values also showed similar trend; the values were 7.23 and 8.48 respectively. Monsoon / Post monsoon values were the lowest for all stations except station 3. The highest seasonal average value for this station was obtained in pre monsoon season. Seasonal variations of pH are presented in Fig. **2.3.**

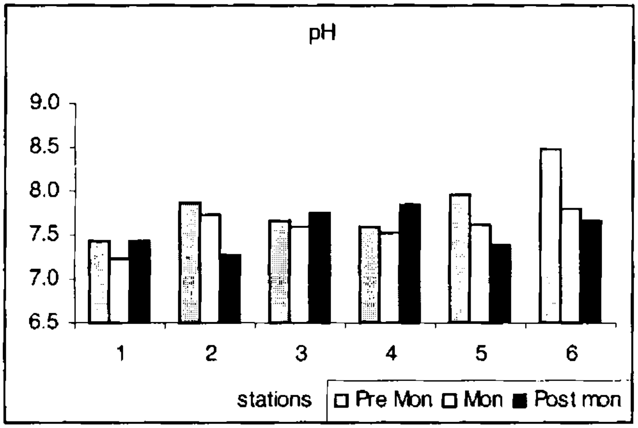

Fig 2.3 Seasonal variation of pH

Temperature

Temperature showed only moderate variations (Fig. **2.4**). The observed variations in temperature are from 23.5^{0}C to 32.1^{0}C. The average seasonal maximum temperature for stations 1, 2, 3 and 6 were noticed in pre monsoon.

Stations 4 and 5 showed the highest seasonal average temperature in post monsoon season. The annual mean temperature varied from 30.5 ^{0}C to 32.5 ^{0}C.

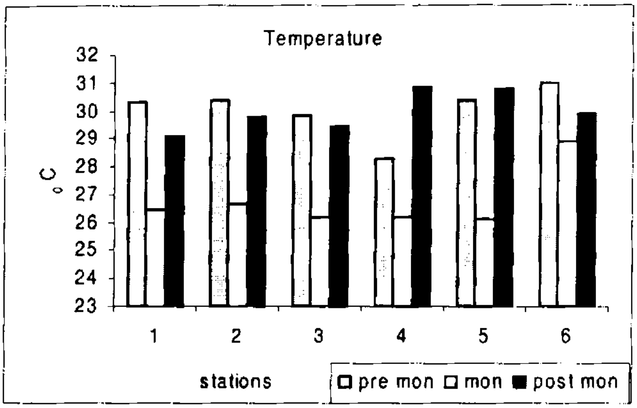

Fig. 2.4 Seasonal variation of temperature (^{0}C)

Salinity

Salinity plays an important role in the precipitation of particulate matter and heavy metals with respect to estuarine mixing. Salinity and pH gradients modify spatial variation of degree of flocculation of Fe – Mn hydrous oxides, which are effective trace metal carriers (Periakkali et al, 2002). Salinity of water is an index of the estuarine mixing processes and tidal effects. Changes in salinity are the combined effect of temperature, photosynthetic activity, and the biochemical oxidation of the waste entering the marine environment. Salinity is also an important ecological and chemical parameter. Variations in salinity affect the retention of pollutants. Seasonal salinity variations are given in Fig **2.5**.

The observed values were in the range of 0.32 – 28.30 ppt. The seasonal average values varied from 4.09 ppt (station 4) to 22.98 ppt (station 6). Pre monsoon values were higher for all stations except stations 3 and 4. For these stations, maximum salinity values were noticed in post monsoon season. Station 5 recorded the lowest value in post monsoon. At all other stations monsoon values were the minimum. The annual mean values of salinity ranged from 11.68 – 15.18 ppt.

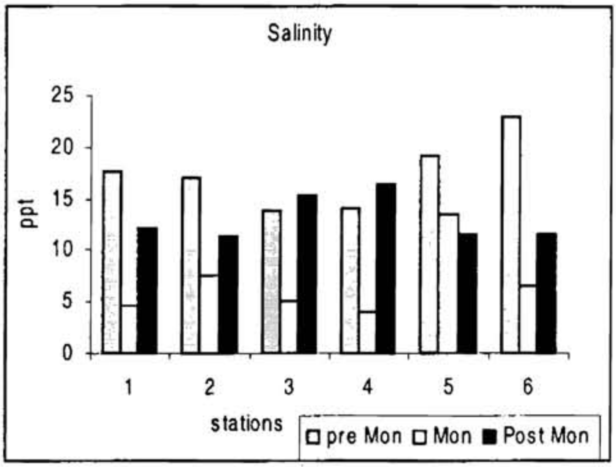

Fig. 2.5 Seasonal variation of salinity (ppt)

Alkalinity

Alkalinity of water is a measure of it's capacity to neutralize acids. The alkalinity of natural water was due to salts of carbonate, bicarbonate, borate, silicates and phosphates along with hydroxyl ions in the free state. However the major portion of alkalinity in natural waters may be caused by hydroxide, carbonate and bicarbonates. Seasonal distribution of alkalinity is presented in Fig. **2.6**

Between seasons, the alkalinity varied from 1.22 m mol/l (station 2) to 3.68 m mol/l. Both the maximum and the minimum values were observed in the post monsoon season. The highest seasonal average values for stations 1 and 5 were noticed in post monsoon. Pre monsoon value was the highest for stations 2, 3,4 and 5.The highest seasonal mean value of alkalinity was observed in monsoon season. The observed alkalinity values ranged from 0.2 (station 1) to 3.96 (station 1). The annual mean concentrations were in the range of 11.68 m mol/l to 15.18 m mol/l.

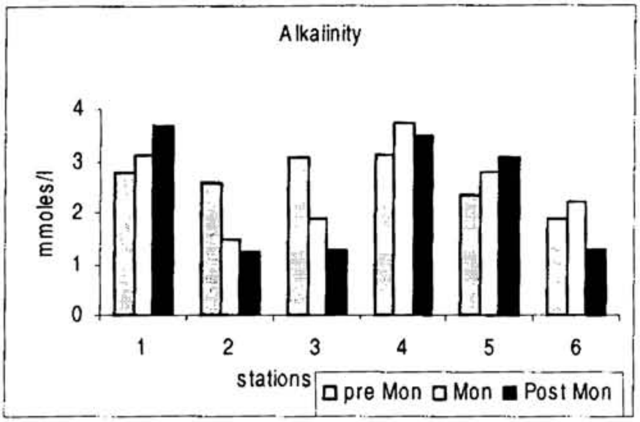

Fig. 2.6 Seasonal variation of alkalinity (m mol/l)

2.5.2 Sediment characteristics

The station wise summary statistics of the sediment parameters as organic carbon and grain size are presented in Table. **2.4**

Organic carbon

Mangroves play a key role towards the contribution of organic matter to the estuarine system in the form of litter which is converted into the detritus by microbial degradation (Sardessai, 1993). Mangroves are one of the most productive ecosystems in the world in terms of gross primary productivity and litter production. Mangroves ecosystems acts as an interface or open systems because of their flow through pathways and transporting matter. These pathways are driven by physical (tides, terrestrial run off and rain fall) and biological (litter production, decomposition, mineral uptake and faunal activities) factors that control the rate of matter import, export and storage (Boto, 1984).

Parameters	Stations	Min	Max	Mean	SD	CV %
OC %	1	0.23	1.61	0.89	0.41	46.64
	2	1.51	2.88	2.27	0.54	23.79
	3	1.52	4.80	2.38	0.93	39.11
	4	0.29	1.02	0.59	0.24	41.39
	5	0.61	2.85	1.50	0.79	52.76
	6	3.64	8.62	5.97	1.41	23.69
Sand (%)	1	14.31	89.78	50.67	25.78	50.87
	2	2.67	65.33	29.36	21.16	72.08
	3	35.48	88.61	62.18	19.01	30.58
	4	49.31	90.52	79.38	14.76	18.59
	5	72.73	96.48	88.02	9.12	10.36
	6	22.63	88.66	51.73	23.45	45.33
Silt (%)	1	2.00	42.19	19.48	13.71	70.38
	2	0.68	48.28	30.31	15.50	51.13
	3	3.68	52.69	25.88	21.53	83.20
	4	1.72	37.15	12.43	12.99	104.48
	5	0.85	13.93	5.51	5.27	95.69
	6	3.28	60.65	25.16	16.38	65.12
Clay (%)	1	3.08	48.26	24.56	16.22	66.06
	2	8.58	66.82	35.77	19.22	53.72
	3	4.87	33.67	13.04	8.92	68.40
	4	2.76	48.96	12.59	14.13	112.29
	5	2.42	11.29	5.47	3.00	54.82
	6	6.60	56.51	23.11	16.62	71.93

Table 2.4 Station wise summary statistics of sediment characteristics.

Organic carbon content in recently deposited sediments has received much attention in environmental monitoring because of their bearing on the physical, chemical and biological processes to which the sediments have been subjected. Org - C plays an important role in the dispersal pattern of many major and trace elements. The sedimentation followed by diagenetic decomposition of organic matter can alter the pH - Eh of aquatic environments. Org - C decreases with increase in grain size of the sediment. High primary production contributed to the increase in organic carbon (Nair *et al.*, 1975).

Abundant supply of organic matter in the overlying water column, rapid rate of accumulation of organic matter and the low oxygen content of the water immediately above the surface sediment favour the preservation of organic matter in sediments. Biological utilization of detrital matter leads to lower organic carbon values. Grain size appears to control the organic matter content of the sediments. Fine grained sediments are richer in organic matter than coarse sand (Tam and Wong, 2000). The factors favouring the high organic matter content are the land derived organic matter from mangrove swamps, good plankton production, and upwelling. Organic matter such as humic acids and organic acids from root exudates are also thought to play an important role in the buffering capacities of the soils. The observed organic carbon content varied from 0.29 % (station 4) to 8.62% (station 6). The station wise mean concentration was the highest at station 6(5.97%) and the lowest at station 4(0.59 %). The seasonal average concentrations varied between 0.46 % (station 4- monsoon) to 7.31 % (station 6- post monsoon).

The seasonal variation of organic carbon (%) is given in Fig.2.7. The seasonal average concentrations increased from pre monsoon to post monsoon through monsoon for stations 2 and 6. The monsoon values were highest at stations 4 and 5; the values are 0.46 % and 1.44 % respectively. The minimum values for these stations were0.85 % (pre monsoon) and 1.71 % (post monsoon) respectively. Monsoon concentrations were the lowest at stations 1 and 3. These stations recorded the highest seasonal average concentration. In all the three seasons, stations 6 and 4 respectively showed the maximum and the minimum average values.

The wide variations observed in the organic carbon contents may be due to various factors. Organic carbon enters the system from the decomposition of plant and animal parts. A portion may be brought from the adjacent coastal areas by tidal action. The increased organic carbon content noticed at station 6 might be due to the dumping of municipal waste in that area.

Organic matter content is high in monsoon. In mangroves primary production is the highest in monsoon. Resuspension of sedimentary particles occurs in monsoon. The observed peak values could be attributed to the influence of land run off containing considerable amounts of terrigenous organic matter and to the high litter fall. In monsoon terrestrial run off contributes high levels of particulate matter with organic and inorganic constituents to mangrove swamps and surrounding waters.

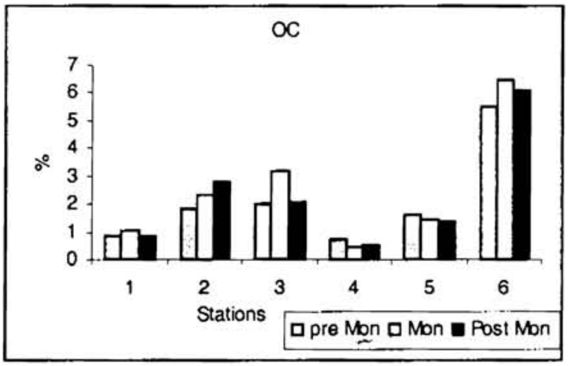

Fig. 2.7 Seasonal variation of OC %

Phytoplanktons contribute significantly to the enrichment of organic carbon. During post monsoon planktonic production leaves behind a large amount of dead planktonic matter due to the grazing of zooplankton. As this dead matter sinks to the bottom, it gets oxidized and on settling it's decomposition releases organic carbon to the interstitial water, a part of which will be released to the overlying water.

Organic matter content in the mangrove sediment is in excess of the estuarine sediment due to the inherent biological productivity within the mangrove. Decomposition of mangrove foliage and other vegetative remains and their resuspension also contributes substantially to the organic matter content in mangrove sediments (Ramanathan, 1997).

Textural Characteristics

Grain size is one of the basic attributes of sediments and its determination is essential to delineate the sedimentary environments. The study of grain size distribution reveals the physical effects on the environment on deposition and the hydrodynamic conditions existing at the time of deposition.

Sediment texture primarily designates the size, shape and mutual relation ship of individual particles constituting the sedimentary deposits The texture of the sediments has a profound bearing on the physico chemical processes as well as on the biological stock/ diversity of the depositional environment (Badarudeen *et al.*, 1996).Textural characteristics of the sediments play a significant role in the distribution of trace metals and nutrients in the ecosystem. Sand represents particles of size greater than 63 μm, silt indicates size between 63 μm and 4 μm and clay includes particles less than 4 μm. The composition of the sediment varied markedly from place to place. Textural characteristics of the sediments from stations 1 to 6 are given in Fig.**2. 8**

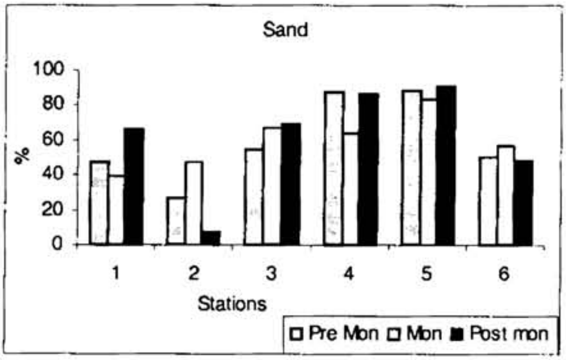

Fig 2.8 a Seasonal variation of sand (%)

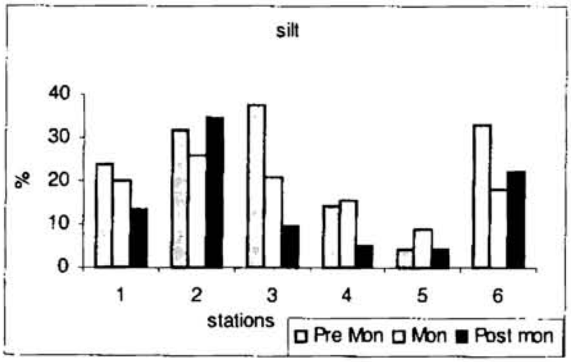

Fig 2.8 b Seasonal variation of silt (%)

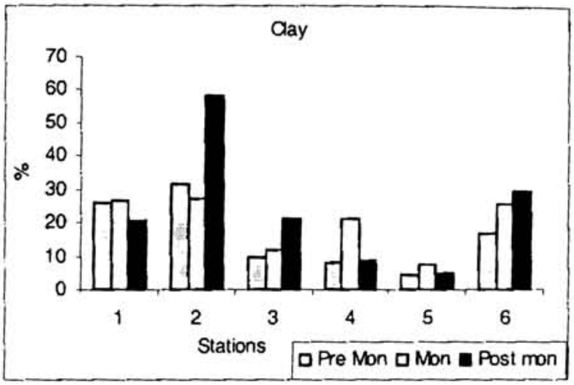

Fig. 2.8 c Seasonal variation of clay (%)

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Chapter 3

DISTRIBUTION OF TRACE METALS IN MANGROVES

Part I Trace metals in mangrove sediments

Part II Trace metals in plant tissues

Part III Trace metals in waters

Part IV Comparison of the metal concentrations in plant tissues, sediments and water

Part I Trace metals in mangrove sediments

Physiochemical factors are likely to influence the concentration and distribution of different metal species. Different processes (post depositional mobility, changes in input etc.) operating in the mangroves may be influencing the metal distribution in this environment. Water circulation and sediment deposition processes (Dyer, 1972; Mackey and Hodgkinson, 1995) controls metal deposition. In wetland systems metals are removed by absorption / adsorption, precipitation and plant uptake. Since the heavy metals are non degradable, they would be transferred and concentrated into plant tissues from soils and pose long term damaging effects on plants. Anthropogenic metals were weakly adsorbed, probably to the negatively charged sites of clays and organics. These loosely bound metals may be desorbed and may re enter the aqueous phase by complex equilibrium reactions or by mass action of more abundant cations. At least some of the retained metals may become a secondary source of metal pollution (Tam and Wong, 1996).

The adsorption of heavy metals by marsh soil involves a series of complex physical, chemical and biological interactions. The four major processes of metal retention include cation exchange, complexation with organics, precipitation as oxides, oxy hydroxides and carbonates and precipitation as sulphides (Dunbabin and Bowmer, 1992). Sulphide precipitation is important for mangrove swamps. Sulphide formation immobilizes the metals. Under anaerobic environment, sulphate reducing bacteria produce H_2S that may precipitate metals as metal sulphides (Lacerda *et al.*, 1993). The degree of retention of heavy metals in sediment is affected by sediment characteristics (Vertacnik *et al.*, 1995; Tam and Wong, 2000). The adsorption and desorption of heavy metals in sediments are influenced by many sediment properties such as pH, CEC, organic matter, clay content, redox potential, salinity, presence of Fe and Mn oxides, presence of other metals, the quantity of heavy metals accumulated, and the alternating aerobic and anoxic conditions (Harter 1992; Orson *et al.*, 1992; Tam and Wong, 1996). Sedimentation and coagulation of particulate and colloidal matter also result in metal fixation in bottom sediments. The organic matter appeared to be the vehicle through which metals are incorporated into tidal marsh sediments (Orson *et al.*, 1992; Tam and Wong, 1996). Organic colloids play an important role in metal transport. Changes in geochemical conditions alter the nature of carrier colloids

(Mc Carthy and Zachara, 1989; Clark *et al.*, 1998). Humic and other organic matter in ground water plays an important role in the distribution of trace metals through chelation with non aggregating organic colloids.

The major influences on the behaviour of metals in natural waters and sediments are pH (Harter, 1992; Tam and Wong, 1996) and Eh (James, 1978; Lu and Chen, 1977; Haribson, 1986). The pH and Eh may affect the migration of metals at the sediment surface and the concentration of the metal ion in the overlying water. Precipitation of metals at the sediment - water interface is encouraged by the high pH values. This along with photosynthetic processes and sulphate reduction in anaerobic sub surface sediments contributes to the retention of metals as sulphides. With reduced tidal movement wide diurnal variations in pH and redox potential are observed in water covering mangrove swamps. Oxidizing conditions at the mid day favour the precipitation of carbonate, oxide and hydroxide phases, while the reducing environment before dawn would facilitate the precipitation of sulphides (Haribson, 1986).

Tidal influence and stratification played a major role in controlling the distribution of trace metals in sediments. Sediment-water interactions on tidal mud flats may also result in the remobilization of metals from sediment surface. Mackey and Hodgkinson (1995) observed that tidal deposition was important in determining the distribution of metals. Transport of metals between mangroves and surrounding coastal waters was associated with the diurnal tides. Metals and other wastes discharged from the industrial areas may be transported by tidal currents and may eventually incorporate into sediments.

Elements show different behaviour during diagenesis. Clark et al. (1998) presented a model that recognized the development of oxidation and reduction horizons, water table fluctuations and bioturbation as major factors controlling the metal behaviour within the mangrove sediments. The development of redox and acidity gradients on rhizospheres may affect the trace metal distribution and geo chemical partitioning in sediments (Lacerda et al., 1993; Clark et al., 1998).

Adsorption and retention mechanisms of heavy metals varied with the soil type and the metal species. Metal binding capacity is dependent on clay content. The amount of heavy metals retained was also affected by the presence of other metals (Tam and Wong, 1996). The amounts of metals retained may be reduced by competitive interactions with other species for similar types of adsorption sites. The degree of competitive adsorption between two similarly charged metal species depended on other environmental conditions.

The investigations on the geochemical role of trace metals in mangroves of Kerala are limited. The present chapter aims to assess the distribution of trace metals in different compartments of mangroves with special emphasis on the metal concentrations in sediments. Metal concentrations in water and plant tissues were determined only to get an idea on the distribution pattern in mangroves and to compare with the trends observed in sediments. Knowledge of trace metal concentrations in sediments can predict the source, fate and the distribution mechanisms of metals in these dynamic environments. The spatial and temporal variations of trace metals in sediments were also discussed in this chapter.

3.1 Results and Discussion:

The observed metal concentrations in sediments from stations 1 to 6 are presented in Appendix IIA. The overall summary statistics on total metal concentrations in mangrove sediments are presented in Table **3.1** and Fig.**3.1.** Seasonal variations of metal concentrations are given in Table **3.2** and Fig.**3.2.**

Cadmium:

The observed values of Cd were between BDL to 12.82 µg/g. The station wise mean concentrations of Cd ranged from 1.42 µg/g (station 4) to 3.53 µg/g (station 2). The seasonal average values varied from 1.178 µg/g (station 4 – post monsoon) to 6.865 µg/g (station 3 – monsoon).

For stations 1 and 5, the seasonal average values increased steadily from pre monsoon to post monsoon season through monsoon. A reverse trend was noticed at station 4.At stations 2 and 6, the lowest seasonal average values were observed in monsoon, the values were 3.00 µg/g and 2.58 µg/g respectively. The highest seasonal average values for these stations were 4.06 µg/g (station 2 - pre monsoon) and 3.79 µg/g (station 6 - post monsoon).

Table 3.1 The station wise summary statistics on the trace metal concentrations in mangrove sediments (min, max and mean in μg/g)

Metal	Stations	Min	Max	Mean	SD	CV %
Cadmium	1	0.00	4.77	2.76	1.50	54.51
	2	1.07	5.26	3.48	1.24	35.76
	3	0.10	12.82	3.53	3.49	99.00
	4	0.00	2.84	1.41	1.00	70.87
	5	0.17	3.64	1.87	1.08	57.96
	6	0.00	5.00	2.98	1.46	49.09
Chromium	1	39.48	163.72	80.68	41.17	51.03
	2	94.97	244.01	173.55	40.56	23.37
	3	1.91	176.55	62.85	50.56	80.44
	4	18.35	71.09	43.04	17.40	40.43
	5	29.77	67.39	47.60	12.10	25.42
	6	45.12	136.08	100.33	32.36	32.25
Cobalt	1	6.52	68.16	23.19	21.48	92.65
	2	26.78	60.28	40.52	12.07	29.78
	3	1.44	25.61	8.15	7.50	92.10
	4	0.00	7.26	3.20	2.56	80.02
	5	0.00	4.60	2.19	1.67	76.41
	6	3.98	23.13	15.32	6.38	41.67
Copper	1	6.03	34.94	14.17	10.47	73.93
	2	27.90	39.95	31.30	3.75	11.98
	3	0.13	34.49	11.77	9.86	83.81
	4	2.79	8.25	5.11	1.68	32.87
	5	1.16	6.69	3.40	1.53	45.07
	6	34.77	243.32	144.88	65.89	45.48
Iron (*1000)	1	0.59	92.54	25.17	25.31	100.57
	2	21.13	86.26	51.48	19.57	38.01
	3	6.50	30.97	14.43	7.73	53.60
	4	3.75	27.39	14.32	7.47	52.16
	5	1.20	95.44	13.63	28.88	211.85
	6	0.53	79.38	22.07	24.64	111.66

Table 3.1 : Contd…

Metal	Stations	Min	Max	Mean	SD	CV %
Lead	1	10.32	43.47	23.82	11.80	49.51
	2	19.08	50.39	41.57	10.28	24.72
	3	0.73	35.44	18.08	10.35	57.23
	4	5.11	58.21	16.36	15.10	92.25
	5	5.06	36.44	14.90	8.39	56.33
	6	11.69	144.36	83.68	50.52	60.37
Manganese	1	12.16	153.91	88.90	42.92	48.28
	2	110.29	325.98	203.51	79.93	39.28
	3	28.00	220.81	79.15	56.62	71.53
	4	12.44	43.62	28.43	9.53	33.52
	5	12.22	43.55	27.24	9.71	35.65
	6	46.57	216.18	165.87	45.44	27.40
Nickel	1	8.38	77.79	27.45	19.77	72.01
	2	66.23	89.97	75.11	7.07	9.41
	3	1.76	75.90	21.17	20.82	98.33
	4	5.20	16.23	10.17	3.44	33.80
	5	3.08	72.91	24.78	26.31	106.17
	6	2.99	51.28	30.91	16.88	54.61
Zinc	1	20.25	103.34	38.78	27.75	71.54
	2	35.55	152.66	106.79	34.62	32.42
	3	75.37	238.48	145.32	58.23	40.07
	4	14.02	153.43	37.63	42.90	114.01
	5	3.88	38.37	13.24	10.01	75.66
	6	61.17	439.70	227.78	114.04	50.07

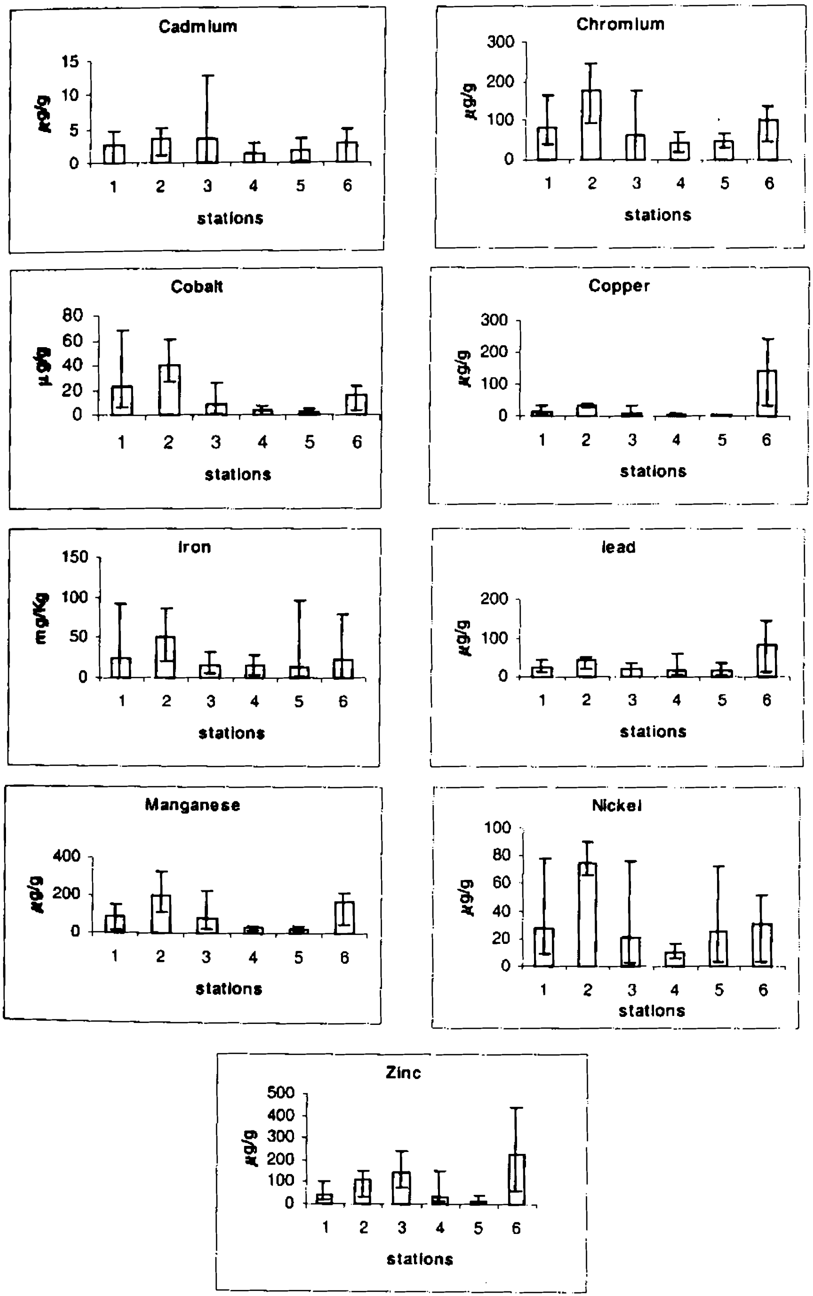

Fig. 3.1 Distribution of trace metals in mangrove sediments

Table 3.2 Seasonal variation of trace metals in mangrove sediments (µg/g)

Metal	stations	pre mon	mon	post mon	Metal	stations	pre mon	mon	post mon
Cd	1	2.62	2.93	3.74	Co	1	10.13	33.17	14.63
	2	4.06	3.00	3.19		2	42.03	45.99	33.06
	3	2.39	6.87	2.51		3	3.37	14.26	11.29
	4	2.04	1.21	1.18		4	4.86	2.15	4.27
	5	1.81	1.97	2.39		5	1.16	3.02	3.50
	6	3.31	2.58	3.79		6	17.17	19.47	17.65
Cr	1	53.88	112.39	72.40	Cu	1	8.82	7.63	10.88
	2	189.63	133.94	191.71		2	30.14	34.23	29.31
	3	38.05	140.83	68.09		3	10.29	13.94	18.52
	4	58.35	38.01	48.90		4	6.05	4.38	4.64
	5	36.77	51.70	57.95		5	2.50	4.52	3.57
	6	109.17	88.79	127.59		6	103.93	184.33	134.47
Fe (*1000)	1	20.16	12.73	24.21	Mn	1	104.69	115.76	95.88
	2	61.26	52.88	37.05		2	278.72	179.11	135.38
	3	9.04	22.27	13.77		3	45.95	126.91	87.84
	4	15.55	9.89	17.12		4	32.48	27.21	24.24
	5	4.57	4.17	5.04		5	27.08	30.46	24.24
	6	21.27	5.74	52.28		6	177.57	179.16	136.99
Ni	1	28.19	15.80	44.71	Pb	1	13.14	32.61	19.17
	2	73.79	75.07	76.91		2	45.97	38.88	38.39
	3	29.23	14.08	25.39		3	14.16	28.50	18.97
	4	10.10	9.40	11.04		4	11.27	10.14	29.37
	5	4.66	39.64	14.00		5	10.39	13.69	22.12
	6	29.37	31.81	46.58		6	115.73	82.79	27.33
Zn	1	23.32	54.36	28.52					
	2	93.08	126.46	124.56					
	3	105.03	119.69	234.44					
	4	36.69	21.63	20.39					
	5	29.37	12.94	8.31					
	6	242.55	244.29	334.71					

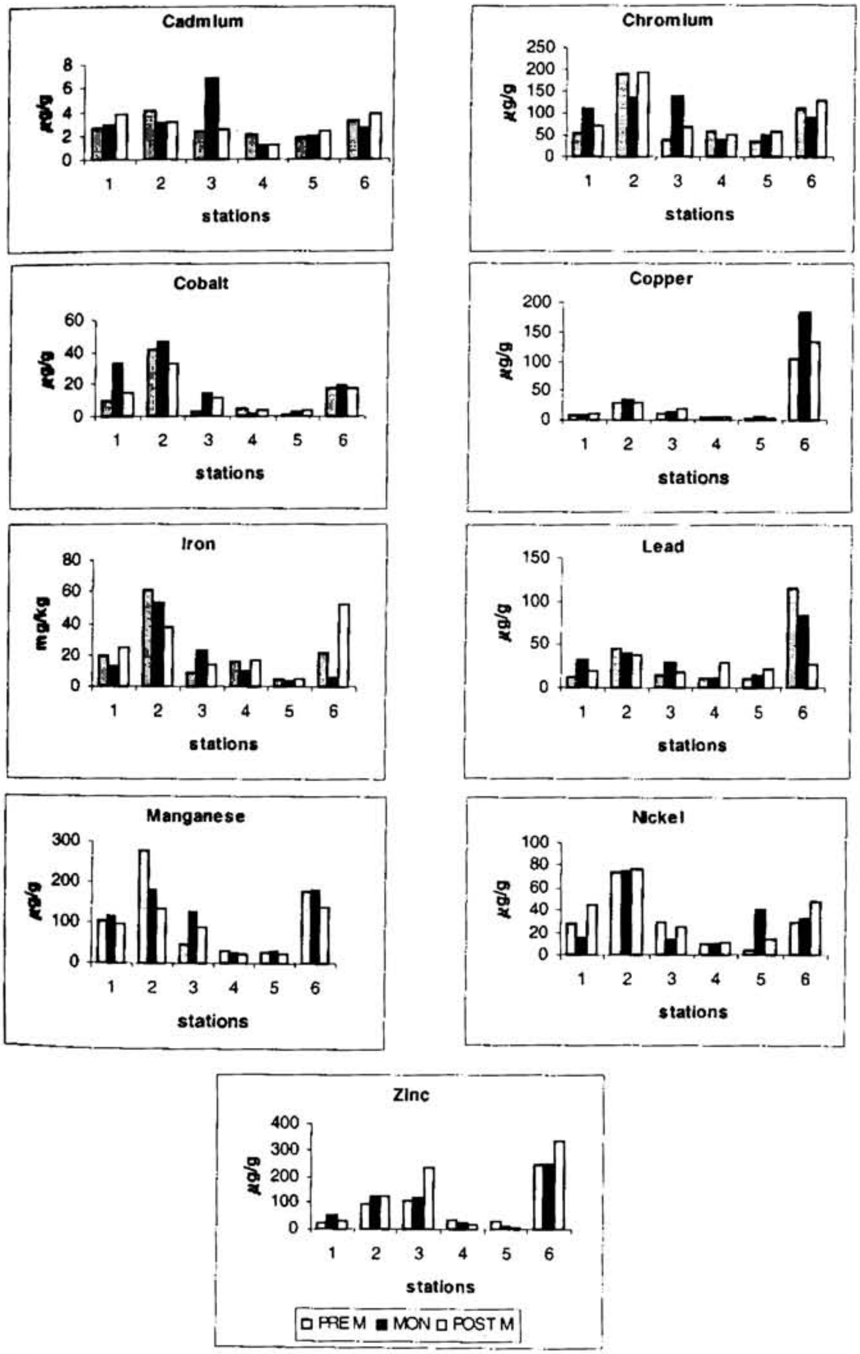

Fig. 3.2 Seasonal distribution of trace metals in mangrove sediments

Chromium:

The observed Cr values were between 1.91 µg/g to 244.01 µg/g. The station wise average values for Cr varied from 43.04 µg/g (station 4) to 173.55 g/g (station 2). The seasonal average values were highest at station 2 (191.71 µg/g - post monsoon) and the lowest at station 5 (36.77 µg/g - pre monsoon).

At stations 1 and 3 the highest and the lowest seasonal average values were noticed in monsoon and pre monsoon seasons respectively. For these stations, seasonal average values ranged from 53.88 µg/ g – 112.33 µg/g (station 1) and 38.05 –140.83 µg/g (station 3). For stations 2, 4 and 6 lowest seasonal average values were noticed in the monsoon; the values were 133.94 µg/g, 38.01 µg/g and 88.79 µg/g respectively. The highest seasonal mean concentration for station 4 was 58.35 µg/g (pre monsoon). For stations 2 and 6 seasonal maximum concentrations were noticed in post monsoon. The values were 197.71 µg/g and 127.59 µg/g respectively. Steady increases in Cr concentrations from pre monsoon to monsoon and further to post monsoon was observed at station 5.

Cobalt:

Observed values were between BDL to 68.16 µg/g. The highest and the lowest station wise average values were 40.53 µg/g (station 2) and 2.18 µg/g (station 5) respectively. The seasonal average value was highest at station 2(45.99 µg/g – monsoon) and the lowest at station 5 (1.16 µg/g - pre monsoon).

The station wise seasonal mean values were observed to be highest in monsoon for stations 1, 2, 3 and 6; the values were 33.17 µg/g, 14.26 µg/g, 45.99 µg/g, and 19.47.µg/g respectively. The lowest seasonal average values for stations 1, 3 and 6 were noticed during the pre monsoon season. For station 2 the lowest seasonal mean value was noticed in post monsoon (33.06 µg/g). At station 4, the seasonal maximum and minimum concentrations were observed in monsoon (4.86 µg/g) and pre monsoon seasons (2.15 µg/g) respectively. At station 5, cobalt concentration increases from pre monsoon to post monsoon.

Copper:

Copper concentrations fluctuated from 0.13µg/ g (station 3) to 243.32 µg/g (station 6). The station wise mean concentration of copper in sediments ranged from 2.5µg/g (station 5) to 144.881 µg/g (station 6). The highest and lowest seasonal average values were 184.33 µg/g (station 6 - monsoon) and 2.51 µg/g (station 5 - pre monsoon).

The minimum seasonal average values for station 1 (7.63 µg/g) and station 4 (4.38 µg/g) were noticed in monsoon. The maximum seasonal average values for these stations were 10.88 µg/g (pre monsoon) and 6.05 µg/g (post monsoon) respectively. Monsoon values were highest for station 2 (34.23µg/g), station 5 (4.52 µg/g) and station 6(184.33 µg/g). The minimum seasonal average value for station 2 was observed during post monsoon (29.31 µg/g). Station 5 recorded the lowest seasonal average concentration in pre monsoon (2.5 µg/g). At station 3, Cu concentrations increased from pre monsoon to post monsoon season.

Iron:

The observed Fe values fluctuated between 0.53 x 1000 µg/g to 92.54 x 1000 µg/g. The station wise mean values varied from 13.63 x 1000 µg/g (station 5) to 51.48 x 1000 µg/g (station 2). The lowest and the highest seasonal average values were observed for stations 5, the values were 4.17 x 1000 µg/g and 61.26 x 1000 µg/g respectively.

The lowest seasonal average values for station 1(12.73 x 1000 µg/g), station 4(9.89 x 1000 µg/g), station 5 (4.17 x 1000 µg/g) and station 6 (5.74 x 1000 µg/g) were observed during monsoon. The highest seasonal average value for station 4 was 15.55 x 1000 µg/g (pre monsoon). Highest seasonal average values for station 1 (24.21 x 1000 µg/g) station 5 (5.04 x 1000 µg/g) and station 6 (52.28 x 1000 µg/g) were obtained in post monsoon season. At station 2 the highest and the lowest seasonal average values were observed in pre monsoon and post monsoon seasons respectively. Cu values increases from pre monsoon to post monsoon at station 3.

Lead:

The observed lead concentrations were between 0.74 µg/g (station 3) to 144.36 µg/g (station 6). The station wise mean value of lead fluctuated from 14.90 µg/g (station 5) to 83.68 µg/g (station 6). The seasonal average values were between 10.14 µg/g (station 4 - monsoon) and 115.73 µg/g (station 6 - pre monsoon).

The station wise seasonal average concentrations were highest in monsoon for station 1(32.61 µg/g) and station 3 (10.14 µg/g). The lowest seasonal average values for these stations were noticed in pre monsoon; the values were 13.14 µg/g and 14.06 µg/g respectively. A decrease in Pb concentrations from pre monsoon to post monsoon was noticed at stations 2 and 6.

At stations 4 and 5 seasonal mean concentrations were highest in pre monsoon; the values were 29.37 µg/g and 22.12 µg/g respectively. The lowest seasonal average values for these stations were 10.14 µg/g (monsoon) and 10.39 µg/g (pre monsoon).

Manganese:

The observed manganese values were between 12.16 µg/g (station 1) and 325.98 µg/g (station 2). The station wise average concentrations of Manganese in sediments were highest at station 2 (186.22 µg/g) and lowest at station 5 (25.40µ g/g). The seasonal average values fluctuated between 24.24 µg/g (station 4 – pre monsoon) to 278.72 µg/g (station 2 – pre monsoon).

The highest seasonal average values for station 1 (115.76 µg/g) station 3 (126.91 µg/g) station 5 (30.45 µg/g) and station 6 (179.16 µg/g) were noticed during monsoon season. The lowest seasonal average values for stations 1, 5 and 6 were noticed in post monsoon season, the values were 95.88 µg/g, 24.24 µg/g and 136.99 µg/g respectively. Station 3 showed lowest seasonal mean values in pre monsoon (45.95 µg/g). For stations 2 and 4 the seasonal average values decreased from pre monsoon to post monsoon.

Nickel:

The observed concentrations of Ni were between 1.76 µg/g (station 3) to 89.97 µg/g (station 2). Station wise mean concentrations ranged from 10.171µg/g (station 4) to 75.11 µg/g (stations 2). The seasonal average values varied from 4.66 µg/g (station 5 – pre monsoon) to 76.91 µ g/g (station 2 - post monsoon).

Station wise seasonal average concentrations were observed to be lowest in monsoon for stations 1 (15.8 µg/g), station 3 (14.08 µg/g) and station 4 (9.4 µg/g). Station 3 recorded the highest seasonal average value in pre monsoon (29.32 µg/g). For station 1 and 4 the highest seasonal average values were 44.71 µg/g and 11.04

μg/g, both in post monsoon season. At stations 2 and 6 Ni concentrations increased regularly from pre monsoon to post monsoon season.

Zinc:

The observed values of zinc were between 3.88 μg/g and 439.70 μg/g. The station wise mean concentration was the highest at station 6 (227.78 μ g/g) and the lowest at station 5(13.24 μg/g). The seasonal average values ranged from 38.31 μg/g (station 4 - pre monsoon) to 334.71 μg/g (station 6 - post monsoon).

Zn concentrations at stations 1 and 2 followed the same seasonal trend. The station wise seasonal maximum and minimum values for these stations were observed in monsoon and pre monsoon seasons. For stations 1 and 3 the seasonal average values were in the range of 23.32 μg/g – 54.36 μg/g and 93.06 μg/g – 126.46 μg/g. At stations 3 and 6 an increase in concentration from pre monsoon to monsoon and further to post monsoon was noticed. Reverse trend was seen at stations 4 and 5.

3.1.1 Spatial variation of trace metals:

In mangrove sediments, the distribution patterns of the nine metals studied were in the following order:

Station 1: Fe > Mn > Cr > Zn > Ni > Co > Pb > Cu > Cd.
Station 2: Fe > Mn > Cr > Zn > Ni > Pb > Co > Cu > Cd.
Station 3: Fe > Zn > Mn > Cr > Ni > Pb > Cu > Co > Cd.
Station 4: Fe > Cr > Mn > Zn > Pb > Ni > Co > Cu > Cd.
Station 5: Fe > Cr > Mn > Pb > Ni > Zn > Co > Cu > Cd.
Station 6: Fe > Zn > Cu > Mn > Cr > Pb > Ni > Co > Cd.

Iron was the most abundant metal in mangrove sediments. Mn was the second most abundant metal at stations 1 and 2. The second highest values at stations 3 and 6 are noticed for zinc. At stations 4 and 5, Cr showed the second highest concentration. Cadmium was the least abundant metal. Copper ranks 8th in the order of abundance at all stations except stations 3 and 6.

The levels of trace metal, which accumulate in mangrove sediments, differ seasonally and spatially. Mangroves at different geographical locations had different heavy metal concentrations, depending on sediment characteristics (Parlude *et al.*, 1992). Origin and composition of the sediment, particle size distribution and post depositional reactions, all play an important role in determining metal concentrations (Barreiro *et al.*, 1994). The mangrove ecosystem being inter-tidal has a varied chemical composition. As the chemical behaviour and the quantities of heavy metals are highly dependent on the physicochemical conditions of the sediments and pore water, sediment heavy metal concentrations fluctuate from place to place, even within an apparently homogeneous habitat (Haribson, 1986; Lacerda *et al.*, 1988). Different plant cover may result in different sediment conditions, patterns of water movement and heavy metal concentrations.

For the metals Co, Cr, Fe, Mn and Ni the highest annual mean concentrations were noticed at station 2. Station 6 recorded the highest annual average concentrations for the metals Cu, Pb and Zn. For all the nine metals studied, the lowest average values (annual) were noticed for stations 4 and 5. The minimum values of Cd, Cr and Pb were noticed at station 4. Station 5 recorded the lowest mean concentrations of Co, Cu, Fe, Mn, Pb and Zn.

Variability of trace metal concentrations between mangroves might be due to the natural variability of the sediments or due to anthropogenic contamination (Tam and Yao, 1998; Tam and Wong, 2000). Different degrees of human activity and anthropogenic input further aggravate the problems of spatial heterogeneity. Elevated metal concentrations reflect the possibility of long term pollution caused by human activities (Everaarts and Fischer, 1989).

A comparison of the metal concentration in the sediments with the world shale[*] is generally taken as a quick and practical method for tracing heavy metal enrichment. The "average geochemical background" or average shale (Turekian and Wedepohl, 1961) represents the standard level of the metals in argillaceous sediments. The background concentration of the metal can be defined as the concentration that can be found in the environment in the absence of human activity. Background values do not reflect regional geochemical variation or the

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[*] **Black Shale** : According to the Glossary of Geology(4 th eds.) Black shale is defined as a a dark thinly laminated carbonaceous shale exceptionally rich in organic matter(50% or more carbon content) and sulphide(especially iron sulphide usually pyrite) and more commonly containing unusual concentrations of trace elements and fossil organisms.

processes that influence marine sedimentation. The metal concentrations in the black shale is given in Table 3.3.

Table 3.3 Metal concentrations in the Black Shale (μg/g) - (Turekian and Wedepohl, 1961)

Metal	World Shale average
Cd	0.3
Co	19
Cr	90
Cu	45
Fe	45700
Mn	850
Ni	68
Pb	20
Zn	95

On comparing the results of the present study with the average shale values, station 1 showed higher average values for the metals Cu, Cr, Cd, Pb and Zn. The values of Cd, Cr, Co, Pb, Fe and Zn were elevated at station 2. Enrichment of Zn and Cd were noticed at station 3. For all the six stations, the observed cadmium values were higher than that reported for average shale concentrations for all the six stations. The average Mn content was lower than the natural background values at all the six stations.

Comparison of the metal concentrations with other mangroves of India and the world (Table.3.4) showed that the metal concentrations were similar in magnitude to those determined for other mangroves with some exceptions The metal content in mangrove sediments were also comparable with the neighboring estuarine sediments (Table.3.5).

Table 3.4 Metal concentrations in mangrove sediments reported from different parts of the world(μg/g)

Location	Metal concentrations(µg/g)				Reference
	Cd	Pb	Co	Fe *1000	
Brisbane river, Australia		7.7-84.7(58.7)			Mackey & Hodkinson, 1995
Sai Keng, Hong Kong		58.2 (8-241)			Tam & Wong, 1995
Sai Keng, Hong Kong	0.73 ± 0.26				Tam & Wong, 1996
Shenzen, Hong Kong	3.91± 0.26		–		Tam & Wong, 1996
Mai Po, Hong Kong	0.6	198.8		4230	Ong Che, 1999
Gunabara Bay, SE Brazil		2.0 -130			Machado *et al.*, 2002
Mangroves of Karachi					Saifullah *et al.*, 2002
New Zealnd		53 - 177.8			Mac Farlane, 2003
UAE Mangroves		13.2 - 49.8 (28.1)	5.70 -14.0 (10.2)		Shriadh, 1992
Saudi Mangroves		6 - 19 (11.8)			Sadiq and Zaidi, 1994
Mangroves of Kerala	1.63	17.74	8.61	18.93	Present study
	(BDL - 2.978)	(0.74 - 144.68)	(7.0-22)	(0.53 - 95.44)	

Table 3.4 Contd ...

Location	Metal concentrations(µg/g)					reference
	Cu	Zn	Mn	Cr	Ni	
Brisbane river, Australia	3.1-34.1(23.1)	40.8 - 144.0 (98.3)		7.6-116.8		Mackey & Hodkinson, 1995
Sai Keng, Hong Kong	12.4 (1-31)	53.3 (17 - 147)	97.9 (34 - 223)			Tam & Wong, 1995
Sai Keng, Hong Kong	16.3 ± 2.2	40.2 ± 3.3	41.3 ± 9.4		1.7 ± 0.2	Tam & Wong, 1996
Shenzen, Hong Kong	44.3 ± 0.5	143.3 ± 22.4	509.2 ± 37.1		10.9 ± 0.6	Tam & Wong, 1996
Mai Po, Hong Kong	46	29.3		13.5	65.7	Ong Che, 1999
UAE Mangroves	5.31 - 29.4(7.21)	4.59 - 22.4 (11.3)	28.8 - 169 (84.1)	8.28 -18.9 (11.9)		Shriadh, 1992
Saudi mangrove	0.1 - 4 (1.8)	2 -- 17	2 - 69 (11.8)			Sadiq and Zaidi, 1994
New Zealnd	26.8 -196.5	133 - 386.1				Mac Farlane, 2003
Gunabara Bay, SE Brazil	53.3 - 610	18 - 80	71.7-273		60.12	Machado *et al.*, 2002
Mangroves of Karachi					28.80 - 103.40	Saifullah *et al.*, 2002
Mangroves of Kerala	15.53	47.92	41.03	32.36	15.71	Present study
	(0.13 - 243.32)	(3.88 - 439.70)	(12.16 - 325.98)	(1.91 - 163.72)	(1.76 - 89.97)	

Table 3.4 Contd ...

Location	Metal concentrations (µg/g)					Source of reference
	Cu	Zn	Mn	Cr	Ni	
Veli Mangroves	23 - 61 (42)	44 - 80 (63)	60 -320 (127)			Badarudeen,1997
Kochi Mangroves	12 - 69 (44)	15 - 83 (40)	60 -171 (102)			,,
Kannur mangroves	19 -77 (52)	56 - 65 (67)	275 - 334 (304)			,,
Mangroves of Kumarakom	10 - 44 (28)	31-155 (100)	318 -1089 (629)			Thomas & Fernandez, 1997
Mangroves of Quilon	652 - 845 (758)	1550 - 2372 (1880)	698 -1124 (881)			Thomas & Fernandez, 1997
Mangroves of Veli	62 - 256 (125)	223 - 370 (313)	158 - 456 (348)			Thomas & Fernandez, 1997
Pichavaram mangroves	14.83 - 135.68		14.83- 135.68			Periakali et al, 2000
Mangroves of Cochin	11.03 - 51.04	3.88 - 439.70	32.78 - 155.66	59.99- 100.91	11.06 - 89.89	Janet, 2002
Pichavaram, Tamil Nadu	20 - 81	63 - 130	385 - 1900	89 -186	38 -86	Ramanathan, 1997
Bhitarkanika, Orissa	2.6 - 6.7	0.7 - 1.7	6.8-10.9			Sarangi *et al.*, 2002
Mangroves of Kerala	15.53	47.92	41.03	32.36	15.71	Present study
	(0.13 - 243.32)	(3.88 - 439.70)	(12.16 - 325.98)	(91.91 - 163.72)	(1.76- 89.97)	

Table 3.4 Contd ...

Location	Metal concentrations(µg/g)				Source of reference
	Cd	Pb	Co	Fe %	
Veli Mangroves		16 - 87 (51)	20 -25 (37)	0.83-1.95(1.13)	Badarudeen, 1997
Kochi Mangroves		20 - 49 (38)	44 - 122 (102)	1.56-6.78 (4.02)	"
Kannur mangroves		22 - 39 (28)	30 - 70 (48)	2.9-5.4 (3.85)	"
Mangroves of Kumarakom		1100 - 1300 (1217)	159 - 261 (205)		Thomas & Fernandez, 1997
Mangroves of Quilon		1800 - 1950 (1888)	148 -248 (168)		Thomas & Fernandez, 1997
Mangroves of Veli		1250 - 1475 (1346)	91-114 (104)		Thomas & Fernandez, 1997
Pichavaram mangroves				0.68-4.41	Periakali et al, 2000
Mangroves of Cochin				1.65 -35.68	Janet, 2002
Pichavaram, Tamil Nadu				21- 68	Ramanathan, 1997
Bhitarkanika, Orissa	0.22 - 1.72	06 -- 17	19 - 54	2.52 - 469	Sarangi *et al.*, 2002
Mangroves of Kerala	1.63	17.74	8.61	1.89	Present study
	(BDL – 2.98)_	(0.74 - 144.68)	(7.0 -22)	(0.05 - 9.55)	

Table 3.5 Metal concentrations in the sediments of mangroves and estuaries of Kerala(μg/g)

Location	Cd	Pb	Co	Fe	Reference
Ashtamudi, Kerala		38		1.8	Nair et al., 1987
Northern part of CES 1			10.0 - 43		Venugopal et al, 1982
Northern part of CES 2	0.8 - 18			4.4 - 29.1	Paul & Pillai, 1983
Northern part of CES 3	0.1 - 6.5	3.0 -46	2.0 - 42	3.1 - 90.6	Malik and Suchindan, 1984
Northern part of CES 4	0.5 - 8.4	10 - 90			Ouseph, 1987
Northern part of CES 5	0.3 - 8.4	3.0 - 50	1.0 - 25	2.8 - 20.2	Nair, 1992
Northern part of CES 6	0.51	2.7	2.9	0.803	Jayasree and Nair, 1995
(range)	0.06 - 4.20	1.40 - 5.32	1.40 - 5.30	0.114-2.694	
Chitrapuzha river, CES 7	12.87	22.4	16.39	25.56	Joseph, 2002
Cochin back waters		21 - 71		1.4-6.2	Balachandran, 2001
Coastal waters near Cochin		36.5 - 60	28.2 - 37.4	2.3 - 4.3	Balachandran, 2003
(average)		47	33.03	3.7	
Cochin estuary	0.97 - 9.4	33.2 -117.1		1.5 - 5.5	Rajammani Amma, 1994
Kerala Coast	1.14 - 5.17	17.9 - 80.9		0.5 - 5.5	Rajammani Amma, 1994
Kayamkulam Estuary	BDL-3.0	4-114		1.0 - 6.3	Reji Sreenivas, 2002
Cochin Estuary	0.48-1.53	14.21-46.68			Babukutty, 1991
Mangroves of Chettuva back waters	BDL-4.77	10.32-43.46	6.53 - 68.16	0.59 - 92.54	Present study
Average	2.76	23.85	23.19	25.17	
Mangroves of Cochin estuary	BDL-12.82	0.74-58.21	BDL-60.28	3.75 - 86.26	"
(average)	2.81	25.34	17.29	26.74	
Mangroves of Kayamkulam estuary	0.170-3.64	5.06-36.44	BDL-4.61	1.20 - 95.44	"
(average)	1.87	14.9	2.19	13.63	
Mangroves of Ashtamudi estuary	BDL-5.01	11.68-144.68	3.98-23.13	.53 - 79.38	"
(average)	2.98	50.52	15.32	22.07	
Present study (mean)	1.63	17.74	8.61	18.93	"
(range)	BDL-2.978	0.734 - 144.68	7.0-22	0.53-95.44	

CES : Cochin Estuarine System

Table 3.5 Contd ...

Location	Cu	Zn	Mn	Cr	Reference
Ashtamudi, Kerala	60	60			Nair et al., 1987
Northern part of CES 1	17 - 71	103 - 664	73 - 318		Venugopal et al, 1982
Northern part of CES 2	5.0 - 61	116 - 1385	15 - 640		Paul & Pillai, 1983
Northern part of CES 3	8.0 - 63	10.0 - 417	44 - 1439		Malik and Suchindan, 1984
Northern part of CES 4		35 - 780		7 - 130	Ouseph, 1987
Northern part of CES 5	1.0 - 50	14 - 259	7 - 170	4.0 - 100	Nair, 1992
Northern part of CES 6	0.35	14	11	1	Jayasree and Nair, 1995
(range)	0.17- 1.12	0.20-192.0	0.50-217.0	0.50 - 3.50	
Chitrapuzha river, CES 7	28.47	177.01	245.18	101	Joseph, 2002
Cochin back waters	5.0 - 53.0	92 - 126.6	151 - 337		Balachandran, 2001
Coastal waters near Cochin	6.9 - 30	52 - 128	124 -773	98.9 - 186.0	Balachandran, 2003
(average)	23	83	293	160	
Cochin estuary	5.5 - 51.3	29.3- 290.5	123 - 280		Rajammani Amma, 1994
Kerala Coast	5.1 - 18.1	7.4 - 148.75	44 - 318		Rajammani Amma, 1994
Kayamkulam Estuary	11.0 - 81	28 - 284	58 - 400	12.0 - 86	Reji Sreenivas, 2002
Cochin Estuary	3.14 - 11.4				Babukutty, 1991
Mangroves of Chettuva back waters	6.03- 34.94	20.25 - 103.34	12.16 - 153.91	39.48 - 163.72	Present study
Average	34.94	38.78	88.9	80.68	
Mangroves of Cochin estuary	0.13 - 39.95	14.02 - 238.48	12.44 - 325.98	1.91 - 244.01	„
(average)	16.06	96.58	103.7	93.15	
Mangroves of Kayamkulam estuary	1.16 - 6.7	3.88 - 38.38	12.217 - 43.549	29.77 - 67.40	”
(average)	3.4	13.236	27.241	47.6	
Mangroves of Ashtamudi estuary	34.77 - 243.32	61.17 - 439.70	45.57 - 216.18	45.12 - 136.08	„
(average)	144.88	227.78	165.87	100.33	
Present study (mean)	15.53	47.92	41.03	32.36	”
(range)	0.128 - 243.3	3.879 - 439.70	12.159 - 325.98	1.908 - 163.722	

3.1.2 Seasonal variation of trace metals in mangrove sediments:

The differences in the seasonal distribution of trace metals could be attributed to the variation of different environmental parameters such as salinity, sediment load, nutrient chemistry, discharge of industrial and domestic effluents, land run off and other activities. Sedimentation and hydrography are influenced by changes in the monsoonal cycle. Enrichment of trace metals in monsoon might also be due to land additions. Washing of coastal areas introduces large amounts of pollutants, both urban and industrial, into the mangroves during monsoon season. The organic matter production in the mangrove swamps is high in monsoon. Increased organic matter content favours the retention of pollutants, especially the metals. Major portion of organic carbon is derived from terrestrial sources as well as biological productivity. During the monsoon, terrestrial run –off contributes high levels of particulate matter with organic and inorganic constituents (Sardessai, 1993). Elevated metal concentrations during post monsoon season might be attributed to increased productivity during this season. The enhanced rate of primary production has lead to increased loading of particulate organic matter into the sediments. With increase in organic production, decay of organisms leads to increased organic load. Higher organic load entering the system favours the sequestration of trace metals and other pollutants into the organic particles. Settling particles stores the contaminants in the sediment. A number of authors have shown that mangrove sediments act as biochemical sinks for pollutants, due to high concentrations in organic matter and sulphides under permanently reducing conditions (Haribson, 1981; Lacerda and Abrao, 1984; Lacerda *et al.*, 1988; Thomas and Fernandez, 1997). Water table fluctuations played a significant role in the cycling of trace metals in these coastal habitats (Clark *et al.*, 1998). Resuspension and settling are also important in deciding the fate of trace metals in sediments. On release into the aquatic environment metals interact with suspended matter and depending on the chemical form of the element get transferred to sediments by subsequent sedimentation.

Even though the processes occurring in these mangroves are similar, geographical and sedimentological characteristics of the stations selected for the present study were different. All these mangroves are water logged, anaerobic and rich in sulphides. Tidal influence is lowest in all these stations. The maximum water circulation occurs in monsoon season. Well-defined seasonal character is not observed in the distribution of metals. The values fluctuate between stations and metals. Seasonal trend of the metals in the stations are presented in Table **3. 6.** The seasonal average values of organic carbon and (silt + clay) are given in Table **3.7**.

Station 1: During monsoon, large amounts of agricultural wastes from the neighbouring Kole wet lands reaches Chettuva backwaters, which form the major portion of the contaminants reaching this site. Here, the chances of resuspension and settling are minimum. Increased land run off and river discharges brings in huge amounts of contaminants. A part of the contaminants reaching the mangroves is retained within the sediments. The lower values observed in pre monsoon season might be due to increased diagenetic activity. The utilization of organic matter by organisms and poor sources of contaminants leads to lower metal levels in pre monsoon season (Senthilnathan and Subramanian, 1997). Similar conditions are observed at stations 3 and 6 also. Increased productivity and the associated increase in organic matter content favours the observed maximum metal concentrations in

Table 3.6 Seasonal trends of metals in the stations (The figures 1 to 6 represent stations 1 to 6)

Metal	Pre monsoon		Monsoon		Post monsoon	
	High	Low	High	Low	High	Low
Cd	2,4	1,3,4	3	5	1,5,6	2,6
Cu	4	1,3,5,6	2,5,6	2	1,3	4
Fe	2,4	1,3	3	2	1,5,6	4,5,6
Ni	3,5,6	3,5,6		2	1,2,4	1,4
Co	4	3	1,2,3,6	2	5	1,4,5,6
Cr	4,5,6	1,3	1,3	2,5,6	2	4
Pb	2,5,6	3	1,3	1,2,4,5,6	4	
Mn	2,4	2	1,3,5,6	6		1,3,4,5
Zn	4	1,2,3,5	1,2		3,5,6	4,6

Table 3.7 Seasonal average values of OC (%) and Silt + Clay (%).

	(silt + Clay)%	OC %		(silt + Clay)%	OC %
Station 1			Station 4		
pre mon	49.60	0.84	pre mon	22.08	0.72
Mon	46.67	1.03	mon	36.48	0.46
post mon	34.00	0.82	post mon	13.68	0.54
Station 2			Station 5		
pre mon	62.75	1.82	pre mon	8.36	1.65
mon	52.71	2.35	mon	16.53	1.44
post mon	92.81	2.80	post mon	8.92	1.35
Station 3			station 6		
pre mon	47.41	2.00	pre mon	49.69	5.48
mon	32.98	3.19	mon	43.49	6.50
post mon	30.83	2.08	post mon	51.15	6.09

post monsoon. The decomposition of organic matter releases organically bound metals into the sediments through pore water. In pre monsoon, diagentic remobilistation of metals from the sediments leads to lower metal concentrations.

Station 2: Mixed silvi – aquacultural practices in this area also leads to enhanced pollutant concentrations. Even though it is closer to the sea than the other stations, tidal activity is minimum in this area. Here, the pollutants reaching through terrestrial run off was greater than that entering through water circulation. Lower metal content in monsoon season could be related to the lowest settling rates observed in this season. Lowest post monsoon concentrations observed for Co, Cu, Fe, Pb and Mn could be attributed to the planktonic uptake of metals.

Station 3: It is a closed mangrove area, in the heart of the Cochin City. Upwelling brings in pollutants from neighbouring coastal areas into the mangroves. Urban and Industrial pollution is the major threat to this mangrove environment. It is separated from the Cochin backwaters through a canal. Lack of direct tidal action is a characteristic of this mangrove area. Microbial activity is maximum here. Once the pollutants reach the mangrove, the chances of removal are very little. Finer particles, organic matter content, reduced conditions and presence of sulphides favour the retention of metals in sediments. Monsoonal run off brings in pollutants, both urban and industrial into this system.

Station 4: The lowest metal concentrations were noticed in monsoon for cadmium and chromium. This might be due the resuspension of metals from sediments to the water column. The lowest values of Co, Cu, Fe, Pb, Ni and Zn were noticed in the monsoon season. Post monsoon values were the highest for Cd and Mn. The highest values of these metals may be associated with the decomposition of organic matter resulting from increased productivity in this season. During this process the metals held through organic associations are released to the system.

It is an open mangrove area with lots of anthropogenic intervention. Prawn farming is the major activity in this area. The lowest retention capacity of metals in sediments at this station might be due to the open nature of the system and the sandy nature of the sediments.

Station 5: This is a man made mangrove area. In monsoon the mangroves are flooded with water. A part of the materials reaching this area are retained in the sediments. Organic carbon content was maximum in pre monsoon (1.65 %). Organic matter concentration was the lowest in post monsoon (1.35 %). This might be due to the utilization of organic matter by the biota. The materials brought in by monsoonal run off are incorporated in to the sediments in post monsoon season.

Station 6: Lowest percentage of finer particles in monsoon might be the result of sediment resuspension in monsoon. Station 6 is being situated on the banks of the estuarine region; the tidal action is minimum in this station. Municipal waste dumping in this area may be the reason for elevated metal levels observed at this station. Organic carbon content is also the highest at this station. Post monsoon/ monsoon values were the highest for most of the metals studied.

3.1.3 Correlation between variables

Correlations between metals:

To assess the elemental associations and origin of heavy metals, correlation (Pearson) tests were carried out. The correlation coefficients (r) for trace metals in sediments are given in Table 3.8.

Table 3.8. Correlations between metals (n = 12)

Correlations - station 1

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.000	.309	.602*	.558	.157	.501	.306	.204	.571
Co	.309	1.000	.658*	.886**	.279	.280	-.108	.656*	.735**
Cr	.602*	.658*	1.000	.900**	.268	.834**	.326	.714**	.942**
Cu	.558	.886**	.900**	1.000	.404	.604*	.143	.743**	.941**
Fe	.157	.279	.268	.404	1.000	-.021	.156	.302	.487
Mn	.501	.280	.834**	.604*	-.021	1.000	.462	.469	.655*
Ni	.306	-.108	.326	.143	.156	.462	1.000	.138	.143
Pb	.204	.656*	.714**	.743**	.302	.469	.138	1.000	.776**
Zn	.571	.735**	.942**	.941**	.487	.655*	.143	.776**	1.000

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

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

Correlations - station 2

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.000	.316	.359	.119	.438	.353	-.135	.457	.047
Co	.316	1.000	-.140	.452	-.111	.033	-.083	.039	.236
Cr	.359	-.140	1.000	-.372	.283	.063	-.077	-.050	-.059
Cu	.119	.452	-.372	1.000	.123	-.209	.616*	-.348	.176
Fe	.438	-.111	.283	.123	1.000	.141	.312	-.148	-.280
Mn	.353	.033	.063	-.209	.141	1.000	-.421	.665*	-.351
Ni	-.135	-.083	-.077	.616*	.312	-.421	1.000	-.734**	-.135
Pb	.457	.039	-.050	-.348	-.148	.665*	-.734**	1.000	.113
Zn	.047	.236	-.059	.176	-.280	-.351	-.135	.113	1.000

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

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

Correlations - station 3

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.000	.142	.560	.298	.813**	.351	-.187	.456	-.044
Co	.142	1.000	.541	.695*	.368	.546	-.025	.399	.118
Cr	.560	.541	1.000	.686*	.638*	.936**	.023	.744**	.322
Cu	.298	.695*	.686*	1.000	.307	.650*	-.009	.532	-.141
Fe	.813**	.368	.638*	.307	1.000	.553	-.167	.249	.311
Mn	.351	.546	.936**	.650*	.553	1.000	-.062	.658*	.544
Ni	-.187	-.025	.023	-.009	-.167	-.062	1.000	-.109	-.056
Pb	.456	.399	.744**	.532	.249	.658*	-.109	1.000	.033
Zn	-.044	.118	.322	-.141	.311	.544	-.056	.033	1.000

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

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

Table 3.8 Contd ....

Correlations - Station 4

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.000	-.178	.524	-.102	.302	.253	-.193	-.151	-.083
Co	-.178	1.000	.211	.400	.148	.022	.472	.205	-.283
Cr	.524	.211	1.000	.581*	.160	.733**	.415	.138	-.082
Cu	-.102	.400	.581*	1.000	-.172	.857**	.856**	-.081	-.053
Fe	.302	.148	.160	-.172	1.000	-.085	-.236	.234	-.350
Mn	.253	.022	.733**	.857**	-.085	1.000	.650*	-.208	-.114
Ni	-.193	.472	.415	.856**	-.236	.650*	1.000	.152	-.271
Pb	-.151	.205	.138	-.081	.234	-.208	.152	1.000	-.331
Zn	-.083	-.283	-.082	-.053	-.350	-.114	-.271	-.331	1.000

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

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

Correlations - station 5

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.000	-.406	.481	.100	.359	-.052	-.010	.102	-.160
Co	-.406	1.000	.019	.082	-.031	-.156	-.209	.228	-.190
Cr	.481	.019	1.000	.708**	.539	.046	-.028	.311	-.367
Cu	.100	.082	.708**	1.000	.370	.485	.072	.048	.088
Fe	.359	-.031	.539	.370	1.000	.104	.036	.049	-.185
Mn	-.052	-.156	.046	.485	.104	1.000	.576	-.093	.696*
Ni	-.010	-.209	-.028	.072	.036	.576	1.000	-.082	.146
Pb	.102	.228	.311	.048	.049	-.093	-.082	1.000	-.122
Zn	-.160	-.190	-.367	.088	-.185	.696*	.146	-.122	1.000

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

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

Correlations - station 6

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.000	.302	.621*	-.273	.269	.211	.334	.173	.324
Co	.302	1.000	.605*	.436	.093	.385	.685*	.528	.485
Cr	.621*	.605*	1.000	.247	.285	.619*	.620*	.442	.690*
Cu	-.273	.436	.247	1.000	-.154	.137	.502	.294	.631*
Fe	.269	.093	.285	-.154	1.000	-.036	.186	-.356	-.083
Mn	.211	.385	.619*	.137	-.036	1.000	.328	.252	.720**
Ni	.334	.685*	.620*	.502	.186	.328	1.000	.415	.652*
Pb	.173	.528	.442	.294	-.356	.252	.415	1.000	.319
Zn	.324	.485	.690*	.631*	-.083	.720**	.652*	.319	1.000

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

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

The following correlations between trace metals were statistically significant. Moderately to good correlations between metals were noticed by many researchers (Ramanathan, 1997). Significant positive correlations between metals indicate their common source of occurrence (Satyanarayana *et al.*, 1985).

Station 1: Positive correlations at 0.05 level exist between Mn and Cu(r = 0.604), Pb and Co(r = 0.656), Cr and Co(r = 0.658),Cr and Cd(r = 0.602). The following correlations are significant at 0.01 level: Cu and Co(r = 0.886), Zn and Co(r =0.735), Pb and Cr(r = 0.714), Pb and Cu(0.743), Zn and Cu (r = 0.941), Pb and Cr (r = 0.714), Zn and Cr(r = 0.942), Zn and Pb (r = 0.776).

Station 2: Correlations statistically significant at 0.05 level were noticed between Mn and Cu (r = 0.616), Mn and Pb(r = 0.665). Pb and Ni correlated negatively at 0.01 level(r = - 0.734)

Station 3: The correlations significant at 0.01 level were Fe and Cd(r = 0.813), Fe and Mn (r = 0.936), Pb and Fe(r = 0.744). The following correlations were found to be significant at 0.05 level: Cu and Co(r = 0.695), Cu and Cr(r = 0.686), Fe and Cr(r = 0.636), Mn and Cu(r = 0.650), Pb and Mn(r = 0.658).

Station 4: The correlations between Mn and Cr (r = 0.733), Cu and Ni (r = 0.856), Cu and Co (r = 0.712) and Mn and Cu (r = 0.857) were significant at 0.01 level. The correlations between Mn and Ni (r = 0.650), and Ni (r = 0.697) and Cr and Cu(r = 0.581) were significant at 0.05 level.

Station 5: The correlations between Mn and Zn (r = 0.696, $p < 0.05$) and Cr and Cu(r = 0.708, $p < 0.01$) are statistically significant.

Station 6: Mn correlated with Cr (r = 0.619, $p < 0.05$) and Zn (r = 0.720, $p < 0.01$). The correlations statistically significant at 0.05 levels were Cr and Ni (r = 0.620), Cr and Zn (r = 0.690), Ni and Zn (r = 0.652), Cu and Zn (r = 0.631), Cr and Cd (r = 0.621), Cr and Co (r = 0.605) and Ni and Co (r = 0.685).

Correlations of trace metals with iron, organic carbon and grain size:

Pearson correlations between trace metals and different hydrographical and sedimentary parameters are given in Table **3.9**

Fe /Mn oxides and hydroxides, clay and organic carbon are recognized as important carriers of metals in sediments. Flocculation occurring in the saline environment favours the formation of hydroxides of Fe and Mn, which have a strong tendency to adsorb other metals. Biogeochemical and sedimentogical processes are important to determine the fate of trace metals. The geochemistry of Fe and organic matter could affect the behaviour of trace metals in the aquatic

Table 3.9 Correlations of metals with other hydrographical and sediment parameters (n = 12)

Correlations - station 1

	Alkalinity	Clay	OC %	pH	Salinity	Sand	Silt
CD	-.349	.040	.399	-.295	.376	-.042	.546
Co	-.608*	.207	.663*	-.234	.081	-.342	.594*
Cr	-.369	.278	.823**	.026	.187	-.384	.732**
Cu	-.584*	.354	.807**	-.111	.260	-.474	.790**
Fe	-.304	.358	.031	.135	.372	-.273	.172
Mn	.034	.265	.779**	.348	.211	-.268	.553
Ni	.285	.080	.254	.230	-.073	-.028	.173
Pb	-.252	.636*	.639*	.047	-.091	-.773**	.473
Zn	-.510	.402	.727**	-.052	.287	-.496	.716**
Alkalinity	1.000	.123	-.197	.508	-.304	.233	-.657*
Clay	.123	1.000	.452	.340	.297	-.854**	.277
OC %	-.197	.452	1.000	.228	.180	-.515	.778**
pH	.508	.340	.228	1.000	.208	-.203	-.129
Salinity	-.304	.297	.180	.208	1.000	-.180	.345
Sand	.233	-.854**	-.515	-.203	-.180	1.000	-.528
silt	-.657*	.277	.778**	-.129	.345	-.528	1.000

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

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

Correlations - station 2

	Alkalinity	Clay	OC %	pH	Salinity	Sand	SILT
Cd	.414	.109	.017	.067	.570	-.103	-.309
Co	.544	-.443	.139	.264	.256	.463	-.418
Cr	.227	-.113	.226	-.187	.277	-.101	-.148
Cu	-.351	.060	.326	-.119	-.382	.149	-.156
Fe	-.009	-.266	-.257	.411	.136	.099	.063
Mn	.543	-.121	-.503	.435	.091	.092	-.103
Ni	-.484	.175	.023	-.045	-.414	-.249	.222
Pb	.498	.171	-.207	.153	.430	-.214	.058
Zn	-.158	.020	.299	-.359	-.028	-.063	.071
Alkalinity	1.000	-.443	-.417	.616*	.520	.179	-.208
Clay	-.443	1.000	.245	-.524	.046	-.674*	.126
OC %	-.417	.245	1.000	-.789**	.074	-.008	-.185
pH	.616*	-.524	-.789**	1.000	.067	.294	.031
Salinity	.520	.046	.074	.067	1.000	-.229	.056
Sand	.179	-.674*	-.008	.294	-.229	1.000	-.696*
Silt	-.208	.126	-.185	.031	.056	-.696*	1.000

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

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

Table 3.9 Contd...

Correlations - station 3

	Alkalinity	Clay	OC %	pH	Salinity	Sand	SILT
Cd	.017	-.303	.147	-.239	-.325	-.114	.231
Co	-.312	.511	.871**	-.078	-.185	-.271	.121
Cr	-.453	.233	.619*	-.164	-.245	-.132	.046
Cu	-.072	.124	.836**	-.320	-.516	.083	-.158
Fe	-.254	.129	.334	-.234	-.210	-.356	.335
Mn	-.572	.283	.675*	-.262	-.074	-.044	-.063
Ni	-.076	.253	-.173	-.214	.143	-.535	.463
Pb	-.312	-.112	.403	-.086	-.259	.076	-.035
Zn	-.659*	.253	.202	-.246	.618*	.002	-.080
Alkalinity	1.000	-.543	-.162	.058	-.040	.085	.177
Clay	-.543	1.000	.270	.413	-.057	-.524	.187
OC %	-.162	.270	1.000	-.220	-.144	.073	-.156
pH	.058	.413	-.220	1.000	-.151	-.060	-.056
Salinity	-.040	-.057	-.144	-.151	1.000	-.089	.201
Sand	.085	-.524	.073	-.060	-.089	1.000	-.924**
Silt	.177	.187	-.156	-.056	.201	-.924**	1.000

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

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

Correlations - Station 4

	Alkalinity	Clay	OC %	pH	Salinity	Sand	Silt
Cd	-.048	-.369	.098	-.171	-.080	.334	.011
Co	.029	-.053	.398	.270	.396	.161	-.278
Cr	.428	-.118	.511	-.445	.460	.144	-.067
Cu	.224	-.082	.881**	-.484	.391	.043	-.089
Fe	.186	-.215	.037	.559	-.271	.395	-.324
Mn	.242	-.014	.800**	-.644*	.263	.007	-.143
Ni	.225	-.083	.796**	-.508	.388	-.056	-.182
Pb	.066	-.098	-.277	.215	.178	.134	-.218
Zn	-.053	-.167	-.126	-.096	.262	.204	.585*
Alkalinity	1.000	-.054	.205	-.202	.046	-.215	.216
Clay	-.054	1.000	-.261	-.231	-.071	-.697*	-.332
OC %	.205	-.261	1.000	-.370	.326	.194	-.139
pH	-.202	-.231	-.370	1.000	-.121	.488	-.241
Salinity	.046	-.071	.326	-.121	1.000	.296	-.118
Sand	-.215	-.697*	.194	.488	.296	1.000	-.244
Silt	.216	-.332	-.139	-.241	-.118	-.244	1.000

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

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

Table 3.9 Contd ...

Correlations - station 5

	Alkalinity	Clay	OC %	pH	Salinity	Sand	Silt
Cd	-.487	.388	-.182	-.740**	-.186	-.186	.088
Co	.789**	.168	-.292	.340	.127	.037	-.060
Cr	.300	.149	-.008	-.438	-.681*	-.238	.254
Cu	.275	.095	.372	.035	-.417	-.001	.027
Fe	.103	-.306	.413	-.210	-.284	.343	-.280
Mn	-.166	.267	.786**	.053	.222	.309	-.301
Ni	-.111	.371	.478	-.295	.208	-.038	-.001
Pb	.151	-.092	-.090	-.435	.230	.026	.040
Zn	-.482	.127	.628*	.301	.349	.213	-.226
Alkalinity	1.000	-.061	-.203	.341	-.217	-.059	.108
Clay	-.061	1.000	-.251	-.333	.008	-.451	.236
OC %	-.203	-.251	1.000	.212	.155	.373	-.254
pH	.341	-.333	.212	1.000	.086	.042	.066
Salinity	-.217	.008	.155	.086	1.000	.327	-.366
Sand	-.059	-.451	.373	.042	.327	1.000	-.928**
Silt	.108	.236	-.254	.066	-.366	-.928**	1.000

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

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

Correlations - station 6

	Alkalinity	Clay	OC %	pH	Salinity	Sand	Silt
Cd	-.203	.250	-.008	.089	.255	-.330	.183
Co	.348	.359	.302	-.143	-.122	-.438	.214
Cr	-.149	.391	.204	.126	.223	-.746**	.591*
Cu	.063	.542	.367	-.517	-.525	-.433	.019
Fe	-.348	-.217	.121	-.031	.329	-.052	.293
Mn	-.105	.502	.604*	.199	.065	-.483	.128
Ni	.287	.296	.423	-.162	-.060	-.537	.411
Pb	.302	.441	.227	-.126	-.038	-.613*	.364
Zn	-.088	.716**	.571	-.236	-.307	-.630*	.104
Alkalinity	1.000	-.402	-.098	.097	-.362	.326	-.022
Clay	-.402	1.000	.641*	-.407	-.172	-.669*	-.137
OC %	-.098	.641*	1.000	-.226	-.090	-.374	-.161
pH	.097	-.407	-.226	1.000	.701*	.187	.169
Salinity	-.362	-.172	-.090	.701*	1.000	-.213	.460
Sand	.326	-.669*	-.374	.187	-.213	1.000	-.645*
Silt	-.022	-.137	-.161	.169	.460	-.645*	1.000

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

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

environment (Lin and Chen, 1996; Zwolsman *et a.l*, 1996; Basaham and El – Sayed, 1998; Fang and Hong, 1999). Concentrations of Fe, Mn and Al oxides (FeO_x, MnO_x, AlO_x) and levels of organic carbon play a major role in determining the bioavailability of trace metals. Following their release to the environment the heavy metals are efficiently scavenged by newly precipitated Fe and Mn oxyhydroxides. The concentration and distribution of heavy metals in aquatic systems are influenced by adsorption and coprecipitaion with Fe and Mn oxides (Jenne, 1968 ; Chester, 2000; Moore, 1991; Stumm and Morgan, 1996; Dassenakis *et al.*, 1997; Szefer, 1998; Hatje *et al.*, 2001).

Sediments form major resipiratories of iron in the costal environments. Iron may be the most sensitive element in the aquatic system to pH changes, forming new solid phases capable of scavenging other trace metals from solution with rise in pH (Boyle *et al.*, 1977; Mayer, 1982). The redox sensitive Fe and Mn hydroxides under oxidizing conditions constitute significant sinks for trace metals in aquatic systems (Jayasree and Nair, 1995). These hydroxides readily adsorb or co precipitate cations and anions. Fe differs from the toxic metals in that it is mobilized in reducing conditions, still it is effective as a trace metal adsorbent (Balachandran *et al.*, 2003). Next to iron, manganese also has an important role in immobilization of toxicants. Mn – oxide coating on settling biogenic particles carries several scavenged metals. Mn is oxidized more slowly than Fe in natural waters (Hatje *et al.*, 2001).

Positive correlations of the metal content with Fe/Mn indicate the significance of inorganic transfer mechanisms (Dassenakis *et al.*, 1997; Fang and Hong, 1999) in aquatic systems. Positive correlations of trace metal contents with the silt and the clay content and Fe and the negative correlations with sand indicate that the trace metals are associated with Fe oxides and hydroxides of the finest fraction (Streckemann *et al.*, 2004). The correlations with Fe and trace metals have also been used to distinguish between the natural levels of trace elements and anthropogenically enriched ones (Windom *et al.*, 1989; Presley *et al.*, 1992; Tkalin *et al.*, 1996). Good correlations between Fe and trace metal concentrations are expected for unpolluted sediments (Presley *et al.*, 1992; Li *et al.*, 2000).

In the present study, significant positive correlations were found for Fe with Cd and Cr at station 3. No significant correlations of metal concentrations with Fe were found at other stations. Concentrations of all metals except lead showed positive correlations with Al and Fe in sediments from Upper Laguna Madre, Texas Mexico (Sharma *et al.*, 1999). Mangroves are somewhat unstable systems. Normal correlations observed between the trace metals and Fe / Mn in the ocean and coastal sediments are not noticed in mangroves due to its dynamic biogeochemical character. Increased input of metals due to lateral additions (both land and terrestrial), biogeochemical transformations occurring at the sediment - water interface, changing redox state, retention and sedimentation processes all these lead to kinetically fluctuating conditions in mangroves. For trace metals and other contaminants, the conventional behaviour observed in other aquatic systems could not be expected for mangroves.

Elemental concentration is dependent on grain size, mineralogy and organic carbon (Al – Ghadban *et al.*, 1994; El –Nandy *et al.*, 1996; Szefer, 1998). The organic carbon plays an important role in the accumulation and release of different metals in sediments. Organic carbon serves as a matrix on particle surface for complexing metals (Daskalakis and O' connor, 1995; Shine *et al.*, 1995). Organic matter has higher complexation ability with trace metals in the aquatic environment (Mantoura *et al.*, 1978). Positive correlation of organic carbon with metals also reflects the high biological uptake of these elements (Newmann *et al.*, 1998).

No significant correlation exists between the metal concentrations in sediment and the organic carbon content at station2. At station 1, organic carbon correlates with the metals Co, Cr, Cu and Mn. Mn, Cu and Ni correlated positively with organic carbon at station 4. Mn and Zn concentrations correlated with organic carbon at station 5. At station 6, the only Mn was noticed to be correlated with organic carbon ($r = 0.641$ $p< 0.05$).

Tam and Yao,.(1988) reported that only Cr showed positive correlation with organic carbon in mangrove sediments of Hong Kong. Organic surfaces have strong affinity for trace metals (Haribson, 1986). Many previous workers reported positive correlations of metals in sediments with organic carbon (Haribson, 1986; Seidemann, 1991; Newman *et al.*, 1998; Fang and Hong, 1999). Orson et al (1992) noticed the absence of any significant correlation between organic matter and the metal concentrations in sediments.

The grain size is the most crucial parameter that controls the spatial distribution of trace metals (Jayasree and Nair, 1995; Fang and Hong, 1999; Harvey *et al.*, 1988,). Metal concentrations in sediments varied with the texture of the sediment. Grain size distributions are primarily influenced by physical processes occurring in the system. The currents and the materials carried determine the grain size distribution. Sediment grain size is important in determining how sediments are transported in the marine environment and in the distribution of metals in the marine sediment.

In the present study, sand correlated negatively with silt at stations 3, 5 and 6.Sand correlated negatively with the clay content at stations 1, 4 and 6. Significant positive correlations were observed between the sand and clay fractions at station 6. These observations are against the previous observations. At station 6, clay content correlated with zinc ($r = 0.716$) and the sand content correlated negatively with the metals Pb($r = -0.613$) and Zn (-0.630). Silt correlated with the Ni content ($r = 0.591, p < 0.05$) at station 6.At station 1, lead correlated positively with clay ($r = 0.636$, $p < 0.05$) and negatively with sand ($r = - 0.773$, $p < 0.01$). No other significant correlations were observed between the trace metals and sediment grain size.

Differences in sediment properties would affect the heavy metal concentration in sediments (Tam and Yao, 1998). The spatial distributions of trace metals are mainly governed by the sediment grain size. Generally the heavy metal concentrations increase with decrease in particle size (Rosental *et al.*, 1986; Harvey *et a.l*, 1988; Francois *et al.*, 1988; Lin and Chen, 1996; Fang and Hong, 1999). The finer particles and sediments especially coated with organic matter have a larger surface area, thus have higher adsorption capacity (Buffle, 1990). The trend of more metals being accumulated within the fine-grained fraction of the sediment varied between the metal species. Tam and Yao, (1988) showed that the high percentage of clay + silt particles (fine particles) favoured immobilization of metals in mangrove sediments. Enrichment of metals in finer fractions was reported by many previous researchers (Katz and Kaplan, 1981; Croudace and Cundy, 1995; Senthilnathan and Subramanian, 1997; Hong *et al.*, 1993). Chakrapani and

Subramanian (1993) reported that Cu, Zn and Mn concentrations increased with the fine size of the sediment. Cr concentrations decreased with the finer size and there was no significant variations of Pb with the fine size. In most mangroves, the fine grained fraction of sediments contained higher concentration of heavy metals than the sand sized fraction (Tam and Wong, 2000). This indicates that more heavy metals were bound to the silt and clay fraction than the sand sized fraction of the sediments. Previous researchers stated that the clay fraction is the most important substrate for metal attachment and metal concentrations tends to increase from sand to silt and from silt to clay (Forstner, 1989; Clark *et al.*, 1998; Tam and Wong, 2000).

Normally, higher concentrations of trace metals were found in fine-grained sediment than sand – sized fractions of the sediment. The differences between the sand and finer fractions become less significant when the mangrove swamp was more contaminated (Tam and Wong, 2000). The accumulation of metals in fine-grained sediments may cause a significant long-term contamination problem, as reworking and possible diagenetic release may cause continued inputs to the environment even after the cessation of industrial inputs (Cearetta *et al.*, 2000).

3.1.4 Analysis of Variance (ANNOVA)

The significance of the variations in observed trace metal concentrations were checked statistically using ANNOVA. The results of two way ANNOVA (stations x months) for metal concentrations in sediments are give in Table **3.10**.

Two way ANNOVA between stations and months for the trace metal concentrations in sediments showed that monthly variations are statistically insignificant. Spatial variations are insignificant only for cadmium. For all the other metals, the spatial variations are statistically significant at 0.01 level.

Table 3.10 The results Two way ANNOVA (stations X months) for metal concentrations in sediments

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Cadmium						
stations	37.1237	5	7.42474	1.886532	0.11558	2.422084
months	5.733472	9	0.637052	0.161867	0.996816	2.095753
Error	177.1045	45	3.935656			
Total	219.9617	59				
Chromium						
stations	117442.2	5	23488.45	16.26704	3.81E-09	2.422084
months	1557.943	9	173.1048	0.119885	0.999016	2.095753
Error	64976.8	45	1443.929			
Total	183977	59				
Cobalt						
stations	10679.68	5	2135.935	19.312	3.2E-10	2.422084
months	1444.123	9	160.4581	1.450777	0.195854	2.095753
Error	4977.065	45	110.6015			
Total	17100.86	59				
Copper						
stations	149531.6	5	29906.33	40.87132	1.22E-15	2.422084
months	8178.108	9	908.6787	1.241841	0.294666	2.095753
Error	32927.36	45	731.7192			
Total	190637.1	59				
Iron						
stations	10516.91	5	2103.382	5.019584	0.000973	2.422084
months	4364.192	9	484.9103	1.157207	0.344803	2.095753
Error	18856.58	45	419.0351			
Total	33737.68	59				
Manganese						
stations	260205.5	5	52041.09	23.29068	1.79E-11	2.422084
months	22639.65	9	2515.516	1.125804	0.36496	2.095753
Error	100548.8	45	2234.417			
Total	383393.9	59				

Table 3.10 Contd…

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Nickel						
stations	25250.88	5	5050.176	15.01079	1.15E-08	2.422084
months	1626.584	9	180.7315	0.537194	0.839539	2.095753
Error	15139.64	45	336.4364			
Total	42017.1	59				
Lead						
stations	35532.42	5	7106.484	11.98695	2.1E-07	2.422084
months	2144.883	9	238.3203	0.40199	0.927463	2.095753
Error	26678.33	45	592.8517			
Total	64355.63	59				
Zinc						
stations	334394.6	5	66878.92	17.73925	1.11E-09	2.422084
months	13079.66	9	1453.296	0.385478	0.935967	2.095753
Error	169654.9	45	3770.11			
Total	517129.2	59				

Part II Trace metals in mangrove plants:

The impact of heavy metal exposure on mangrove plants has been considered as minor and non existent (Peters *et al.*, 1997). The relatively low uptake by plants seems to be a general pattern for most ecosystems (Peters *et al.*, 1997; Lacerda, 1998; Silva *et al.*, 1990; Chi and Chou, 1991; Sadiq and Zaidi, 1994; Machado *et al.*, 2002). Most mangrove species have developed strategies to minimize the metal uptake. This includes oxidation and preferential metal fixations within root tissues (Doyle and Otte, 1997; Ong Che, 1999). These attributes of mangroves have been proposed as a way to mitigate metal pollution in coastal areas.

In mangrove soil metals were bound by adsorption onto ion exchange sites, incorporation to the lattice structures or by precipitation as insoluble sulphides. Only the non residual fraction of the sediment is considered to be mobile and therefore is likely to become available (Waldichuk, 1985; Machado *et al.*, 2002). Hence only a very small fraction of metals is bioavailable to the plants, and a larger portion is precipitated as sulphides in the sediments (Lacerda and Rezende, 1987). Other factors favouring the immobilization of trace metals from sediments include complexation with organic matter (Lacerda *et al.*, 1991) and the adaptive mechanism of the plant, which reduces the metal uptake at the root level.

The presence of mangrove plant cover may reduce the physical disturbance of sediments and preserve the metal sedimentary record better than adjacent unvegetated environments (Wassermann *et al.*, 2000; Machado *et al.*, 2002). Plant cover reduces sediment disturbance, resuspension and consequent oxidation associated to frequent storms that can increase the remobilization of metal contaminants (Salomons and Forstner, 1984).

Plant growth and uptake by heavy metals are affected by a number of environmental conditions such as light intensity and duration. The metal uptake by plants also depends on changes in pH and redox conditions. Sarkar and Wyn Jones (1982) showed that small changes in pH in the rhizosphere could make the trace metals more available for uptake. Metal solubility and bioavailability are directly affected by the pH and the redox potential of the soil. Reduced conditions of the mangrove soil might reduce the solubility and limit the bioavailability of heavy metals for plant uptake. Exudation of H_2CO_3 by roots may also help to solubilse metal carbonates and make them more bio available (Xian and Shokohifard, 1989; Ong Che, 1999).

Distribution pattern of some selected trace metals in plant tissues are determined to understand the roles of mangrove plants in meal cycling.

3.2 Results and Discussion:

For convenience, the most common mangrove plants *Acanthus ilicifolius, Avicennia.officinalis* and *Rhizhophora mucronata* species were considered together as group I plants. The remaining plants, were taken as group II plants. Group II plants include *Aegiceras corniculatum, Bruguiera cylindrica, Bruguiera gymnorhiza, Clerodendrum inermi and Excoaecaria agallocha.* species Group I plants were collected from all the six sampling stations. Only random samples of group II plants were analysed for metal content. The metal concentrations in group I and group II mangrove plants from stations 1 to 6 are presented in Table **3.11** and **3.12** Observed metal concentrations in plant tissues are given in Appendix II B. (Fig. **3.3**).

Cadmium

In group I plants, cadmium values varied between BDL to 3.61μg/g. The maximum concentrations were observed for the root tissues of *A.ilicifolious* at station 6. For group I plants observed Cd values were below the detectable limit for all the three species. Station 2 exhibited the highest concentrations for *A. officinalis* and *R.mucronata*; the values were 2.87μg/g (leaves) and 1.52μg/g (stem) respectively.

In all plant parts, the minimum values were below the detectable limit of AAS. The minimum concentrations for leaves and roots were observed for *A.ilicifolious* at station 6; the values were 2.98μg/g and 3.61μg/g respectively. In stem tissues the maximum concentration 1.59 μg/g was noticed for *A.officinalis* species at station 2.

Among group II plants, *E.*agallocha and *A. corniculatum* recorded the highest (3.51 μg/g) and *B.gymnorphiza* (BDL) the lowest values for cadmium.

Table 3.11. Trace metal concentrations in group I plants (µg/g)

Species	Metal concentrations in group I plants (µg/g dry weight)								
	Cd			Co			Cr		
	L	S	R	L	S	R	L	S	R
A.ilicifolious	0.25-2.98	BDL-0.78	BDL-3.61	1.45-46.72	BDL-7.95	7.22-41.27	0.06-3.47	0.59-1.78	1.61-11.43
A. officinalis	0.31-2.87	BDL-1.59	0.02-1.45	BDL-35.53	2.77-26.21	5.00-42.92	0.05-4.83	0.48-5.47	1.90-5.30
R.mucronata	BDL-1.11	BDL-1.5	BDL - 1.08	BDL-11.96	0.36-40.2	1.36-9.12	0.05-1.72	0.68-0.85	0.85-8.37

Species	Metal concentrations in group I plants (µg/g dry weight)								
	Cu			Fe			Mn		
	L	S	R	L	S	R	L	S	R
A.ilicifolious	4.09 - 10.06	2.63 - 13.43	3.15 - 22.21	92.17 - 296.72	30.79 - 294.83	66.35 - 2659.2	6.32 - 56.78	6.61 - 74.46	18.54 - 72.69
A. officinalis	1.73-9.59	2.06 - 10.36	6.15 - 13.97	9.61 - 278.23	55.1 - 1070.3	61.69 - 301.93	32.24 - 125.97	17.07 - 41.76	9.8 - 75.89
R.mucronata	1.21-4.91	1.21-7.61	2.85 - 8.21	20.35 - 203.97	26.17 - 151.00	19.15 - 947.41	5.41 - 92.32	5.29 - 69.53	9.15 - 21.67

Species	Metal concentrations in group I plants (µg/g dry weight)								
	Ni			Pb			Zn		
	L	S	R	L	S	R	L	S	R
A.ilicifolious	3.48 - 12.87	2.7 - 45.06	0.18 - 20.51	0.55 - 36.75	0.49 - 4.39	3.03 - 41.06	10.41 - 135.58	14.2 - 68.56	10.31 - 31.54
A. officinalis	0.38 - 6.71	1.89 - 9.84	0.56 - 7.36	0.44 - 18.08	0.33 - 33.4	0.07 - 14.49	7.64 - 41.96	9.65 - 30.72	20.92 - 80.51
R.mucronata	0.91 - 6.3	1.7 - 10.48	1.24 - 4.38	0.69 - 14.05	1.36 - 29.7	1.34 - 5.73	3.17 - 12.59	4.61 - 17.05	3.02 - 33.12

Table 3.12. Trace metal concentrations in Group II plants (μg/g)

species	Metal concentrations in group II plants (μg/g dry weight)								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
A.corniculatum	0.09 - 3.51	1.25 - 19.7	0.8 - 2.63	2.96 - 15.45	29.89 - 411.04	3.74 - 96.91	4.46 - 9.73	0.12 - 1.21	7.21 - 56.33
B.cylindrica	0.39 - 1.46	BDL - 8.46	0.69 - 17.49	2.44 - 8.76	39.1 - 578.48	6.42 - 29.85	2.94 - 29.85	0.1 - 34.42	2.82 - 20.73
B.gymnorphizha	BDL - 0.58	5.89 - 34.62	0.37 - 2.58	4.16 - 24.7	107.18 - 141.12	16.19 - 28.29	0.74 - 2.79	3.39 - 6.14	5.16 - 26.66
C.inermi	0.13 - 0.94	BDL - 8.86	2.07 - 4.13	9.23 - 22.21	25.29 - 287.66	4.48 - 38.09	0.57 - 16.73	1.03 - 5.61	17.18 - 140.95
E. agallocha	0.02 - 3.51	5.59 - 50.23	0.02 - 2.56	3.58 - 10.65	6.21 - 497.3	8.27 - 101.88	2.18 - 4.57	0.41 - 4.44	11.25 - 65.36

Chromium

In group I plants, Cr content varied from 0.05 μg/g (station 2) to 11.43 μg/g (station 4). Lowest concentrations were noticed for leaves. In *A.officinalis* and *R.mucronata*, the stem tissues showed the maximum values. Root concentration was the highest in *A.ilicifolious* species. For *A. ilicifolius*, the maximum and the minimum values were 11.43 μg/g (station 4) and 0.06 μg/g (station 1) respectively. In *A.officinalis* the lowest Cr values were noticed at stations 3 and 6. *A.officinalis* recorded a maximum value of 5.47 μg/g at station 5. The values varied from 0.05 μg/g (station 2) to 14.37 μg/g (station 1) for *R. mucronata.*

For leaves, the values ranged from 0.05 μg/g (station 2) to 14.37 μg/g (station 1). In stem parts, Cr content varied from 0.48 μg/g (station 4) to 14.37 μg/g (station 1). The concentrations varied between 0.85 μg/g (station 3) to 11.43 μg/g (station 4) for roots.

The maximum (17.49 μg/g) and the minimum (0.02 μg/g) values for groupII plants were noticed for *B. cylindrica* and *E. agallocha* species respectively.

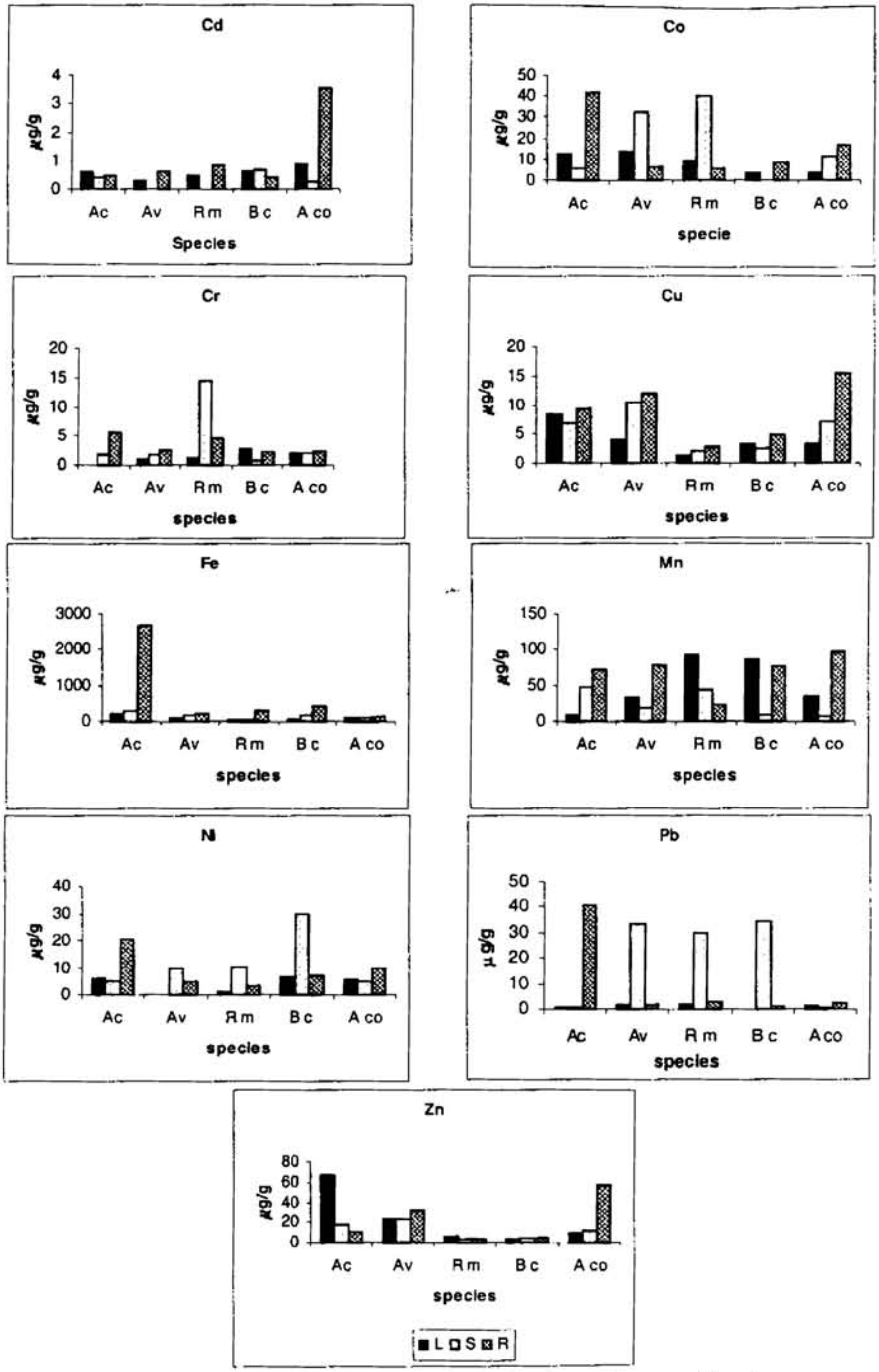

Fig 3.3.1 Distribution of trace metals in plant tissues - Station 1

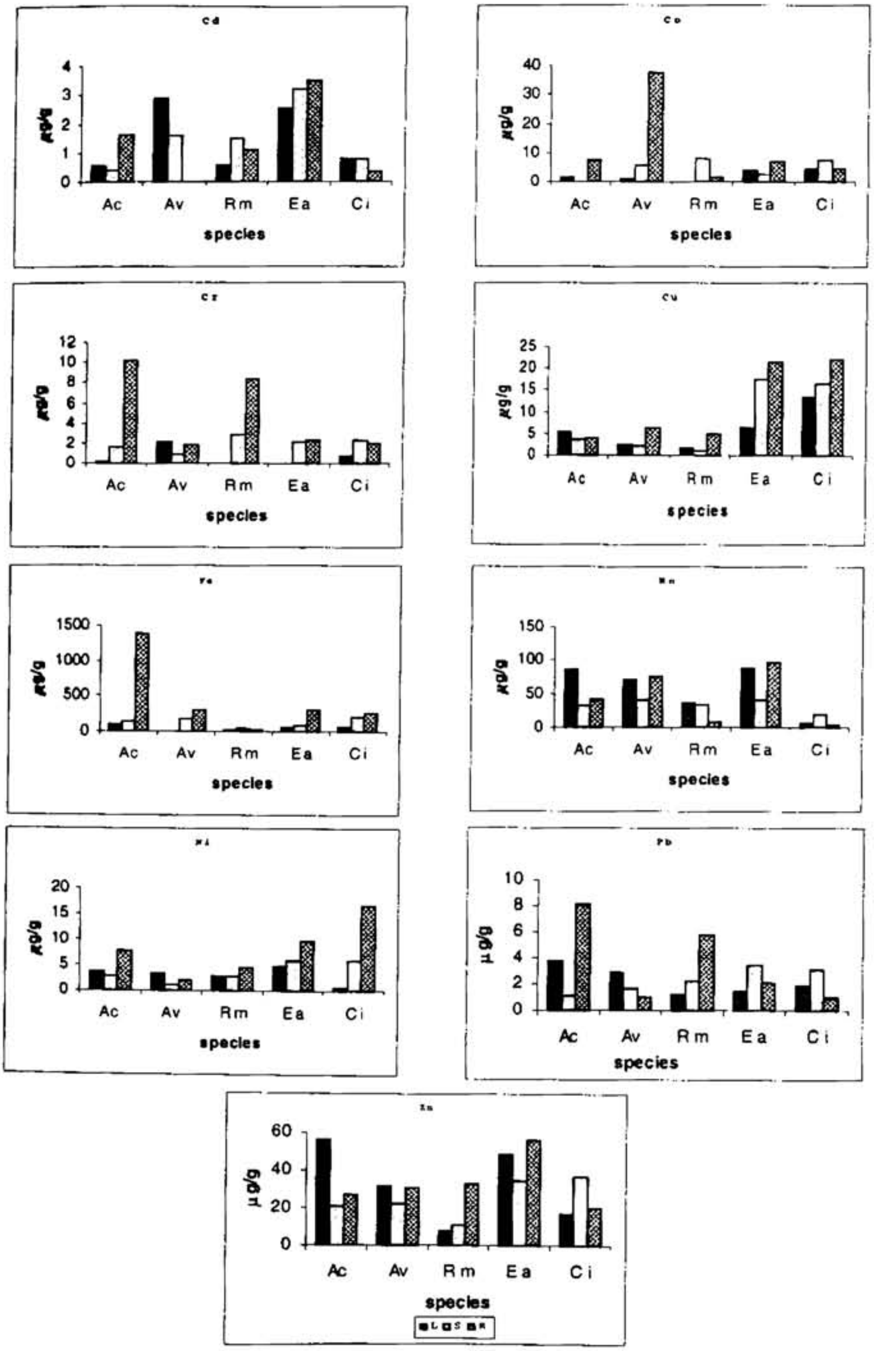

Fig. 3.3.2 Trace metal concentration in plant tissues - Station 2

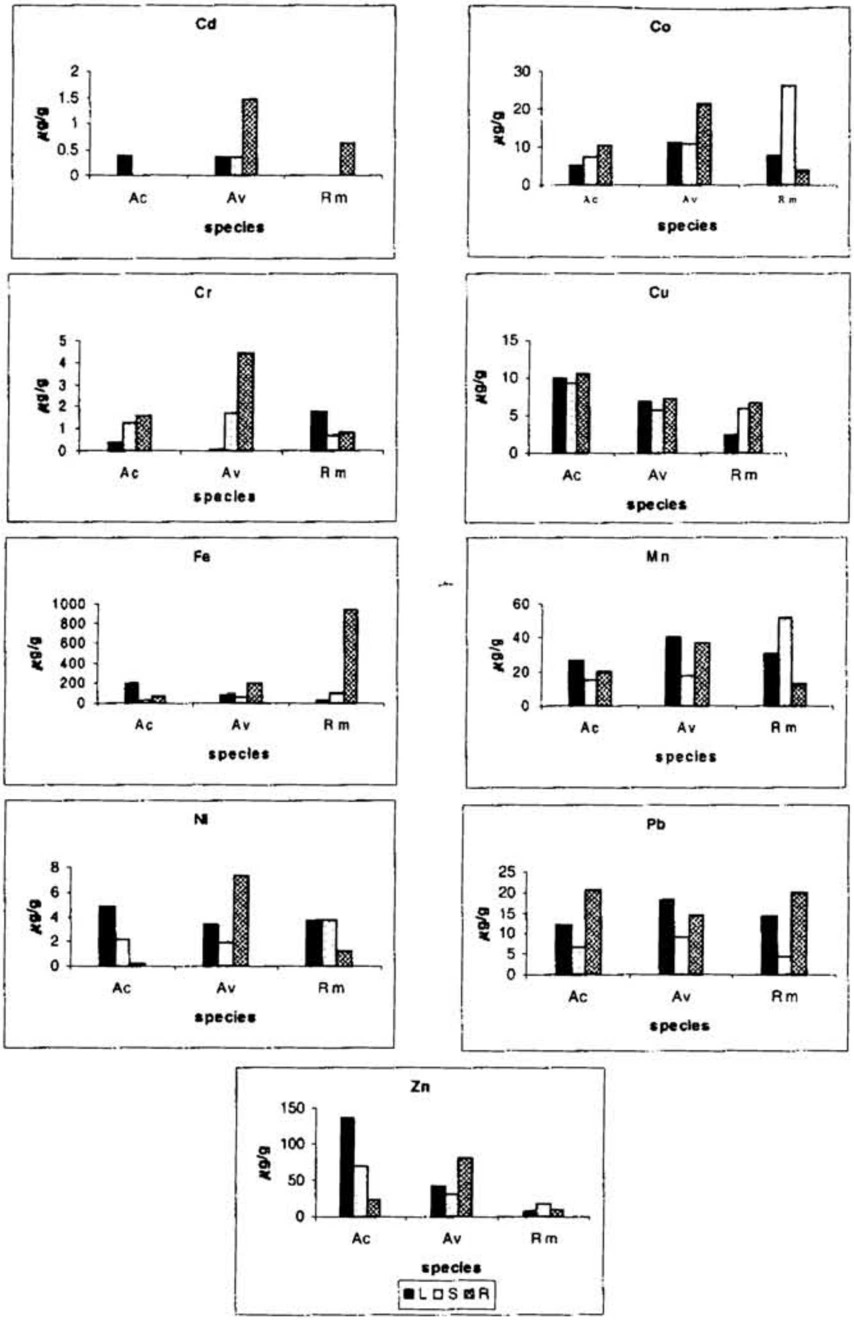

Fig 3.3.3 Trace metal concentration in plant tissues - Station 3

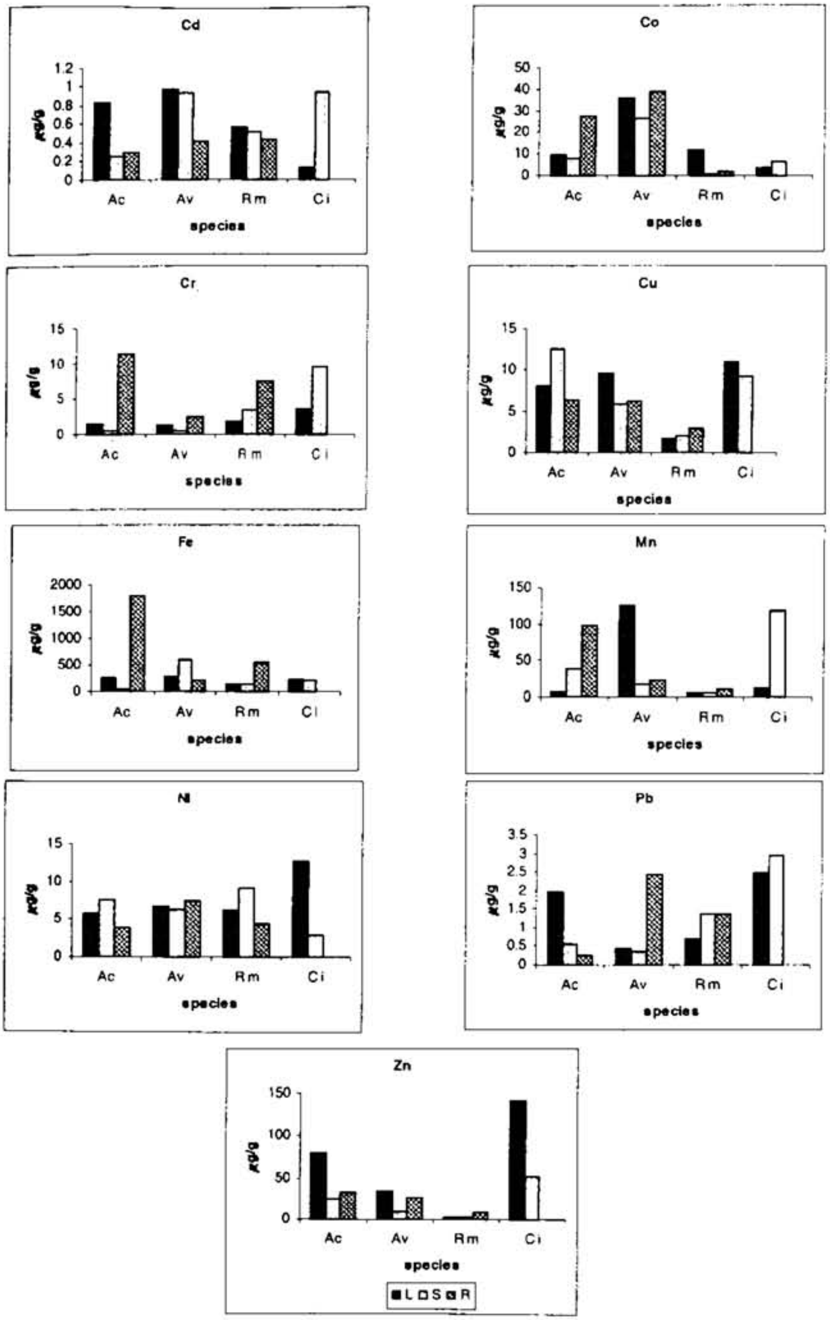

Fig 3.3.4 Trace metal concentration in plant tissues - Station 4

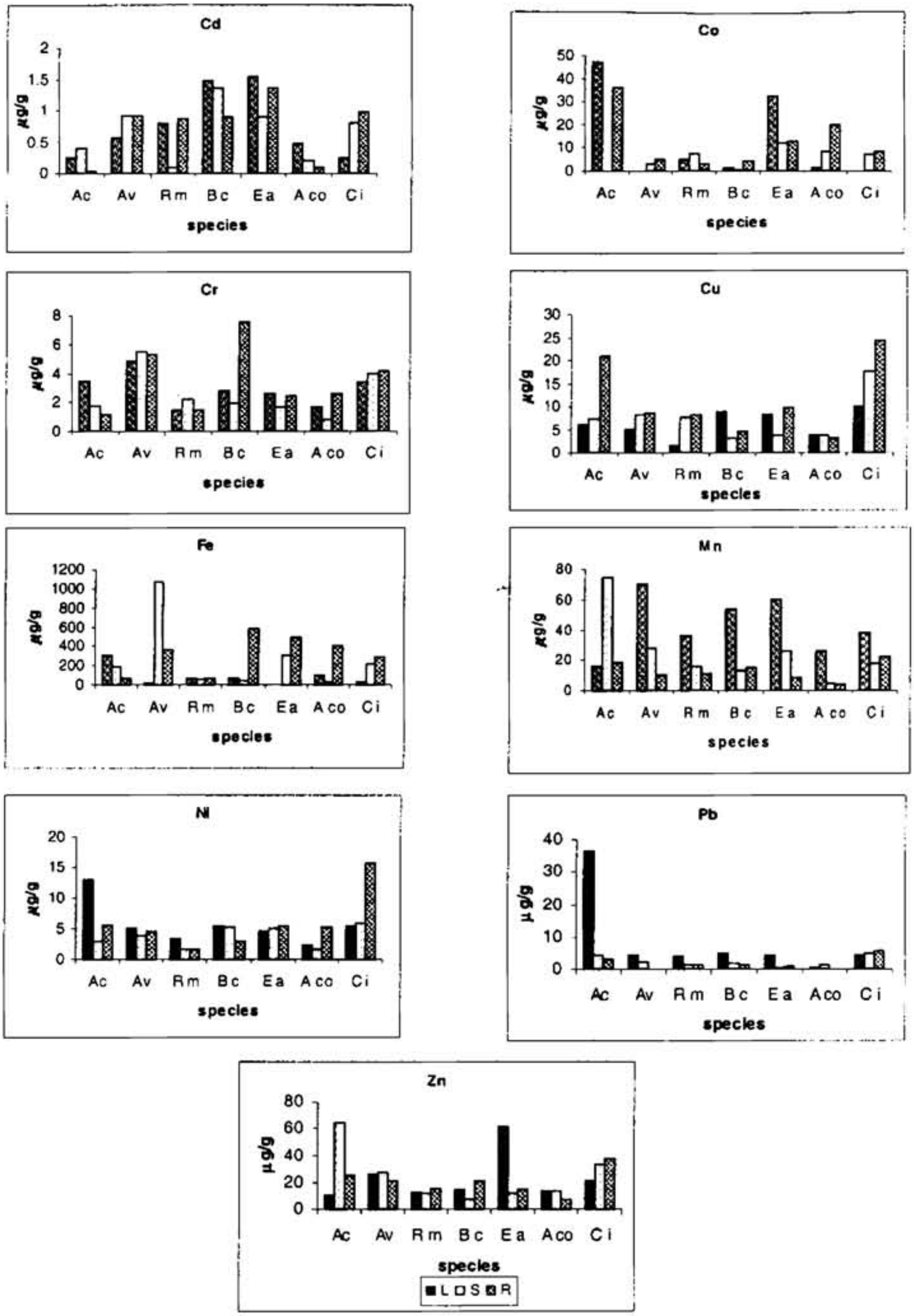

Fig 3.3.5 Trace metal concentration in plant tissues - Station 5

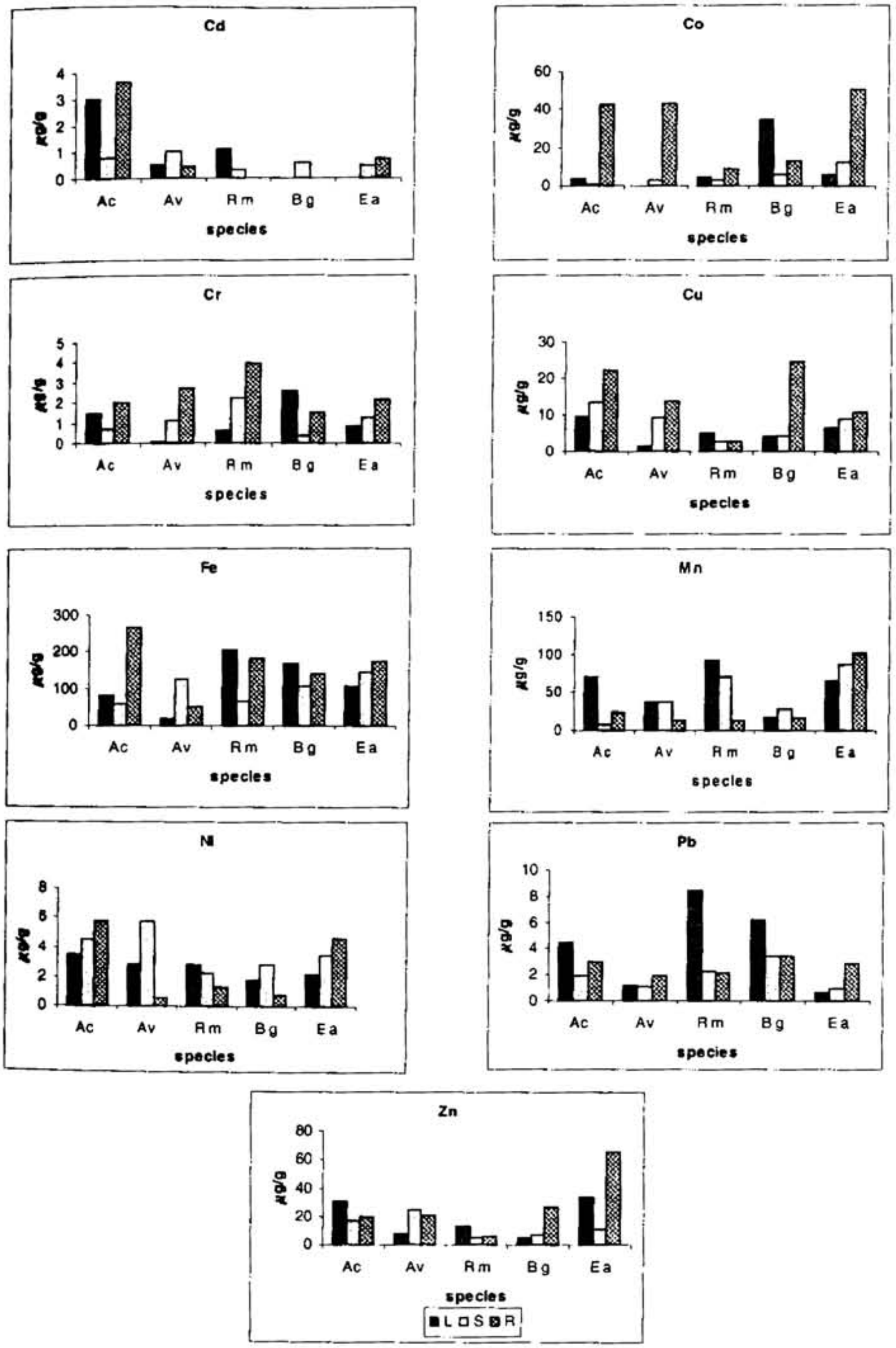

Fig 3.3.6 Trace metal concentration in plant tissues - Station 6

Cobalt

Cobalt content in plant parts varied from BDL to 46.72 µg/g for groupI plants. Leaves of *A.ilicifolious* at station 5 showed the highest Co value (46.72 µg/g). The lowest values for *A. ilicifolius*, *A.officinalis* and *R.Mucronata* were below the detectable limit of AAS. In *A.officinalis* the observed maximum concentration was for the root tissues at station 6 (40.2 µg/g). *R.Mucronata* recorded a maximum concentration of 40.2 µg/g for stem tissues at station 1.

The lowest values for leaves and stem tissues were below the detectable limit of AAS. Leaf tissues recorded a maximum concentration of 46.72 µg/g for *A.ilicifolious* species at station 5.The highest Co values for stem parts were noticed at station 1 for R.M species (40.2 µg/g).

In group II plants, the values were below the detectable limit for *B.cylindrica* (Stem) and *C. Inermi* (leaves). Observed maximum Co concentration was 50.23 µg/g (*E. agallocha*).

Copper

Copper concentrations for groupI plants varied from 1.21µg/g (station 1) to 22.21µg/g (station 6). For *A.ilicifolious sp.* the observed maximum and the minimum values were 2.63 µg/g (station 2) and 22.21µg/g (station 6) respectively. In *A.officinalis* the values ranged from 2.06 µg/g (station 2) to 13.97 µg/g (station 6). Copper concentrations ranged from 1.21 µg/g (station 1) to 8.21 µg/g (station 5) in *R.mucronata* species. Root tissues showed the highest and stem parts showed the lowest copper content.

In leaf tissues, the values fluctuated from 1.21 µg/g (station 1) to 10.06 µg/g (station 4). Stem concentrations ranged between 1.21 µg/g (station 1) to 13.43 µg/g (station 6). For root tissues the observed maximum and the minimum concentrations were 22.21 µg/g (station 6) and 2.85 µg/g (station 1) respectively. For all plant parts *A.ilicifolious* recorded the maximum and *R.mucronata* the minimum copper values.

For group II plants, the values ranged from 3.58 µg/g (*E.agallocha*) to 24.7 µg/g (*B.gymnorphiza*).

Iron

Iron content in group I plants varied from 9.61 µg/g for leaves to 2659.2 µg/g for roots. The maximum and the minimum concentrations were noticed for *A.ilicifolious* (station 1) and *A.officinalis* (station 2) species respectively. In *A.ilicifolious* the minimum Fe concentration (30.79 µg/g) was observed for stem tissues at station 3. *Avicennia officinalis* recorded a maximum concentration of 1070.3 µg/g in stem parts at station 5. Root tissues showed the maximum and the minimum concentrations for *R.mucronata* species. The values ranged between 19.15 µg/g (station 2) and 947.41 µg/g (station 3).

For leaves and stem *A.ilicifolious* species showed the highest values. The values were 296.72 µg/g (station 5) and 2659.2 µg/g (station 1) respectively. Lowest Fe content in leaves (9.61µg/g) was observed at station 2 for Avicennia officinalis species. Root tissues showed a minimum concentration of 19.15 µg/g for *R. mucronata* at station 2. For stem parts the highest and the lowest values in stem parts were noticed for *Avicennia officinalis* and *A.ilicifolious* respectively; the values ranged from 30.79 µg/g (station 3) to 1070.3 µg/g (station 5).

In group II plants, the values ranged from 6.21 µg/g (*E.agallocha*) to 578.48 µg/g (*B. cylindrica*).

Lead

In Group I plants, Pb content varied from 0.07 µg/g (station 5) to 41.06 µg/g (station1), both for root tissues. *A.officinalis* species at station 2 showed minimum Fe content and all plants of this group showed maximum concentration at station1. For *A. ilicifolius*, the highest (41.06 µg/g) and the lowest (0.49 µg/g) values were noticed at station 1. Stem concentrations were the highest in *A.officinalis* and *R.mucronata*. Root tissues exhibited maximum values in *A.ilicifolious sp*. In *A.officinalis*, the values varied from 0.07 µg/g to 33.4 µg/g. For R.M, the highest and the lowest values were 0.69 µg/g and 29.7 µg/g respectively.

For leaves, stem and roots the lowest Pb content was observed for *A.officinalis*. The maximum values in leaves and roots were noticed for *A. ilicifolius*. For stem parts, the maximum values were noticed for *A.officinalis* sp. Pb content in leaves varied from 0.44 µg/g (station 4) to 36.75 µg/g (station 5). The values were between 0.33 µg/g (station 4) and 33.4 µg/g (station 1) for stem parts of the plants. In root tissues the observed maximum and the minimum values were 0.07 µg/g (Station 5) and 41.06 µg/g (station 1) respectively.

The maximum and the minimum concentrations in Group II plants were 34.42 µg/g and 0.1 µg/g respectively. Both the values were for *B. Cylindrica* species.

Manganese

Concentrations in Group I plants ranged from 5.29 µg/g to 125.97 µg/g; both at station 4.The lowest values for *A.ilicifolious* and *A.officinalis* were noticed at station 4.The highest manganese values for theses species were 86.78 µg/g (station 2) and 92.36µg/g (station 2) and 92.36µg/g (station 6) respectively. The values varied from 9.8 µg/g (station 5) to 125.97 µg/g (station 4) for *R. Mucronata* species. Leaf Mn values were the highest for all group I plants.

Leaves and stem parts recorded the lowest values at station 4, the values were5.41 µg/g and 5.29 µg/g respectively. The highest manganese concentrations for leaves were 125.97 µg/g (station 4). Stem tissues showed a maximum concentration of 74.46 µg/g at station 5. In roots, the highest (75.89 µg/g) and the lowest (9.15 µg/g) were noticed for *A.officinalis* species at station 2. R. M showed lowest values for all plant parts. The highest Zn content for roots and leaves were noticed in *A.officinalis* species. Maximum Mn values in stem tissues were observed for *A.ilicifolious*species.

In Group II plants, the values fluctuated from 3.74µg/g (*A. corniculatum*) to 140.95 µg/g (*C. inermi*), both for roots.

Nickel

In group I plants, nickel content varied from 0.18 µg/g (station 3) to 45.06 µg/g (station 1), both for *A.ilicifolious*. In *A.ilicifolious* species, the maximum and the minimum concentration were for the root and stem parts. For *A.officinalis* and *R.mucronata* the highest and the lowest values were noticed at station 1 for stem and leaves respectively. The values ranged from 0.38µg/g to 9.84 µg/g in *A.officinalis* and 0.91 µg/g to 6.3 µg/g in *R.mucronata*.

A.ilicifolious showed maximum values for all plant parts. In leaves, the observed values varied from 0.38µg/g (station1) to 12.87µg/g (station 5). For stem parts, Ni content in plant parts ranged between 1.7 μg/g and 45.06 μg/g, both at station 1.The highest and the lowest values in root tissues were 0.18 μg/g (station 3) and 20.51 μg/g (station 1) respectively.

Among group II plants, *C. inerme* showed the lowest Nickel content (0.57 μg/g). The observed maximum Ni content was 29.85 μg/g (*B cylindrica*).

Zinc

The observed maximum (80.51 μg/g) and the minimum (3.02 μg/g) concentrations for group I plants were noticed for root tissues at station 3 and 1 respectively. The maximum and the minimum values for *A.officinalis* (80.51 μg/g) and *R..mucronata* (33.12 μg/g) were observed for root tissues. The minimum zinc content for these species were 7.64 μg/g leaves) and 3.02 μg/g (roots) respectively. For *A.ilicifolious*. The values ranged from 10.31 g/g (roots) to 135.58μg/g (leaves). The maximum zinc values for *A.ilicifolious* and *A.officinalis* were noticed at station 3. The highest values were observed at station 2 for *R.mucronata*. The lowest values in root tissues at station 1 were noticed for *A.ilicifolious* and *R.mucronata* species. The minimum Zn content in leaves was noticed only for *A.officinalis*.

Rhizhophora sp. showed lower values for all plant parts – leaves, stem and roots. The values were 3.71 μg/g (station 4), 4.61 μg/g (station 5) and 3.02 μg/g (station 1) respectively. The highest values for leaves (135.58 μg/g) and stem (68.56 μg/g) were observed for *A.ilicifolious*. Root tissues showed a maximum concentration of 80.51 μg/g in *A.officinalis species*.

In Group II plants, Zn concentrations varied from 2.82 μg/g (*B.cylindrica*) to 65.36 μg/g (*E. agallocha*).

3.2.1 Spatial variation of trace metals in plant tissues:

Metal concentrations in plant tissues differ between stations. This might be due to the variations in sediment characteristics, which would affect metal availability and consequently, plant uptake. In this study, interspecies variations were also noticed. Metal content in different plant species can vary greatly because of different uptake mechanisms operating in plant tissues. Wide variations in plant metal content can also occur in different populations of the same species as plants respond to the concentration of the metal in the soil and the speciation pattern of metals have a major role in the metal uptake.(Ong Che, 1999).

Station 1 recorded the highest average values for manganese (48.24 μg/g) and nickel (8.30 μg/g) and the lowest average values of cobalt.(6.89 μg/g) and zinc (18.11μg/g) and (Table **3.13**). The highest station wise mean concentration for cadmium (1.42 μg/g) was noticed at station 2. Station 3 showed the maximum average value of zinc (46.07μg/g) and lead (13.30 μg/g) and the minimum values for cadmium (0.45 μg/g), chromium (1.42 μg/g).and nickel (3.17 μg/g). The station wise maximum concentrations of chromium (3.98 μg/g) and iron (406.84 μg/g) were noticed at station 4. The lowest average value of manganese was noticed at station 5 (26.92 μg/g). The highest average values for cobalt.(16.44 μg/g) and copper (9.31μg/g), and the lowest average value for iron (125.94μg/g)were noticed at station 6.

Table 3.13. Station wise average metal concentrations in plant tissues (μg/g)

Metal	Stations					
	1	2	3	4	5	6
Cu	6.23	8.59	7.18	6.85	8.22	9.31
Zn	18.11	30.20	46.07	37.22	22.26	19.49
Mn	48.24	45.51	27.56	42.06	26.92	45.22
Ni	8.30	5.25	3.17	6.60	5.05	2.99
Pb	10.17	2.72	13.30	1.35	4.13	2.93
Cr	2.99	2.49	1.42	3.98	2.97	1.57
Cd	0.67	1.42	0.45	0.57	0.72	0.96
Co	14.09	7.02	11.55	15.40	11.90	16.44
Fe	325.95	211.20	188.63	406.84	227.82	125.94

3.2.2 Interspecies variation of trace metals in plant tissues:

Distribution of trace metals in different plant tissues varied with the metal species (Table **3.14**). The distribution of trace metals within the plant depends on the ability of these metals to be transported. In the present study, the distribution of trace metals in the three common mangrove plants follows the decreasing order:

Acanthus ilicifolius:
Fe > Mn > Zn > Co > Cu > Pb > Ni > Cr > Cu
Avicennia officinalis:
Fe > Mn > Zn > Co > Cu > Pb > Ni > Cr > Cu
Rhizhophora mucronata:
Fe > Mn > Zn > Co > Pb > Ni > Cu > Cr > Cu

The highest average values for iron (514.95 μg/g) and chromium (3.29 μg/g) were noticed for *A.ilicifolious* species. *R. mucronata* species recorded the highest average concentration for chromium (3.29 μg/g) and the lowest value of copper (3.52μg/g). *B.gymnorphizha* species recorded the highest species wise average values for cadmium (19 μg/g) and cobalt (17.87 μg/g) and the lowest mean values for chromium, iron and nickel. The lowest average values of cadmium 0.66 μg/g), manganese (18.17 μg/g) and the highest values for copper (17.31 μg/g) were noticed for the species *C. Inerme*. The lowest mean value of copper was for the *A.corniculatum* species. *B. Cylindrica* plants recorded the maximum for nickel and the minimum values for cobalt (3.00 μg/g) and zinc (9.09 μg/g). The maximum mean values for manganese, lead and zinc were noticed for *E. Agallocha* species; the values were 63.59 μg/g, 91.65 μg/g and 38.04 μg/g respectively.

Table 3.14 Species wise average concentration of trace metals in plant tissues (μg/g)

Metal	Species							
	Ac	Av	R m	B c	A.co	E a	C i	B g
Cd	0.77	0.79	0.54	0.9	0.9	1.58	0.66	19
Co	14.8	16.28	8.17	3	10.26	15.4	5.32	17.87
Cr	2.58	2.23	3.29	2.96	1.91	1.71	2.72	1.49
Cu	8.7	6.94	3.52	4.48	6	10.3	17.31	11.07
Fe	514.95	206.52	167.74	216.59	136.44	186.23	176.83	137.9
Mn	38.82	42.76	32.84	42.08	28.95	63.59	18.17	20.49
Ni	5.82	4.27	3.7	9.47	4.91	5.79	8.41	1.77
Pb	8.4	5.45	5.81	7.13	0.96	91.65	3.43	4.33
Zn	37.66	28.43	9.62	9.09	18.37	38.04	27.31	12.77

Ong Che (1999) recorded higher concentrations of Zn, Fe and Cu in the root tissues of mangrove plants of Mai Po, Hong Kong. In Plant parts iron concentrations were highest. Fe, Cu and Zn are micronutrients essential for plant growth. So their elevated concentrations in the roots may reflect the physiologic requirements of the plants. High concentrations of Fe could be due to the formation of iron plaque on the roots. Plaques are formed when mangrove plant roots leak oxygen and oxidize the rhizosphere sediments. This in turn leads to the oxidation of the iron and manganese in the soil and the deposition of Fe on the roots (Otte, 1991). Oxidation processes in the rhizosphere and iron plaque formation can further change the speciation of metals. Iron and manganese hydroxides are capable of adsorbing large quanities of heavy metals. Zn accumulates in the iron plaque to higher concentrations than those found in the bulk sediment and Cu may also be adsorbed (Ong Che, 1999).Zn and Cu are plant micro nutrients, essential for plant growth and metabolism (Chakrabarthi *et al.*, 1993; Tam and Wong, 1997; Ong Che, 1999). Fe is a constituent of cytochromes and of non heme iron proteins involved in photosynthesis, nitrogen fixation and respiration, while Cu is an essential component of ascorbic acid oxidase, uricase, cytochrome oxidase (Ong Che, 1999).

Of the non essential metals, lead showed higher concentrations. Lead is a multimedia pollutant and the high concentrations of lead in the roots may result not just from soil and water borne lead but also from atmospheric inputs from industrial processes and combustion of fuels and waste materials, which have been adsorbed by the foliage. The high levels of Pb in roots suggest a possible function of sequestering toxic metals in the organ.

Among the nine metals studied, cadmium showed lowest accumulation tendency. Certain higher plant families do accumulate higher levels of Cd in their aerial parts (Ong Che, 1999). Some metals, such as Cr, Pb and Hg have low translocation rates, and are therefore more concentrated in roots than in stems and leaves (Alberts *et al.*, 1990; Ong Che, 1999). Translocation and transport processes may also alter metal concentrations in plant organs (Gleason *et al.*, 1979; Markert, 1993).

The average metal concentrations in different plant parts of mangrove plants are given in Table **3.15**. Generally, higher trace metal concentrations were found in roots with little translocation to other leaf and stem portions. Leaves are found to possess lowest concentrations among the mangrove parts and the sediments the highest (Machado *et al.*, 2002; Saifullah *et al.*, 2002). In *A. ilicifolius*, the leaf tissues recorded the highest mean concentration only for Zinc. For all the other 8 metals studied, the root concentrations were the highest. In *A.officinalis* plants, leaves showed highest average concentration for manganese. Stem parts showed higher values for Fe, Ni, and Pb. Leaf concentrations of Mn and stem concentrations of Co, Ni and Pb were maximum in *R. mucronata* species.

Table 3.15 Average metal concentrations in different plant parts (μg/g)

Metal	Leaves	Stem	Roots
Cu	5.81	7.5	9.86
Zn	32.94	26.14	27.12
Mn	47.19	32.09	28.65
Ni	4.6	4.15	5.78
Pb	5.04	2.78	4.97
Cr	1.58	2.38	4.32
Cd	0.8	0.8	0.83
Co	9.79	7.74	13.82
Fe	107.63	198.44	461.6

Jayasekara (1988) found higher concentrations of metals in roots of *R mangle* compared to stem and leaves. Generally higher trace metal concentrations were found in roots with little translocation to other leaf and stem portions. The roots have been known as a good adsorptive sponge to heavy metals in soils and water. Metals adsorbed or absorbed by plant tissues are often bound to the cell wall material or other macromolecules to prevent them from translocation to the sensitive plant parts (Tam and Wong, 1997; Yim and Tam, 1999). In general, very small quantities of trace metals are accumulated in leaf tissues. Stem tissues reported to have more concentration of trace metals, even more than roots due to their higher bio mass content (Yim and Tam, 1999). Metal concentrations in plant tissues from different other mangrove ecosystems are given in Table **3.16**.

Table 3.16. Metal concentrations in mangrove plant parts from different parts of the world (μg/g)

References	Zn	Fe	Cu	Mn	Pb
Bhosale, 1979 leaves	8.3-107.1		4.1-10.8	5.7-7.2	
Chakrabarthi et al, 1993 Sunderbans - leaves			11.0-29.0		5.0-24
Ong Che, 1999 Mai Po, Hong Kong - root tissues	137.5	4275.6	32.6		34.4
Machado et al, 2002 - Gunabara Bay, SE Brazil - leaves	14.0-31.0		7.0-10.0	28.0-65.0	1.0-8.9
Sarangi et al, 2002 - Bhitarkanika, Orissa leaves	0.3-2.0	7.0-61.0	0.8-3.7	5.7-7.2	
Mac Farlane, 2003 - New Zealnd leaves	0.38		0.14		0.02
Mac Farlane, 2003 - New Zealnd root tissues	4.51		1.58		0.79

References	Ni	Cd	Cr	Co
Ong Che, 1999 Mai Po, Hong Kong -- root tissues	16.3	0.4	3.5	
Chakrabarthi et al, 1993 leaves				1.4 -5.9
Saifullah etal, 2002, Karachi - Leaves	0.10-12.50			
Saifullah etal, 2002, Karachi - Bark	1.10-14.40			
Saifullah etal, 2002, Karachi - Pnematiphores	6.60-12.40			

3.2.3 Correlations of the metal concentrations in plant tissues, sediment and water

An attempt has been made to link the metal content in plant tissues with that in sediments and in water (dissolved and particulate).Correlations between the metal content in different plant parts were also determined. Correlation coefficients (r values) are given in table 3.17. The results of the analysis are the following:

Table 3.17.a Correlation coefficients (r) of trace metal concentrations in plant tissues (*A. ilicifolious*), sediment and water

Correlations - Chromium

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.273	-.548	-.406	-.409	.018
LEAVES	-.273	1.000	-.383	-.394	-.508	.029
PARTICULATE	-.548	-.383	1.000	.969**	.246	-.348
ROOTS	-.406	-.394	.969**	1.000	.141	-.245
SEDIMENT	-.409	-.508	.246	.141	1.000	.295
STEM	.018	.029	-.348	-.245	.295	1.000

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

Correlations - Copper

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.394	.034	-.187	-.262	.117
LEAVES	.394	1.000	-.349	.511	.430	.861*
PARTICULATE	.034	-.349	1.000	-.622	-.251	-.503
ROOTS	-.187	.511	-.622	1.000	.530	.820*
SEDIMENT	-.262	.430	-.251	.530	1.000	.728
STEM	.117	.861*	-.503	.820*	.728	1.000

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

Correlations - Cobalt

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.283	.398	-.190	-.264	-.698
LEAVES	-.283	1.000	-.139	.576	-.623	-.143
PARTICULATE	.398	-.139	1.000	.060	-.432	-.619
ROOTS	-.190	.576	.060	1.000	-.383	.268
SEDIMENT	-.264	-.623	-.432	-.383	1.000	.580
STEM	-.698	-.143	-.619	.268	.580	1.000

Correlations - Iron

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.201	.034	-.209	.240	.402
LEAVES	.201	1.000	-.088	.062	-.138	.254
PARTICULATE	.034	-.088	1.000	.785	-.173	.265
ROOTS	-.209	.062	.785	1.000	-.223	.559
SEDIMENT	.240	-.138	-.173	-.223	1.000	-.368
STEM	.402	.254	.265	.559	-.368	1.000

Table 3.17.a Contd…

Correlations - Manganese

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.019	-.544	-.390	-.299	-.479
LEAVES	-.019	1.000	-.497	-.452	.112	-.532
PARTICULATE	-.544	-.497	1.000	-.065	-.272	.783
ROOTS	-.390	-.452	-.065	1.000	.337	.162
SEDIMENT	-.299	.112	-.272	.337	1.000	-.019
STEM	-.479	-.532	.783	.162	-.019	1.000

Correlations - Nickel

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.342	.346	.732	.801	-.263
LEAVES	-.342	1.000	-.415	-.024	-.611	-.136
PARTICULATE	.346	-.415	1.000	.249	.745	.113
ROOTS	.732	-.024	.249	1.000	.682	.221
SEDIMENT	.801	-.611	.745	.682	1.000	.041
STEM	-.263	-.136	.113	.221	.041	1.000

Correlations - Lead

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.063	-.540	.210	-.363	.725
LEAVES	-.063	1.000	.143	-.302	-.314	.611
PARTICULATE	-.540	.143	1.000	.204	-.093	-.361
ROOTS	.210	-.302	.204	1.000	-.149	-.022
SEDIMENT	-.363	-.314	-.093	-.149	1.000	-.316
STEM	.725	.611	-.361	-.022	-.316	1.000

Correlations - Zinc

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.715	.225	.359	.621	.808
LEAVES	.715	1.000	-.166	.060	.204	.890*
PARTICULATE	.225	-.166	1.000	.049	.592	-.301
ROOTS	.359	.060	.049	1.000	-.228	.131
SEDIMENT	.621	.204	.592	-.228	1.000	.251
STEM	.808	.890*	-.301	.131	.251	1.000

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

Table 3.17 b Correlation coefficients (r) of trace metal concentrations in plant tissues, sediment and water – *A. officinalis*

Correlations - Cobalt

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	STEM	SEDIMENT
DISSOLVED	1.000	.205	-.383	-.540	.699	.268
LEAVES	.205	1.000	-.391	.158	.770	-.382
PARTICULATE	-.383	-.391	1.000	.421	-.370	.580
ROOTS	-.540	.158	.421	1.000	-.223	.281
STEM	.699	.770	-.370	-.223	1.000	-.166
SEDIMENT	.268	-.382	.580	.281	-.166	1.000

Correlations - Cadmium

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.854*	.512	.929**	-.239	-.242
LEAVES	.854*	1.000	.090	.939**	-.120	.021
PARTICULATE	.512	.090	1.000	.180	-.173	-.660
ROOTS	.929**	.939**	.180	1.000	-.085	.073
SEDIMENT	-.239	-.120	-.173	-.085	1.000	.452
STEM	-.242	.021	-.660	.073	.452	1.000

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

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

Correlations - Chromium

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.403	-.548	.449	-.409	-.051
LEAVES	-.403	1.000	-.119	.476	-.239	.798
PARTICUL	-.548	-.119	1.000	-.840*	.246	-.665
ROOTS	.449	.476	-.840*	1.000	-.555	.825*
SEDIMENT	-.409	-.239	.246	-.555	1.000	-.200
STEM	-.051	.798	-.665	.825*	-.200	1.000

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

Correlations - Copper

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.883*	.034	-.571	-.262	-.294
LEAVES	.883*	1.000	-.149	-.613	-.569	-.142
PARTICULATE	.034	-.149	1.000	-.448	-.251	-.704
ROOTS	-.571	-.613	-.448	1.000	.762	.809
SEDIMENT	-.262	-.569	-.251	.762	1.000	.352
STEM	-.294	-.142	-.704	.809	.352	1.000

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

Table 3.17.b Contd…

Correlations - Iron

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	STEM	SEDIMENT
DISSOLVED	1.000	.010	.034	-.357	.121	.240
LEAVES	.010	1.000	.280	-.132	.137	-.220
PARTICULATE	.034	.280	1.000	-.791	-.274	-.173
ROOTS	-.357	-.132	-.791	1.000	.645	.492
STEM	.121	.137	-.274	.645	1.000	.907*
SEDIMENT	.240	-.220	-.173	.492	.907*	1.000

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

Correlations - Manganese

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.289	-.544	.026	-.299	-.317
LEAVES	-.289	1.000	.137	-.250	-.436	-.114
PARTICULATE	-.544	.137	1.000	-.533	-.272	-.149
ROOTS	.026	-.250	-.533	1.000	.839*	.073
SEDIMENT	-.299	-.436	-.272	.839*	1.000	.062
STEM	-.317	-.114	-.149	.073	.062	1.000

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

Correlations - Nickel

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.883*	.346	-.095	.801	.297
LEAVES	-.883*	1.000	-.018	.360	-.653	-.381
PARTICULATE	.346	-.018	1.000	-.205	.745	-.114
ROOTS	-.095	.360	-.205	1.000	-.376	.087
SEDIMENT	.801	-.653	.745	-.376	1.000	.285
STEM	.297	-.381	-.114	.087	.285	1.000

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

Correlations - Lead

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.938**	-.540	.992**	-.363	-.002
LEAVES	.938**	1.000	-.368	.939**	-.387	.021
PARTICULATE	-.540	-.368	1.000	-.580	-.093	.237
ROOTS	.992**	.939**	-.580	1.000	-.324	.073
SEDIMENT	-.363	-.387	-.093	-.324	1.000	-.119
STEM	-.002	.021	.237	.073	-.119	1.000

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

Table 3.17.b Contd…

Correlations - Zinc

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.451	.225	.740	.621	.190
LEAVES	.451	1.000	-.278	.698	-.355	-.028
PARTICULATE	.225	-.278	1.000	-.279	.592	-.174
ROOTS	.740	.698	-.279	1.000	.233	.474
SEDIMENT	.621	-.355	.592	.233	1.000	.282
STEM	.190	-.028	-.174	.474	.282	1.000

Table 3.17.c Correlations of trace metal concentrations in plant tissues, sediment and water – *R. Mucronata.*

Correlations- Cadmium

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.549	.512	-.345	-.239	-.346
LEAVES	-.549	1.000	.414	-.462	.266	.094
PARTICULATE	.512	.414	1.000	-.844*	-.173	-.270
ROOTS	-.345	-.462	-.844*	1.000	-.180	.344
SEDIMENT	-.239	.266	-.173	-.180	1.000	-.004
STEM	-.346	.094	-.270	.344	-.004	1.000

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

Correlations - Cobalt

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.425	-.383	.108	.268	.971**
LEAVES	.425	1.000	-.790	-.060	-.575	.269
PARTIULATE	-.383	-.790	1.000	-.306	.580	-.353
ROOTS	.108	-.060	-.306	1.000	.001	.131
SEDIMENT	.268	-.575	.580	.001	1.000	.321
STEM	.971**	.269	-.353	.131	.321	1.000

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

Table 3.17.c Contd ...

Correlations- Chromium

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.488	-.548	-.579	-.409	-.357
LEAVES	.488	1.000	-.355	-.518	-.345	-.028
PARTICULATE	-.548	-.355	1.000	.982**	.246	.220
ROOTS	-.579	-.518	.982**	1.000	.253	.169
SEDIMENT	-.409	-.345	.246	.253	1.000	.929**
STEM	-.357	-.028	.220	.169	.929**	1.000

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

Correlations- Copper

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.150	.034	-.189	-.262	-.133
LEAVES	-.150	1.000	-.387	-.306	.951**	-.076
PARTICULATE	.034	-.387	1.000	-.266	-.251	-.703
ROOTS	-.189	-.306	-.266	1.000	-.507	.870*
SEDIMENT	-.262	.951**	-.251	-.507	1.000	-.286
STEM	-.133	-.076	-.703	.870*	-.286	1.000

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

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

Correlations - Iron

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.873*	.034	-.192	.240	-.516
LEAVES	-.873*	1.000	-.317	-.121	-.495	.352
PARTICULATE	.034	-.317	1.000	-.233	-.173	-.050
ROOTS	-.192	-.121	-.233	1.000	.789	.613
SEDIMENT	.240	-.495	-.173	.789	1.000	.114
STEM	-.516	.352	-.050	.613	.114	1.000

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

Correlations - Manganese

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.287	-.544	-.174	-.299	.320
LEAVES	-.287	1.000	.049	.722	.654	.740
PARTICULATE	-.544	.049	1.000	.133	-.272	-.430
ROOTS	-.174	.722	.133	1.000	.740	.318
SEDIMENT	-.299	.654	-.272	.740	1.000	.313
STEM	.320	.740	-.430	.318	.313	1.000

Correlations - Nickel

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.804	.346	.177	.801	.376
LEAVES	-.804	1.000	.011	.218	-.566	.001
PARTICULATE	.346	.011	1.000	.894*	.745	.244
ROOTS	.177	.218	.894*	1.000	.602	.555
SEDIMENT	.801	-.566	.745	.602	1.000	.394
STEM	.376	.001	.244	.555	.394	1.000

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

Correlations - Lead

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	.789	-.540	.968**	-.363	-.140
LEAVES	.789	1.000	-.659	.790	.113	-.209
PARTICULATE	-.540	-.659	1.000	-.356	-.093	.284
ROOTS	.968**	.790	-.356	1.000	-.307	-.102
SEDIMENT	-.363	.113	-.093	-.307	1.000	-.034
STEM	-.140	-.209	.284	-.102	-.034	1.000

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

Correlations - Zinc

	DISSOLVED	LEAVES	PARTICULATE	ROOTS	SEDIMENT	STEM
DISSOLVED	1.000	-.101	.225	.130	.621	.566
LEAVES	-.101	1.000	.014	.076	.276	.284
PARTICULATE	.225	.014	1.000	.571	.592	-.203
ROOTS	.130	.076	.571	1.000	-.070	.391
SEDIMENT	.621	.276	.592	-.070	1.000	.038
STEM	.566	.284	-.203	.391	.038	1.000

In *A. ilicifolious*, cadmium content in roots and leaves were positively correlated ($r = 0.909$, $p<0.05$). Correlations between the stem tissues and leaves were found to be statistically significant at 0.05 level for the metals copper ($r = 0.939$) and lead ($r = 0.939$). The metal content in stem and root tissues showed significant correlations for chromium ($r = 0.825$) in *A.officinalis species*. In *R. mucronata* species, copper content in stem and root tissues were positively correlated.

In A.*ilicifolius*, the particulate chromium content correlated with that in root tisssues ($r = 0.839$, $p< 0.05$). The manganese and iron content in root tissues correlated with that in sediments at 0.05 level ($r = 0.839$ for Man and $r = 0.97$ for

Fe) in *A. officinalis*. Dissolved metal concentrations of copper, lead, nickel in sediments correlated with the respective metal content in leaves for copper and lead ($r = 0.883$, $p < 0.05$) and the metal content in root tissues for the metals cadmium($r = 0.929$, $p< 0.05$) and lead ($r = 0.992$, $p < 0.01$) in *Avicennia*. Particulate Cr values correlated with that in root tissues in Avicennia plants ($r = 0.840$, $p < 0.05$). Positive correlations were found for the leaf copper content in *R. Mucronata* species with that in sediments. In *R.mucronata* species, the iron content in leaves, the Co content in stem parts and the lead content in roots correlated with the respective dissolved metal concentrations ($r = 0.873$, $p< 0.05$; $r = 0.971$, $p < 0.01$ and $r = 0.968$, $p< 0.05$ respectively). In this species, the root metal levels for Cd, Cr and Ni showed significant metal concentrations with the particulate metal content ($r = 0.844$, $p< 0.05$; $r = 0.982$, $p < 0.01$; $r = 0.894$, $p< 0.05$).

3.2.4 Analysis of Variance (ANNOVA)

The significance of the observed variations in trace metal concentrations were analysed statistically using one way ANNOVA (Table **3.18**). The results of one way ANNOVA for the metal concentrations in plant tissues between stations and species (separately) are given in table. The variations between stations were statistically significant only for cadmium ($p< 0.05$). Significant interspecies variations were found for the metals Cd, Cu and Zn at 0.01 level and for Fe at 0.05 level.

Table.3. 18.a The results of one way ANNOVA for the metal concentrations in plant tissues (between stations)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Cadmium						
Between Groups	149.5948	5	29.91897	1.026199	0.412945	2.408513
Within Groups	1399.446	48	29.15512			
Total	1549.041	53				
Cobalt						
Between Groups	1089.814	5	217.9629	1.460061	0.220412	2.408513
Within Groups	7165.601	48	149.2834			
Total	8255.415	53				

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Chromium						
Between Groups	39.47376	5	7.894753	0.90099	0.488238	2.408513
Within Groups	420.5908	48	8.762308			
Total	460.0646	53				
COPPER						
Between Groups	171.1602	5	34.23205	1.911031	0.109903	2.408513
Within Groups	859.8178	48	17.91287			
Total	1030.978	53				
Iron						
Between Groups	729727.1	5	145945.4	0.63551	0.673595	2.408513
Within Groups	11023233	48	229650.7			
Total	11752960	53				
Lead						
Between Groups	1238.753	5	247.7507	3.222116	0.013755	2.408513
Within Groups	3690.752	48	76.89066			
Total	4929.505	53				
Manganese						
Between Groups	2854.728	5	570.9456	0.662297	0.653752	2.408513
Within Groups	41379.31	48	862.069			
Total	44234.04	53				
Nickel						
Between Groups	118.0527	5	23.61054	2.227349	0.066682	2.408513
Within Groups	508.8138	48	10.60029			
Total	626.8665	53				
Zinc						
Between Groups	5372.077	5	1074.415	2.106599	0.080745	2.408513
Within Groups	24481.13	48	510.0236			
Total	29853.21	53				

Table 3.18.b The results of one way ANNOVA for the metal concentrations in plant tissues (between species)

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Cadmium						
Between Groups	276.2572	2	138.1286	5.534764	0.006678	3.178798
Within Groups	1272.784	51	24.95654			
Total	1549.041	53				
Chromium						
Between Groups	10.53183	2	5.265913	0.597424	0.554032	3.178798
Within Groups	449.5327	51	8.814367			
Total	460.0646	53				
Cobalt						
Between Groups	833.2267	2	416.6134	2.862671	0.066332	3.178798
Within Groups	7422.189	51	145.5331			
Total	8255.415	53				
Copper						
Between Groups	265.1053	2	132.5527	8.826776	0.000511	3.178798
Within Groups	765.8727	51	15.01711			
Total	1030.978	53				
Iron						
Between Groups	1835632	2	917816	4.719882	0.013162	3.178798
Within Groups	9917328	51	194457.4			
Total	11752960	53				
Lead						
Between Groups	93.45494	2	46.72747	0.492778	0.613805	3.178798
Within Groups	4836.05	51	94.82451			
Total	4929.505	53				

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Manganese						
Between Groups	899.0643	2	449.5322	0.529045	0.592365	3.178798
Within Groups	43334.97	51	849.7054			
Total	44234.04	53				
Nickel						
Between Groups	43.31227	2	21.65613	1.892648	0.161104	3.178798
Within Groups	583.5542	51	11.44224			
Total	626.8665	53				
Zinc						
Between Groups	7348.814	2	3674.407	8.327029	0.000742	3.178798
Within Groups	22504.39	51	441.2626			
Total	29853.21	53				

Part III Dissolved and particulate trace metal concentrations in mangroves:

Trace metals exist in different forms in the aquatic environment. This includes ionic forms, inorganic and organic complexes, and those associated with colloidal material, particulate matter, bottom sediment and biota. They undergo numerous changes during their transport as a result of dissolution, precipitation and sorption.

Distribution of elements in water is greatly influenced by the physiochemical character of water and anthropogenic activities in the area. The study of the distribution of trace metals in water is essential to understand their role in various biogeochemical processes in the aquatic system. In aquatic systems, different processes controlling the trace metal distribution tends to be superimposed. Inputs can be from rivers, sediments or by atmospheric deposition. The removal can be by biological uptake, sorption in or on to the sedimentary particles both organic and inorganic and by flushing with coastal and ocean waters. It is important to distinguish between particulate and dissolved species to understand the effects of the toxicities of heavy metals in the marine environment (Ouseph, 1992). The partitioning of metals between the dissolved and particulate phases in coastal waters varies greatly from element to element.

The solid - water interface mostly established by the particles in natural waters and soils plays a commanding role in regulating the concentrations of most of the dissolved reactive trace elements in soil and natural water systems and in the coupling of various hydrogeochemical cycles. Particles play an important role in the sequestration of reactive elements during the transport cycle. Transfer of dissolved constituents to the particulate phase and the subsequent sinking of particulate trace material are responsible for the removal of dissolved metals from water. The transformations themselves involve a wide variety of biogeochemical processes.

Metals are partitioned among soluble, suspended and bottom sediment and biota in aquatic systems. The soluble phase represents the principal source of bioavailable metals. The dissolved fraction is favoured under conditions of low pH, low particulate loads and high concentrations of dissolved organic matter. At low pH, the solubility of metal hydroxides increases, the adsorption capacity of H+ decreases and H+ ions compete with metals for co- ordination sites on organic molecules.Increase in salinity, usually results in reduced dissolved metal concentrations because the organic particles form flocs with high settling velocity.

3.3 Results and Discussion:

The observed metal concentrations in water (dissolved and particulate) are given in Appendix II C. The distribution of trace metals in water are presented in Figure 3.4.

Cadmium

Particulate Cd values fluctuated from 0.15 µg/l to 0.90 µg/l (Station 6 - Monsoon). Generally, the observed Cd values were higher in the monsoon season.

The maximum and minimum values for dissolved Cd were respectively 1.04 µg/ l (station 3) and 0.01 µg/l (station 1). Stations 3 and 4 showed enrichment in dissolved Cd values during the rainy season.

Pre monsoon concentrations of Cd in both the dissolved and particulate fractions were lowest at station 1.Dissolved and particulate Cd concentrations were always less than or nearer to 1 µg/l.

Chromium

Dissolved Cr values ranged from 0.07 µg/l to 49.58 µg/l. Comparatively higher values were noticed for stations 3,5 and 6. For Cr also an increase in concentration during monsoon is noticed.

Particulate Cr values were between 0.16 µg/l (station 6) and 4.55 µg/l (station 4). Particulate Cr values were higher during pre monsoon season.

Cobalt

Dissolved Co values ranged between BDL to 0.11 µg/l. Dissolved Co concentrations were lowest for station 4. Monsoon values were greater than pre monsoon values for stations 1, 2, 5 and 6.

Particulate Co values were between 0.01 µg/l and 1.12 µg/l. All observed values were close to zero. Only station 2 recorded a concentration of 1.12 µg/l. The highest particulate cobalt concentration in monsoon season was for station 1(0.28 µg/l).

exceptions. For station 2 higher dissolved Mn values were noticed in monsoon season (5.16 μg/l).

The maximum particulate Mn values were reported for station 5, (pre monsoon –9.62 μg/l) and the minimum at station 6 (monsoon – 0.03 μg/l). Observed particulate Mn values were lower at station 3 in both the investigations. Station 5 recorded higher particulate Mn values in monsoon and pre monsoon seasons. Very little seasonal variations were noticed for particulate Mn values at stations 1,3 and 4.Higher particulate Mn values were noticed during monsoon season for stations 2 and 5.

Nickel

Both the highest and lowest dissolved Ni values were observed in monsoon, the values were 0.27 μg/l (station 4) and 14.63 μg/l (station 2) respectively. For all stations other than 1 and 4, monsoon values were higher than pre monsoon values.

During monsoon particulate Ni values were always less than 5 μg/l. In pre monsoon values greater than 5 μg/l were observed at stations 1, 2 and 4; with a maximum concentration of 20.15 μg/l at station 2.

Zinc

Dissolved Zn values were between 0.79 μg/l (station 5 – pre monsoon) and 89.38 μg/l (station 1 – monsoon). Zn values in pre monsoon season were higher than monsoon values for stations 2, 4 and 6. Lowest dissolved Zn concentration was observed at station 5.

The highest and the lowest concentrations for particulate Zn were 0.89 μg/l and 16.28 μg/l respectively. Pre monsoon values of particulate zinc were higher than the monsoon values like dissolved zinc. In both the investigations, station 5 recorded lower values in particulate fraction. Station 6 showed higher values in monsoon and pre monsoon seasons. Only a little variation in the temporal distribution of particulate Zn was noticed at station 3.

Copper

Dissolved Cu values were lowest at station 1 and highest at station 4, the values were 0.57 μg/l and 38.04 μg/l. Monsoon concentrations were generally higher for dissolved copper.

Particulate Cu values were greater during pre monsoon. Monsoon concentrations were higher only for stations 5 and 6. Little seasonal variations were observed for particulate copper values for stations 5 and 6. The values of particulate copper ranged from 4.07 μg/l to 26.88 μg/l. The highest and the lowest values were observed for stations 2 and 4 respectively.

Iron

Dissolved iron values ranged from 5.00 μg/l to 99.25 μg/l. Stations 3 and 4 showed higher values in monsoon season. For all other stations pre monsoon values were higher. Dissolved Fe concentrations were lower for station 6(<10 μg/l). During monsoon maximum Fe values were noticed for station 3.

Particulate iron concentrations were also lower at station 6. Stations 1,3,4 and 5 showed higher values in pre monsoon. Particulate Fe values were higher at stations 1 and 2. Highest particulate Fe values were noticed for station 2 (628.24 μg/l).

Lead

Dissolved lead values were between 0.01 μg/l and 8.84 μg/l. Monsoon values were generally higher, station 4 being an exception. The maximum observed value of dissolved lead was 8.84 μg/l (station 6 - monsoon). Concentrations of Pb in the dissolved phase were lower at station 4.Dissolved lead concentrations at station 5 were always less than 1 μg/l.

Particulate lead concentrations varied from 1 μg/l to 4.15 μg/l. Pre monsoon values were higher at stations 1, 2, 3 and 5 than monsoon concentrations. Higher particulate lead values in monsoon were noticed for the other two stations.

Manganese

Wide variations in dissolved Mn values were observed in the present study from 0.40 μg/l (station 5 – pre monsoon) to 30.50 μg/l (station 3 – monsoon). Like most metals monsoon values were higher also for dissolved Mn with little

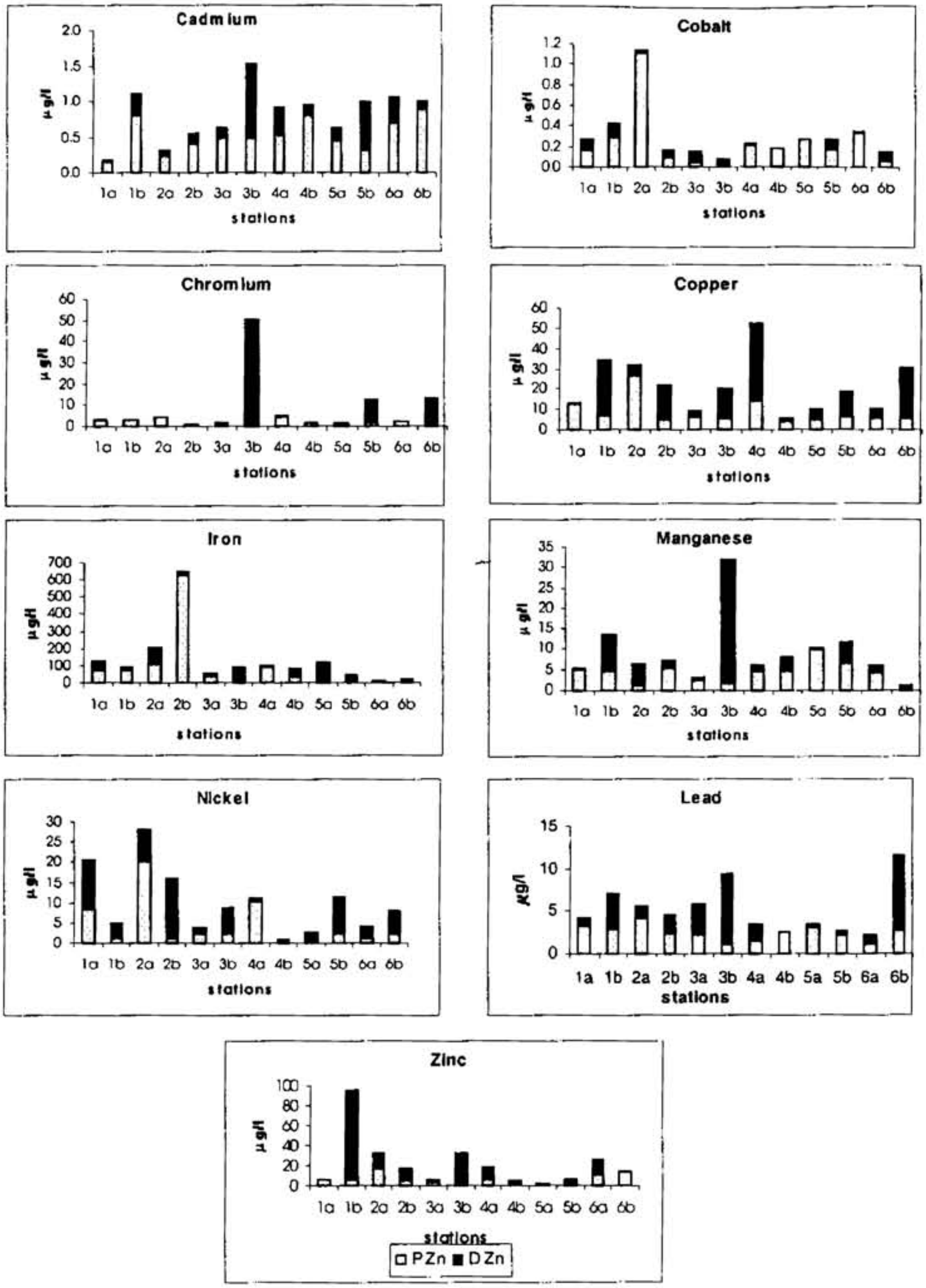

Fig. 3.4. Distribution of trace metals in water (µg/l) (a:pre monsoon, b: monsoon)

3.3.2 Pearson Correlations:

The results of Pearson correlation analysis is presented in Table 3.19

a) Between dissolved metals

Significant positive correlations were found for dissolved chromium with cadmium manganese and lead. Dissolved cadmium values were also correlated with Mn values.

b) Between particulate metals:

The following correlations between the metals were statistically significant at 0.01 level. Co and Cu (r = 0.853), Co and Ni (r = 0.799), Cr and Cu(r = 0.77), Cr and Ni(r = 0.776).The correlations between Co and Cr, Co and Pb, Co and Zn, Cu and Zn are significant at 0.05 level.

3.3.3 Student's *t* – test:

The significance of the seasonal variations of the dissolved and particulate trace metal concentrations were analysed statistically using student's *t* - test.(Table **3.20**) For all the nine metals the variations were statistically insignificant at 0.05 level.

Table 3.19.a Correlations between dissolved metals

Correlations - Dissolved Trace metals

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.000	.026	.813**	.234	.078	.819**	-.036	.347	.245
Co	.026	1.000	.093	.231	-.369	.079	.403	.402	.415
Cr	.813**	.093	1.000	.119	.235	.907**	.106	.695*	.092
Cu	.234	.231	.119	1.000	-.512	.116	-.091	.432	.435
Fe	.078	-.369	.235	-.512	1.000	.310	.066	-.210	-.156
Mn	.819**	.079	.907**	.116	.310	1.000	.057	.562	.399
Ni	-.036	.403	.106	-.091	.066	.057	1.000	.030	-.085
Pb	.347	.402	.695*	.432	-.210	.562	.030	1.000	.255
Zn	.245	.415	.092	.435	-.156	.399	-.085	.255	1.000

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

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

Table 3.19.b Correlations between particulate metals

Correlations - Particulate trace metals

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.000	-.326	-.297	-.526	-.226	-.220	-.549	-.295	.098
Co	-.326	1.000	.633*	.853**	-.036	-.137	.799**	.592*	.622*
Cr	-.297	.633*	1.000	.777**	-.024	-.029	.776**	.211	.340
Cu	-.526	.853**	.777**	1.000	-.016	-.310	.993**	.527	.591*
Fe	-.226	-.036	-.024	-.016	1.000	.092	.001	.073	.006
Mn	-.220	-.137	-.029	-.310	.092	1.000	-.321	.063	-.633*
Ni	-.549	.799**	.776**	.993**	.001	-.321	1.000	.475	.573
Pb	-.295	.592*	.211	.527	.073	.063	.475	1.000	.316
Zn	.098	.622*	.340	.591*	.006	-.633*	.573	.316	1.000

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

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

Table 3.20 a) Results of student's t – test for dissolved metal concentrations.

	Cd - D		Co - D		Cr - D	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*
Mean	0.195958	0.407938	0.044017	0.07875	0.365417	12.44094
Variance	0.023385	0.145085	0.002122	0.002079	0.041861	364.98
Observations	6	6	6	6	6	6
Pooled Variance	0.084235		0.0021		182.5109	
Hypothesized Mean Difference	0		0		0	
df	10		10		10	
t Stat	-1.26505		-1.31271		-1.54818	
P(T<=t) one-tail	0.117269		0.109304		0.076309	
t Critical one-tail	1.812462		1.812462		1.812462	
P(T<=t) two-tail	0.234537		0.218609		0.152619	
t Critical two-tail	2.228139		2.228139		2.228139	

Table 3.20.a) Contd ...

	Cu - D		**Fe - D**		**Mn - D**	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*
Mean	9.4154	16.32727	48.16667	33.14583	1.689896	8.447698
Variance	199.5598	90.75125	1647.867	654.6651	3.212268	124.2669
Observations	6	6	6	6	6	6
Pooled Variance	145.1555		1151.266		63.73958	
Hypothesized Mean Difference	0		0		0	
df	10		10		10	
t Stat	-0.99366		0.766773		-1.46609	
P(T<=t) one-tail	0.171911		0.230468		0.086675	
t Critical one-tail	1.812462		1.812462		1.812462	
P(T<=t) two-tail	0.343822		0.460935		0.173349	
t Critical two-tail	2.228139		2.228139		2.228139	

Table 3.20. a) Contd ...

	Ni - D		**Pb - D**		**Zn-D**	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*
Mean	4.488433	6.6831	1.536542	4.054	8.246458	23.01856
Variance	21.32663	23.91713	1.421574	14.8026	54.15612	1159.537
Observations	6	6	6	6	6	6
Pooled Variance	22.62188		8.112085		606.8464	
Hypothesized Mean Difference	0		0		0	
df	10		10		10	
t Stat	-0.79922		-1.53093		-1.03864	
P(T<=t) one-tail	0.221367		0.078393		0.161718	
t Critical one-tail	1.812462		1.812462		1.812462	
P(T<=t) two-tail	0.442734		0.156785		0.323435	
t Critical two-tail	2.228139		2.228139		2.228139	

Table 3.20 b) Results of student's t – test for particulate concentrations

	Cd - P		Cr- P		Co -P	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*
Mean	0.426667	0.622833	2.4565	1.181167	0.357587	0.129018
Variance	0.041664	0.060087	2.638982	0.724177	0.147639	0.00981
Observations	6	6	6	6	6	6
Pooled Variance	0.050876		1.681579		0.078724	
Hypothesized Mean Difference	0		0		0	
df	10		10		10	
t Stat	-1.50637		1.703435		1.41099	
P(T<=t) one-tail	0.081446		0.059655		0.094296	
t Critical one-tail	1.812462		1.812462		1.812462	
P(T<=t) two-tail	0.162891		0.119309		0.188592	
t Critical two-tail	2.228139		2.228139		2.228139	

Table 3.21.b) Contd …

	Cu-P		Fe-P		Mn -P	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*	*Variable 1*	*Variable 2*
Mean	11.64017	5.421833	54.146	128.0185	4.3985	3.713167
Variance	69.61383	0.898955	1874.025	60583.65	8.452588	5.945874
Observations	6	6	6	6	6	6
Pooled Variance	35.25639		31228.84		7.199231	
Hypothesized Mean Difference	0		0		0	
df	10		10		10	
t Stat	1.81391		-0.72404		0.442404	
P(T<=t) one-tail	0.049882		0.242816		0.333806	
t Critical one-tail	1.812462		1.812462		1.812462	
P(T<=t) two-tail	0.099764		0.485632		0.667612	
t Critical two-tail	2.228139		2.228139		2.228139	

Table 3.20.b) Contd ....

	Ni –P		**Zn -P**	
	Variable 1	*Variable 2*	*Variable 1*	*Variable 2*
Mean	7.2205	1.586	7.209	5.1325
Variance	55.76475	0.623722	30.91706	21.56042
Observations	6	6	6	6
Pooled Variance	28.19424		26.23874	
Hypothesized Mean Difference	0		0	
df	10		10	
t Stat	1.837959		0.702136	
P(T<=t) one-tail	0.047959		0.249305	
t Critical one-tail	1.812462		1.812462	
P(T<=t) two-tail	0.095919		0.498611	
t Critical two-tail	2.228139		2.228139	

Part IV Comparison of the metal concentrations in plant tissues, sediment and water:

Acanthus ilicifolius:

Distribution pattern of zinc in plant tissues were comparable with that in the dissolved fraction. The average zinc content in plant tissues increases with the metal content in sediments for all stations except station 6. At station 6, zinc content in plant tissues was comparatively higher. The higher metal concentration in sediments does not imply higher values in plant parts. The highest Zn content in plant tissues was noticed at Station 3. Both the dissolved and the sedimentary zinc concentrations were maximum at station 3. For the metals Fe, Mn and Zn, the tissue metal concentrations were comparable with the sedimentary metal concentrations at stations 4 and 5. At station 5, Ni and Pb concentrations in plant tissues were comparable with the metal content in sediments. The highest average Ni content in plant tissues were noticed at station 1. The dissolved and sedimentary Ni concentrations were the highest at station 1.

Cd was detected in the plant tissues from station 4. Lower cadmium concentrations were noticed for sediments at this station. Higher average cadmium content in plant tissues were noticed only at station 6. Particulate and sedimentary metal concentrations were also the highest at station 6. Cd content in plant tissues from all the other stations was lower than 1 μg/g. For copper, the tissue metal concentrations and the sedimentary metal values were the highest at station 6.

Spatial variations in plant tissues were noticed for the metals Zn and Co.

Avicennia officinalis

For *A.officinalis* species, manganese concentrations in plant tissues were comparable with that in sediments. Manganese concentrations in plant parts do not necessarily increase with the metal content in sediments. Highest and the lowest Mn content in plant tissues were noticed at station 2 and station 5 respectively.

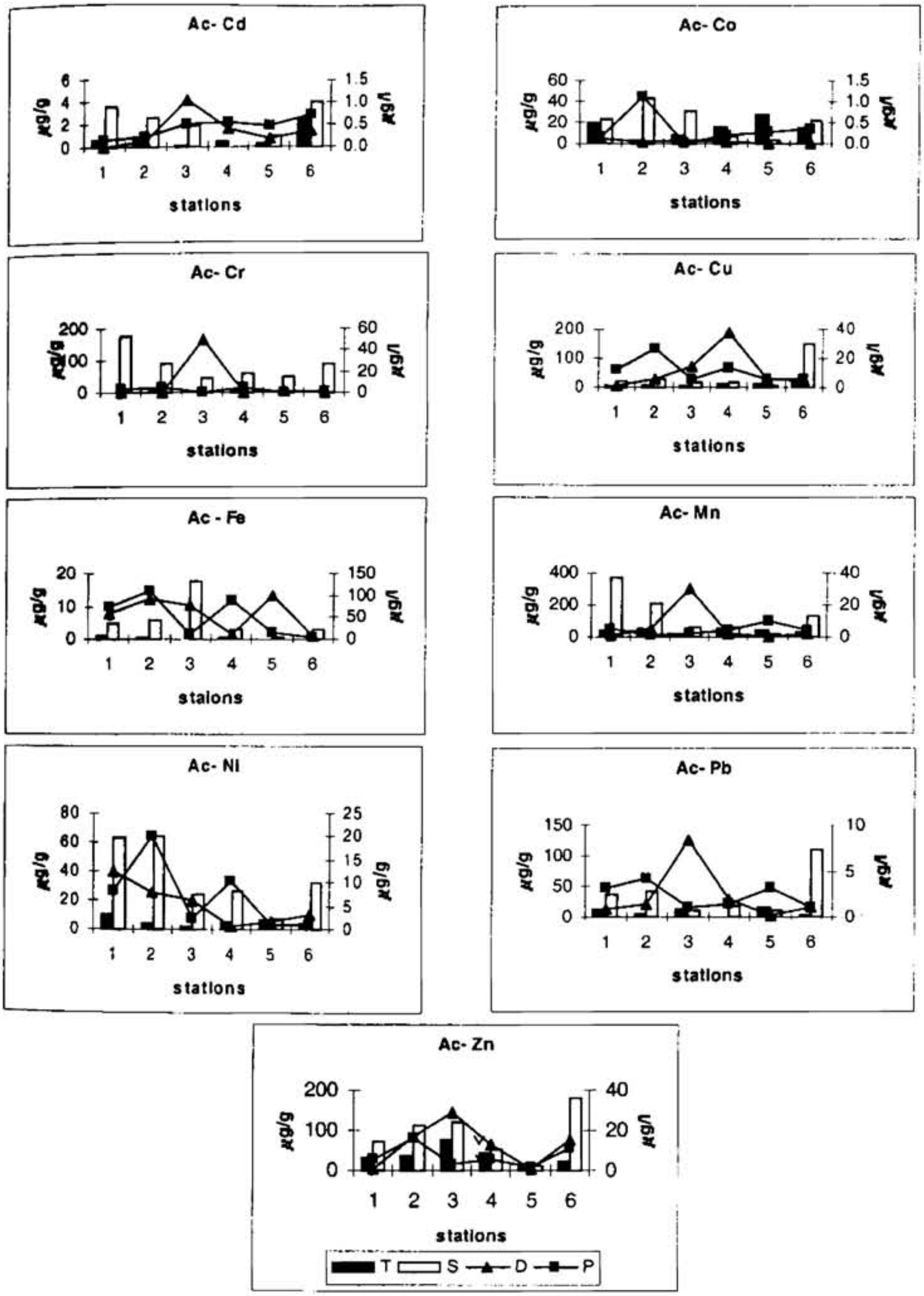

Fig 3.5.1. Distribution of trace metals in plant tissues, sediment and water- *A. ilicifolious*

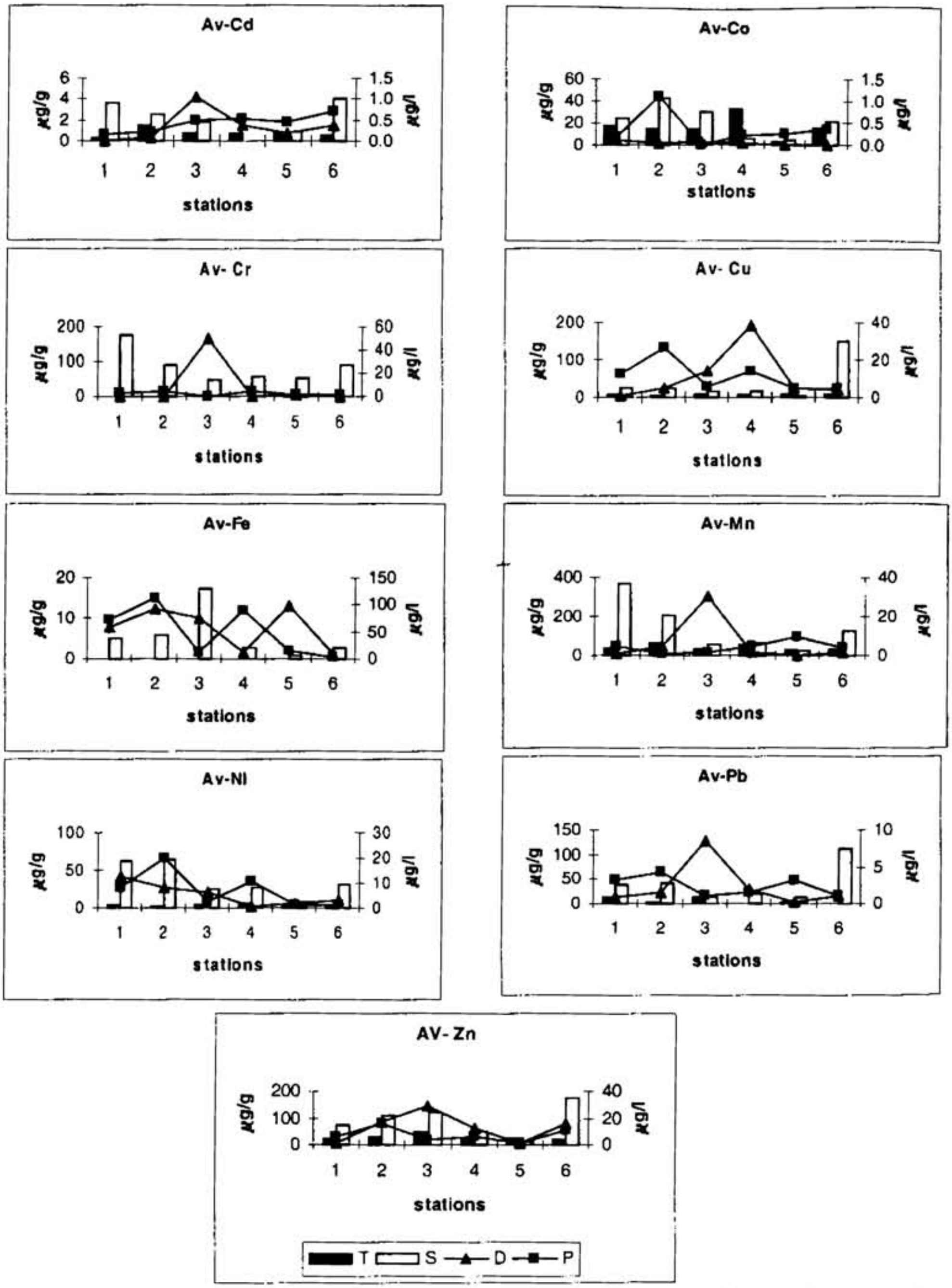

Fig 3.5.2. Distribution of trace metals in plant tissues(*A.officinalis)*, sediment and water

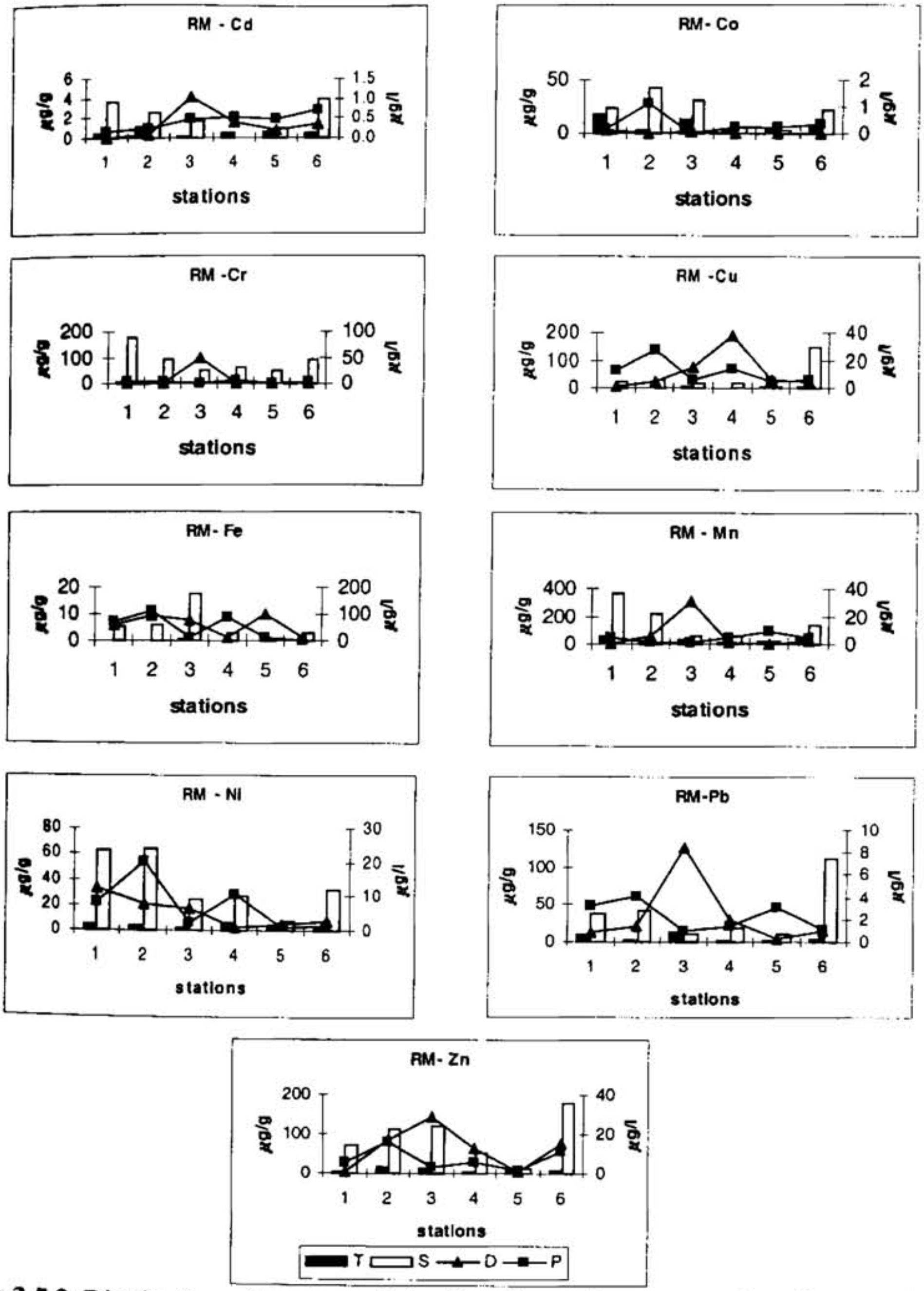

Fig 3.5.3. Distribution of trace metals in plant tissues(*R.mucronata*), sediment and water.

Sedimentary metal concentrations were the highest at station 1, the second highest Mn content was observed at station 2.At station 5, copper content in plant parts were lower than that in sediments. Copper concentrations in plant parts were comparable at all the six stations. Copper content in plant tissues did not vary with the sedimentary copper content. At station 6, the elevated copper values for sediments do not result in higher tissue metal concentrations.

Distribution pattern of zinc in plant parts were comparable with that of sediments and dissolved zinc for stations 1, 2, 3 and 4. Average zinc content in plant tissues was higher than the zinc content in sediments. The highest zinc content in plant tissues and sediments were noticed at station 3. Zinc content in plant tissues was higher than that in sediments at stations 4 and 5.

Lead content in plant tissues were higher than that found in sediments at station 3.Dissolved and sedimentary metal concentrations were also highest at station 3. Nickel content in plant tissues were comparable with that in sediments at station 4. Lead content in plant parts were higher than that in sediments at stations 3 and 5.

At station 4, Cd and Co concentrations in plant tissues were higher than that found in sediments. Cadmium concentrations in plant tissues were comparable with that in sediments.

Rhizhophora mucronata

Copper and Zinc concentrations in plant tissues were higher than that found in sediments. Elevated metal levels in sediments did not reflect in the metal concentrations in plant tissues. At stations, 1, 4 and 5 cobalt content in plant tissues were comparable to that in sediments. Sedimentary Ni content increases with that in particulate matter. Cd, Co and Mn concentrations in plant tissues varied among stations. Cd content in plant tissues was highest at station 2 and the lowest at station 3. Dissolved Cd concentration was the highest at station 3. Mn content in plant parts was the highest at station 6. The second highest Mn value was noticed at station 1. Sedimentary Mn content was the highest at station 1. At station 5, the sedimentary Co values were lower than the tissue metal concentrations. The lowest average Co content in plant tissues were noticed at station 2. Co content in the sediment was the highest at station 2. Particulate Co concentrations were also the highest at station 2.

Spatial variations in metal concentrations in plant tissues were negligible for all the three species studied. Machado et al.(2002) observed less accentuated variations in leaf metal concentrations among stations than the sediments. He also noticed that the leaf metal concentration seems to be related to the metal content in sediments. Lacerda et al. (1997) observed lowest metal concentrations in mangrove leaves than the sediments. Though in some cases the metal content in plant tissues increases/decreases with the metal concentrations in sediments. It is not the general pattern. Various other factors should also be considered to understand the accumulation and fate of trace metals in mangrove plants. The mangrove soils has a large capacity to retain heavy metals and the role of mangrove plants in retaining metals will depend on plant age and their biomass production (Tam and Wong, 1997). Mangrove sediments possess the ability to immobilize metals in unavailable forms through complexation with organic matter and precipitation with iron sulphides under permanently reducing conditions. Only small portions of metals are available to plants and a larger portion is precipitated as sulphides in sediments. Most of the studies reveal relatively small transfer of trace metals from sediments to mangrove plants (Silva *et al.*, 1990; Chiu and Chou, 1991; Sadiq and Zaidi, 1994, Machado *et al.*, 2002). The metal concentration does not vary with the metal content in sediments or water even in systems with elevated metal levels. The mangrove plants have the capacity to be extremely tolerant to metals. Mangroves avoid higher concentrations of metals in their tissues in several ways, including shedding of leaves, fruits and flowers. Larger amounts of tannins present in them also render metals inactive by binding and delaying the re entry into system and slowing down their cycling. The export of metals from mangrove forests through plant detritus is also found to be very small (Lacerda *et al.*, 1988, Silva *et al.*, 1998; Machado *et al.*, 2002).

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Chapter 4

SPECIATION OF TRACE METALS IN MANGROVE SEDIMENTS

Metals accumulated in sediments may be subsequently released to the water column as a result of either physical disturbance (Boughriet *et al.*, 1992) or diagenesis (Peterson *et al.*, 1995; Jones and Turkey, 1997). The mobility and bioavailabilty of metals bound to sediments depends on a multitude of factors such as sediment characteristics, chemical conditions of the system and the physiochemical forms of the metals. Changes in the forms the sediment occurs by changes in the environmental conditions.

The major factors controlling the release of metals are pH, organic matter content, major element chemistry and biological activity. Higher mobility was observed at low pH values. A decrease in pH may cause the release of metals from complexes and from solid surface by increased competition for sorption sites by H+ ions (Prokop *et al.*, 2003). The oxidation of sulphides and organic matter may also generate acidic conditions, which favors the mobility of metals. The introduction of oxygen mobilizes metals originally bound to sulphides under anoxic conditions. Oxidation of organic matter is considered as one of the important mechanisms inducing mobilization of metals.

Redox conditions during sediment deposition and diagenesis played an important role in the speciation, mobility, and preservation of trace metals (Farmer and Lowell, 1984; Cundy and Croudace, 1996; Mortimer and Rae, 2000). Diagenesis is particularly significant in association with the transition from aerobic to anaerobic conditions, sulfate reduction and biogenic decomposition of organic matter. Transformations during early diagenesis and changing redox state characterize chemical forms of metals in aquatic systems.

With the onset of sulphate reduction, metals bound to oxide phases were initially transformed to mono sulphides and fixed as pyrite with the progress in sulphidization. The efficiency with which this transfer occurs differs significantly among metals. When the the sulphidization of iron minerals is complete, pyrite will the dominant host for non silcate bound transition metals.

Many sequential extraction procedures have been developed for partitioning trace metals in sediments, soils and sludges (Tessier *et al.*, 1979; Lake *et al.*, 1984; Shuman, 1985). The most widely used one is that of Tessier with slight modifications. Many researchers have pointed out the limitations of this procedure.

The limitations of sequential extractions include the technical difficulties associated with achieving complete and selective dissolution and recovery of trace metals from different geo chemical phases. Basically it is intended that at each step, a reagent attacks a well defined component only without affecting the rest (that is, it is selective) and that there are no problems with readsorption of the already solubilised elements. The overlap of chemical reagents and readsorption of trace metals from different geo chemical phases (chances of overestimating and under estimating the metal content in different fractions) cannot be neglected. The selectivity of a reagent for a particular phase is limited or extracted elements get readsorbed during extraction sequence(Bunzl *et al.,* 1999). Redox sensitive elements may change their oxidation state during an extraction sequence. Reducible oxides may not be completely removed at steps II and III. A portion of these two interferes with fraction IV. Metals associated with humic materials are not leached at step IV of the scheme. Humic materials are even resistant to oxidation. Metals occluded in humic substances are estimated along with mineral components. In all these conventional sequential extraction schemes, chemical discrimination between organic and sulphide bound metals is difficult (Kersten and Forstner, 1989).

Inspite of all these limitations, the sequential extraction scheme is a very useful method for characterizing solid – phase solid phase associated trace metals in soils and sediments (Shuman, 1979; Belzile *et al.,* 1989; Kim and Fegusson, 1991; Tessier and Campbell, 1991). These techniques are useful for monitoring the relative changes in contaminant partitioning as a consequence of changing physiochemical conditions (La Force *et al.,* 1999).

In our experiments, the protocol of Tessier's et al. (1979) with slight modifications as suggested by Calmano and Forstner (1983) was used. The five step sequential extraction yields the following operationally defined fractions.1) Exchangeable cations, 2) Moderately reducing phases (Mn oxides and partly amorphous Fe- oxy hydrates and carbonate phases), 3) Easily reducing fraction (Amorphous and poorly crystallized Fe – oxy hydrates), 4) Organic fraction including sulphides and 5) Residual fraction.

The first fraction is extracted with ammonium acetate. $MgCl_2$ extraction (step I of Tessier's Scheme) is avoided due to the possibility of formation of soluble metal – chloro – complexes. An additional step is included for moderately reducing fractions. Though this aspect is of little importance while considering the bioavailability, it is valuable in the determination of origin and distribution as well as diagenetic effects (Calmano and Forstner, 1983).

The conventional schemes may be significant under experimental conditions encountered in the laboratory. But the natural environment is highly variable. Mangrove sediments are anoxic in nature. Sulphide formation and and co precipitation of metals on these sulphides plays a major role in trace metal cycling in these sediments. Sulphides can be released to the water column by the direct advantage of pH. Most heavy metal sulphides are soluble at acidic pH. Trace metal complexes, which are not oxidizable under these mild conditions, are released during anaerobic diagenesis. During early diagenesis microbially mediated reactions will result in the dissolution of Fe (III) and Mn (IV) oxides and possible release of the associated metals. Some of the metals originally bound in oxide phases may be fixed as pyrite as sulphidization progresses (Huerta – Diaz and Morse, 1992). Mineralization of organic matter in the sediment can result in the removal of bound metals, and a significant flux of these metals from the sediment to the overlying water (Peterson *et al.*, 1995; Jones and Turkey, 1997).

To understand the behavior of metals in reducing sediments, the leachability of metals over a wide pH range, from 8 to 2 were examined. As strong oxidizing agents as HNO_3 were not used in extractions, only weakly bound and hence bioavailable fractions were separated using this scheme. Considering, the impact on the environment, characterization of bioavailable fractions were more important than the fractionation into different geochemical associations. In natural environment, the possible influences on metal fractionation include ion interactions (eg. salinity change), changes in pH and redox potential. In surface sediments, strong oxidizing conditions were not practically feasible. The extraction by strong acids is poorly related to the natural environmental conditions and to questions of bioavailability and mobility (Ure, 1996). These extractions give information on lithogenous associations, which is insignificant while considering biological uptake. Only the fractions becoming available through environmental changes are important while considering bioavailability.

Soluble complexes will be transferred to the aqueous phase and the insoluble complexes will wait for mineralization. Metals associated with humins will be more or less storage; no release is expected under natural conditions. What we can envisage is that the assessment of available metal species (biological uptake and chemical transformations) can be obtained by considering pH modifications, salinity changes and diagenetic activity. When we consider sediments, the short-term release will be purely based on pH and salinity variations. These are fast inorganic chemical reactions. Because of these considerations, in anoxic sediments, a speciation scheme based on pH can better predict the labile concentrations of metals.

The mangrove sediments are under anoxic conditions. The mobility of the metal under natural conditions was better predicted by extraction at pH 6 and 7. The oxidation and reduction reactions occurring in mangrove sediments are not pure chemical oxidation and reduction reactions. Microbial activities played a major role in controlling the redox state of the sediment. In highly oxidized conditions, observed maximum concentrations might be due to the decomposition of organic matter. Hence, the two schemes used in the present study were not comparable.

Results and Discussion

Samples were analyzed seasonally. In our study, seasonal cycle starting from pre monsoon and moving to post monsoon through monsoon was considered. The results of these two sequential schemes are presented separately under headings: I) Speciation based on the modified Tessier's scheme and II) Speciation based on pH.

For the fractions leached using the modified Tessier's Scheme, the numbers representing the fractions are used along with the chemical symbol to represent the respective fractions of the element. Total metal concentrations were denoted by adding the subscript T to the chemical symbol of the metal.

The fractions leached at pH values varying from 8 to 2 were represented as f 8, f 7, f 6, f 5, f 4, f 3 and f 2respectively; the number denotes the pH of the extracting solution.

4.1 Speciation based on the modified Tessier's scheme

Even though, the values showed a tendency to decrease from pre monsoon to post monsoon through monsoon season no significant seasonal variation was observed. So seasonal description on the speciation data is avoided.

The mean and range of heavy metal concentrations in various operationally defined fractions are given in Table **4. 1**(Fig. **4.1.1** to **4.1.6)**

Copper

In all the fractions, the concentration of copper was fairly high at station 6. Organic fraction including sulphides made a significant role in the speciation of copper in mangrove sediments. This fraction made higher contribution to total copper. Comparatively lower values for this fraction were obtained at station 2. Exchangeable and easily reducing fractions made only small contribution to the total Copper content.

The exchangeable copper concentrations (Cu_1) were highest at station 6(4.63 μg/g) and the lowest at station 4 (0.08 μg/g). Station wise average concentrations varied from 0.21 μg/g (station 1) to 2.78 μg/g (station 6). Stations 2, 3, 5 and 6 exhibited the general seasonal pattern.

In the easily reducing fraction copper concentrations (Cu_2) ranged from 0.01μg/g (station 4) to 1.40 μg/g (station 6). The highest and the lowest station wise average values were noticed at station 6 (0.95 μg/g) and at station 4 (0.10 μg/g) respectively.

The concentrations of copper in the moderately reducing component (Cu_3) were below the detectable limit at stations 1 and 2. The observed maximum concentration for Cu_3 was 68.06 μg/g (station 6 – monsoon). The station wise average values fluctuated from 1.06 μg/g (station 5) to 32.13 μg/g (station 6).

The observed copper values in the organic fraction (including sulphides) - Cu_4 - ranged from 0.20μg/g (station5) to 109.54 μg/g (station 6). Station wise average concentration was the highest at station 6 (67.05 μg/g) and the lowest at station 5 (1.09 μg/g). General seasonal trend was noticed for stations 1 and 4.

Table 4.1.1 Concentrations of copper in different fractions of sediments extracted using modified Tessier's Procedure (µ/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
Cu_1	1	0.148	10.75	3.07	Cu_2	1	0.058	8.29	3.18
	2	0.104	23.13	6.03		2	0.313	22.32	6.85
	3	0.128	6.15	2.06		3	0.024	12.84	4.16
	4	0.199	4.68	1.21		4	0.007	3.62	0.88
	5	0.145	0.79	0.50		5	0.258	2.27	0.90
	6	1.252	59.41	20.79		6	1.403	104.27	36.88
Cu_3	1	0.238	4.97	2.18	Cu_4	1	0	15.44	4.82
	2	0	20.66	5.86		2	0.205	17.76	5.31
	3	0.215	8.50	2.48		3	0.158	6.44	2.50
	4	0.123	1.78	0.73		4	0.118	8.13	3.26
	5	0.1	1.61	0.71		5	0.174	1.79	0.74
	6	0.295	69.16	26.80		6	0.92	109.54	29.99
Cu_5	1	0.075	9.56	2.76					
	2	0.154	16.60	6.71					
	3	0.013	13.34	3.47					
	4	0.019	4.49	1.72					
	5	0.122	1.19	0.56					
	6	0.616	70.10	34.36					

Residual copper concentrations (Cu_5) varied between 0.18 µg/g (station 5) to 109.54µg/g (station 6). Station wise mean concentrations were in the range of 0.83 µg/g (station 5) to 45.89 µg/g (station 6). General seasonal pattern was noticed at station 2. A reverse trend was obtained for stations 4 and 5.

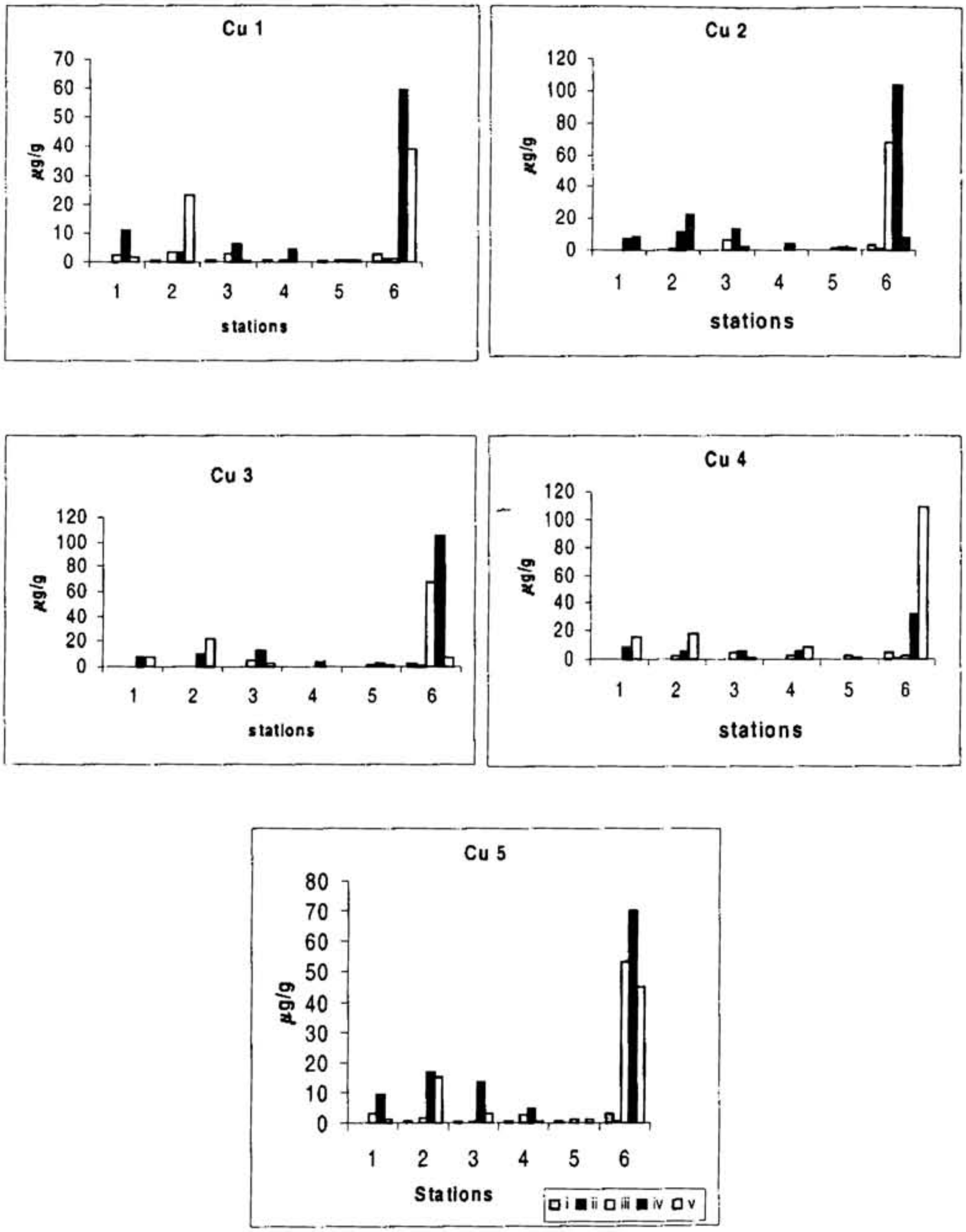

Fig. 4.1.1 Distribution of copper in different fractions of the sediment

Analysis of the mean percentage values of copper indicates a very high percentage in the organic / sulphide fraction. Complexation with organic matter is also important in systems rich in organic load. Sulphide formation is important in anoxic sediments. Sulphide formation is expected under anoxic conditions. Of the six stations, station 6 recorded the highest copper values for all the fractions. Increased Cu 4 values at station 6 may be attributed to higher organic load which is the result of municipal waste dumping at station 6. Here the sediment is reducing with anoxic overlying waters. The presence of large amounts of H_2S at this station is evident from its intense smell.

Iron

Through out the study, the residual fraction was the major contributor to total iron. Most observed values were greater than 85 %. Exchangeable and moderately reducing fractions made only a little contribution to the iron content (less than 1 %)

Exchangeable iron concentrations (Fe_1) varied from 0.05 µg/g (station 4) to 34.34 µg/g (station 6). The station wise average concentrations ranged between 2.30µg/g (station 3) to 10.60µg/g (station 6). General seasonal trend was noticed at station 4. A reverse behavior was noticed for station 5.

Easily reducing fraction of iron concentrations (Fe2) showed values fluctuating from 2.08 µg/g (station 4) to 117.9 µg/g (station 5). The maximum (36.83 µg/g) and the minimum (4.84 µg/g) seasonal average values were noticed at stations 5 and 3 respectively. Reverse seasonal trend was observed at station 5.

The values of iron in the moderately reducing fraction (Fe3) varied between 16.51 µg/g (station 1) and 786.54 µg/g (station 6). The station wise mean values ranged between 208.33 µg/g (station 4) to 510.66µg/g (station 6). Fe3 values decreased from pre monsoon to post monsoon for stations 3 and 4. At station 6, a reverse trend was observed.

Table 4.1.2 Iron content in different fractions of sediments extracted using modified Tessier's Procedure (μg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
Fe_1	1	2.16	7.85	4.63	Fe_2	1	4.402	48.45	20.85
	2	1.741	15.02	8.34		2	2.548	39.69	19.96
	3	1.172	6.32	3.30		3	2.417	8.49	4.84
	4	0.048	4.33	2.30		4	2.078	12.35	5.93
	5	2.761	6.09	4.46		5	9.807	117.79	36.83
	6	2.038	34.34	10.60		6	5.034	58.83	26.75
Fe_3	1	16.514	696.58	306.57	Fe_4	1	123.9	568.67	427.44
	2	72.565	712.76	285.76		2	269.2	993.65	642.93
	3	226.51	551.04	401.84		3	153.8	1077.81	567.70
	4	88.199	368.17	208.93		4	146.6	1951.86	583.10
	5	211.52	596.67	399.82		5	85.32	674.78	242.91
	6	275.55	786.54	510.66		6	442.1	2274.90	1538.31
Fe_5	1	4092.7	37832.57	17141.92					
	2	5207.2	92789.40	49272.80					
	3	1.158	20922.36	11658.71					
	4	765.52	16825.98	11323.34					
	5	125.15	34319.66	9577.99					
	6	1870.3	38158.58	20126.88					

Iron concentration in the organic fraction (including sulphides)- Fe_4 ranged from 85.32 μg/g (station 5) to 2274.90 μg/g (station 6). The maximum and the minimum station wise average concentrations were 242.91 μg/g (station 5) and 1538.31 μg/g (station 6) respectively. For Fe_4 concentrations, the general seasonal pattern was noticed at stations 2 and 6.

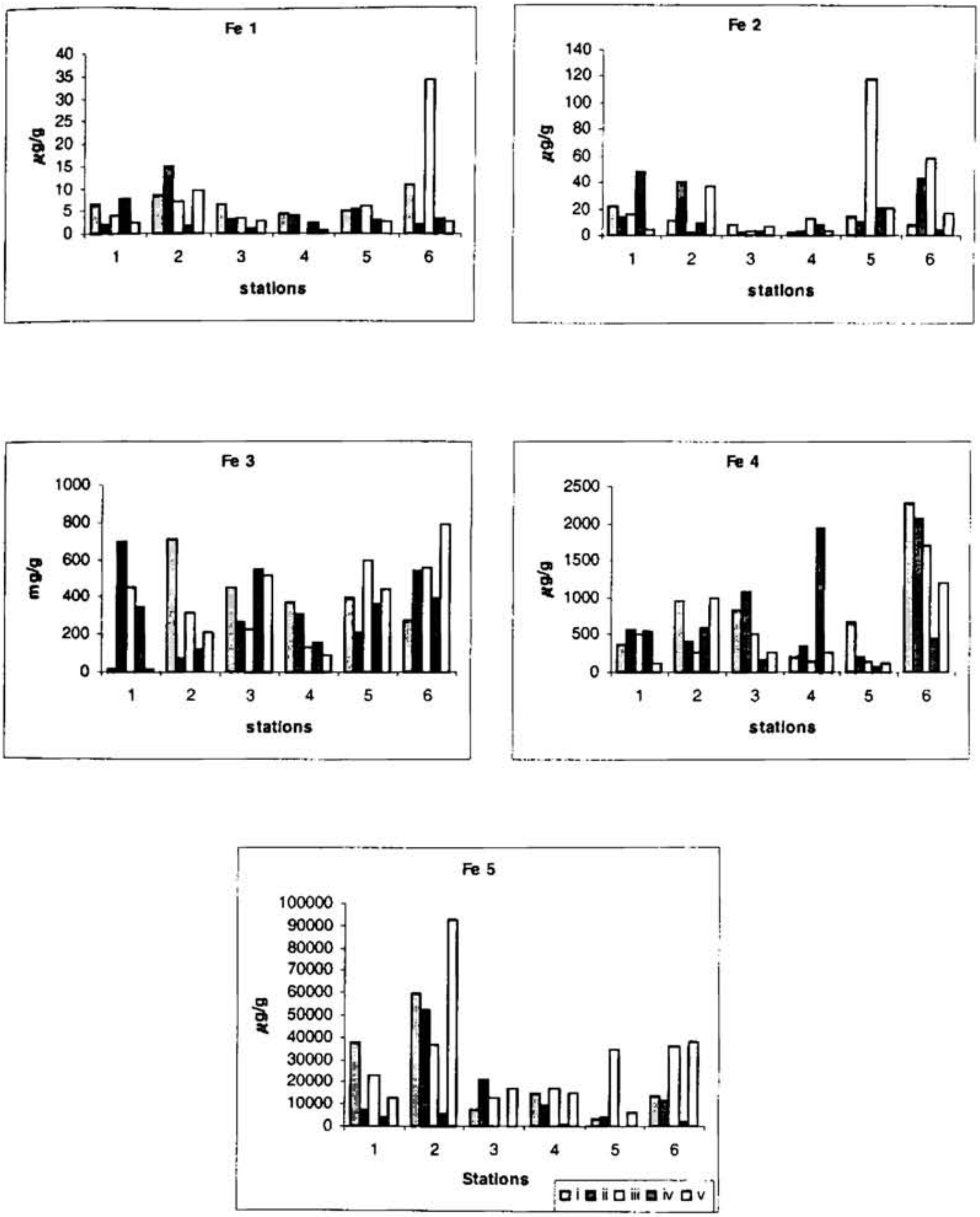

Fig 4.1.2 Distribution of iron in different fractions of the sediment

Residual Fe (Fe_5) concentrations fluctuated between 1.16 µg/g (station 3) to 97789.4 µg/g (station 2). Station wise mean concentrations varied from 9577.99 µg/g (station 5) to 49272.8 µg/g (station 2). General seasonal behavior was noticed at station 2.A reverse trend was observed at station 6.

The major contributing component in the speciation of iron was the residual fraction. Most previous researchers observed this trend. In sediments, iron present as iron oxides, are sparingly soluble under acidic conditions. Sulphide formation also occurs under anoxic conditions. In anoxic sediments, pyrite formation is important in fixing iron in sediments. Pyrites being insoluble in hot acids, iron bound to sulphides were estimated along with the residual component. This is one of the reasons for the observed higher values in the residual fraction

Lead

Concentrations of lead in different chemical fractions were higher at station 6.The easily reducing concentrations (Pb_2) were lower than exchangeable lead (Pb_1) values. Contribution of Pb_3 to the total lead concentration was negligible. The residual or organic fraction including sulphides forms the dominant phase in the speciation of lead. For most of the samples residual fraction made a larger contribution to total lead content.

Exchangeable Pb concentrations (Pb_1) varied between BDL (station 5) to 4.81 µg/g (station 6). The station wise average concentration was the highest at station station 6 (3.01 µg/g) and the lowest at station 3(1.10 µg/g). At station 6, Pb_1 concentrations showed the general seasonal trend.

The lead concentrations in the easily reducing fraction (Pb_2) were below the detectable limit at stations 1,2 and 5.Observed maximum concentration was 2.58 µg/g (station 6). Station wise mean concentrations varied from 0.60 µg/g to 1.38 µg/g. Station 6 recorded the maximum station wise average value.

Moderately reducing component showed lead concentrations (Pb_3) fluctuating from 0.05µg/g (station 5 – pre monsoon) to 16.64 µg/g (station 6 – post monsoon). The highest and the lowest station wise average concentrations were 7.85µg/g (station 6) and 0.79 µg/g (station 2) respectively.

Table 4.1.3 Concentrations of lead in different fractions of sediments extracted using modified Tessier's Procedure (μg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
Pb_1	1	0	11.62	4.14	Pb_2	1	0.581	22.78	6.52
	2	0.69	34.28	9.19		2	0.561	32.37	7.78
	3	0.592	7.36	2.83		3	0.86	20.91	5.70
	4	0.974	4.25	2.25		4	0	4.98	1.71
	5	0	6.43	2.08		5	1.291	5.23	2.74
	6	1.503	53.81	19.47		6	1.009	39.28	16.56
Pb_3	1	0.518	12.86	3.83	Pb_4	1	0.305	30.02	7.49
	2	0	34.46	7.68		2	0.606	34.29	8.51
	3	0.295	5.49	2.58		3	0.153	6.99	2.79
	4	0.245	23.74	5.87		4	0.196	10.67	3.64
	5	0.703	15.99	4.42		5	0.579	5.57	2.29
	6	1.016	40.25	13.27		6	1.518	89.03	22.27
Pb_5	1	0	42.25	12.46					
	2	0.908	21.70	5.76					
	3	0.551	7.11	2.30					
	4	0.33	1.90	1.01					
	5	0	15.11	3.85					
	6	0.788	27.68	9.36					

The observed values of lead in the organic fraction (Pb_4) varied between 1.21μg/g (station 4) and 53.81 μg/g (station 6). The station wise mean concentration was maximum at station 6 (30.42 μg/g) and the minimum at station 5 (3.45 μg/g). For stations 1,2 and 5 the values decreased from pre monsoon to post monsoon.

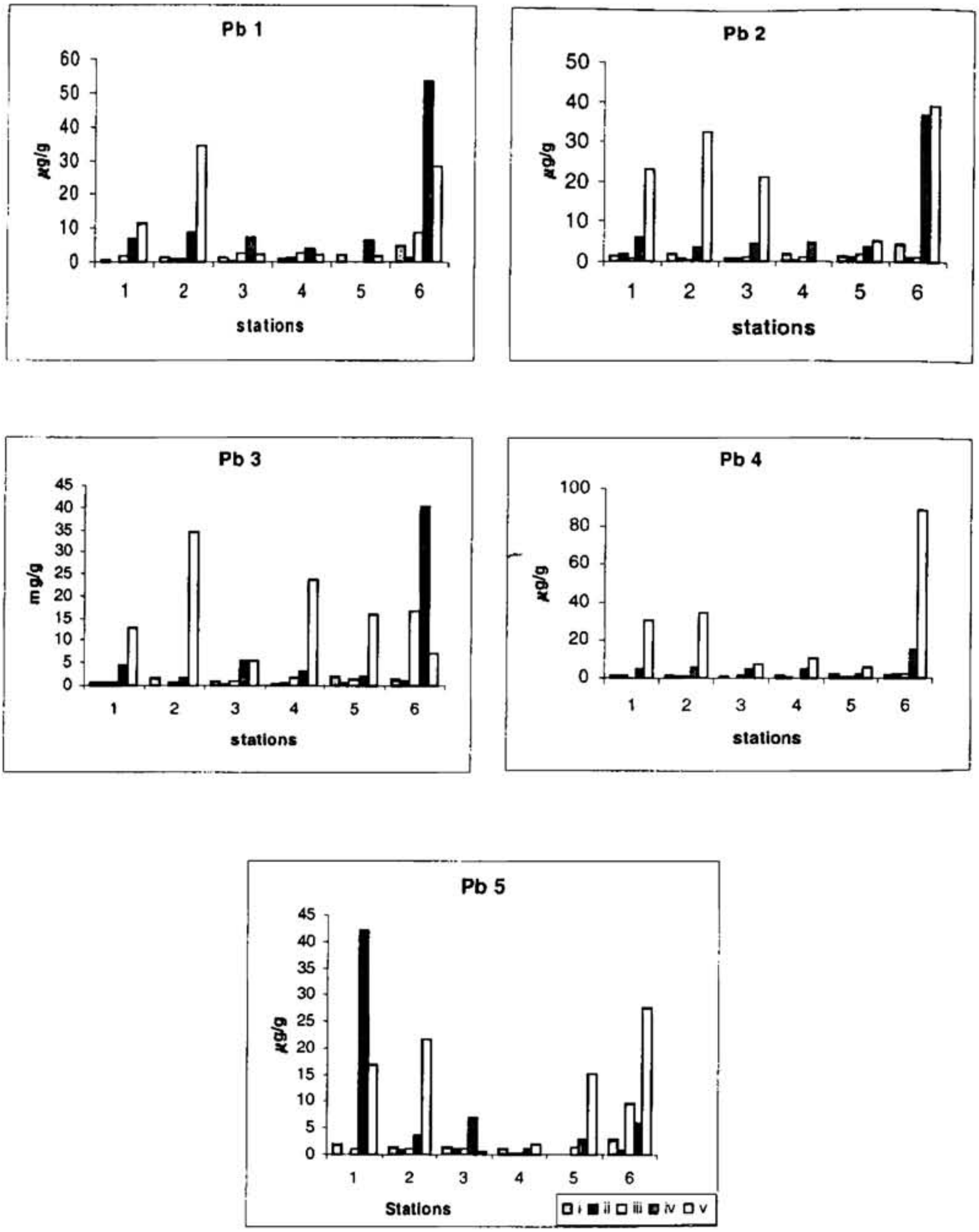

Fig. 4.1.3 Distribution of lead in different fractions of the sediment

Residual lead concentrations (Pb_5) varied from BDL (station 4) to 89.03 μg/g (station 6). Station wise mean values fluctuated between 7.23 μg/g (station 3) and 38.27 μg/g (station 6). Reverse seasonal trend was observed at station 5.

The speciation pattern of lead is similar to that of copper. The higher Pb_4 values might be attributed to the formation of stable organic compounds of lead. The organic/sulphide fraction exhibited higher values as in the case of copper. The use of HNO_3 as an extracting agent modifies the solubility character of lead, since lead nitrate being the most soluble form of inorganic lead.

Manganese

Residual fraction made greater contribution to the total manganese content. Most values of exchangeable Mn were less than 1μg/g. Similar to Pb, easily reducing component showed values lower than exchangeable component. Easily reducible phase and the moderately reducing phases made only a little contribution to the speciation of manganese. The first three phases made only a little role in manganese speciation.

Manganese concentrations in the exchangeable fraction (Mn_1) varied between 0.32μg/g (station 3) and 21.19 μg/g (station 2). The station wise mean concentration was the highest at station 2(12.70 μg/g) and the lowest at station 3(0.72 μg/g). At station 3, general seasonal behavior was noticed for Mn_1 concentrations. Station 6 showed an opposite trend in seasonal distribution.

Observed maximum concentration for the easily reducible fraction (Mn_2) was 18.96 μg/g (station1). Values were below the detectable limit at station 3. The staion wise average concentrations varied from 0.07 μg/g (station 3) to 9.84 μg/g (station 2).

Manganese concentration in the moderately reducing fraction (Mn_3) varied between BDL (station 2) to 16.90 μg/g (station 1). The maximum and the minimum station wise average concentrations were 8.42 μg/g (station 1) and 2.05 μg/g (station 3) respectively. General seasonal trend was noticed for stations 2,3 and 5.

The organic fraction including sulphides showed Mn values (Mn_4) ranging from 2.23 μg/g (station 5) to 55.67 μg/g (station 6). The highest and the lowest station wise mean concentrations were 44.68 μg/g (station 6) and 4.90μg/g (station 5) respectively. General seasonal trend was observed at station 1. A reverse seasonal behavior was noticed for stations 2 and 5.

Residual manganese concentrations (Mn_5) ranged from 6.91 μg/g (station 5) to 280.28 μg/g (station 1). Station wise average concentrations varied between 15.66 μg/g (station 5) and 32.18 μg/g (station 2). General seasonal behavior was noticed for stations 1, 2 and 6.

This being an essential plant nutrient, the export occurs through plant detritus. During diagenesis, the organically bound manganese is released as soluble Mn (II).

Table 4.1.4 Concentrations of manganese in different fractions of sediments using modified Tessier's Procedure (μg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
Mn_1	1	1.9	73.68	18.40	Mn_2	1	4.316	71.03	23.15
	2	3.462	235.55	55.74		2	2.817	115.67	35.82
	3	0.035	28.15	9.19		3	0	88.68	25.38
	4	1.054	23.61	6.50		4	1.433	12.81	5.44
	5	0.099	12.51	5.42		5	0.561	22.30	6.09
	6	1.914	103.09	35.51		6	5.194	99.17	35.83
Mn3	1	6.759	49.81	19.18	Mn_4	1	2.092	280.28	73.54
	2	0	56.93	18.05		2	0.28	177.00	42.33
	3	0	32.12	11.80		3	0.148	40.39	11.35
	4	0.936	14.66	4.85		4	0.519	51.29	12.39
	5	1.054	14.10	4.85		5	0.37	17.57	4.43
	6	5.109	63.32	27.40		6	1.003	92.07	26.39
Mn_5	1	0.253	34.45	14.26					
	2	0.976	75.73	24.60					
	3	0.044	41.94	11.61					
	4	0.283	11.05	4.26					
	5	0.305	17.42	4.61					
	6	5.663	45.70	21.16					

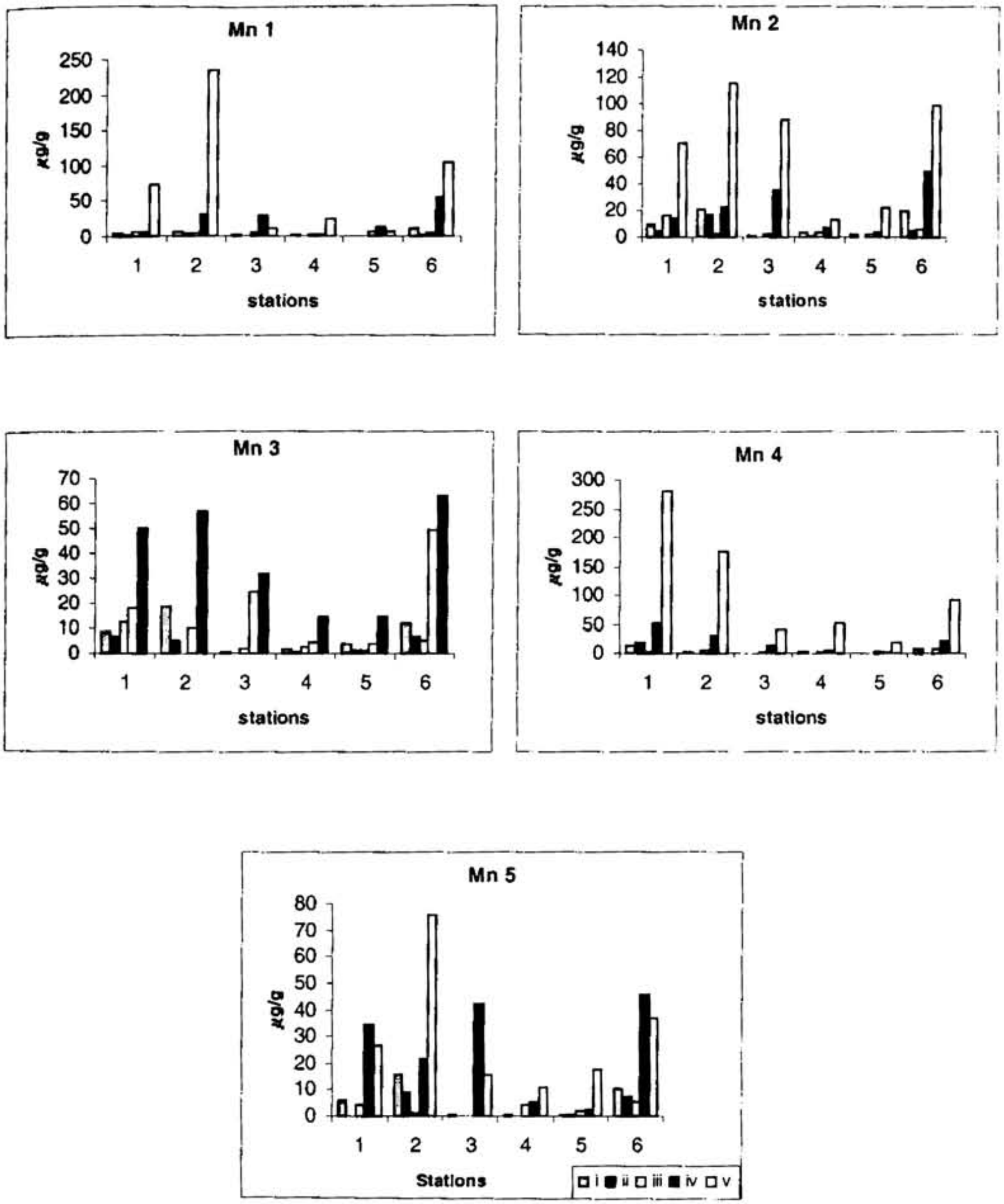

Fig. 4.1.4 Distributions of manganese in different fractions of the sediment

Nickel

The first three fractions made almost equal contribution to the speciation; the average value for each fraction was less than 10 % of the total. Residual phase forms the major contributing component followed by the organic fraction including sulphides. For all the different fractions, the highest average concentration was observed at station 6. For Residual component, the highest average concentration was observed at station 2.

Table 4.1.5 Nickel concentrations in different fractions of sediments extracted using modified Tessier's Procedure (μg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
Ni_1	1	0.367	12.86	4.65	Ni_2	1	1.098	8.26	3.16
	2	0	54.21	14.76		2	0.604	62.04	15.01
	3	0.528	12.17	5.85		3	1.819	3.97	2.82
	4	0.478	4.16	2.02		4	1.23	2.85	1.88
	5	0.947	9.41	4.34		5	0.276	31.67	7.93
	6	2.76	13.21	5.87		6	2.09	11.47	6.36
Ni_3	1	0.549	31.32	8.94	Ni_4	1	0	51.69	12.58
	2	0	65.47	15.38		2	1.814	50.02	12.91
	3	1.418	8.19	3.50		3	0.883	3.22	2.04
	4	0.789	4.10	2.21		4	1.018	15.36	5.44
	5	0.065	9.21	2.80		5	0.606	2.51	1.55
	6	0.648	15.47	6.41		6	2.042	11.97	6.41
Ni_5	1	1.224	14.83	6.88					
	2	0.79	80.74	19.62					
	3	0.262	10.55	4.80					
	4	1.571	5.11	3.47					
	5	0.025	4.94	2.35					
	6	2.674	43.25	11.51					

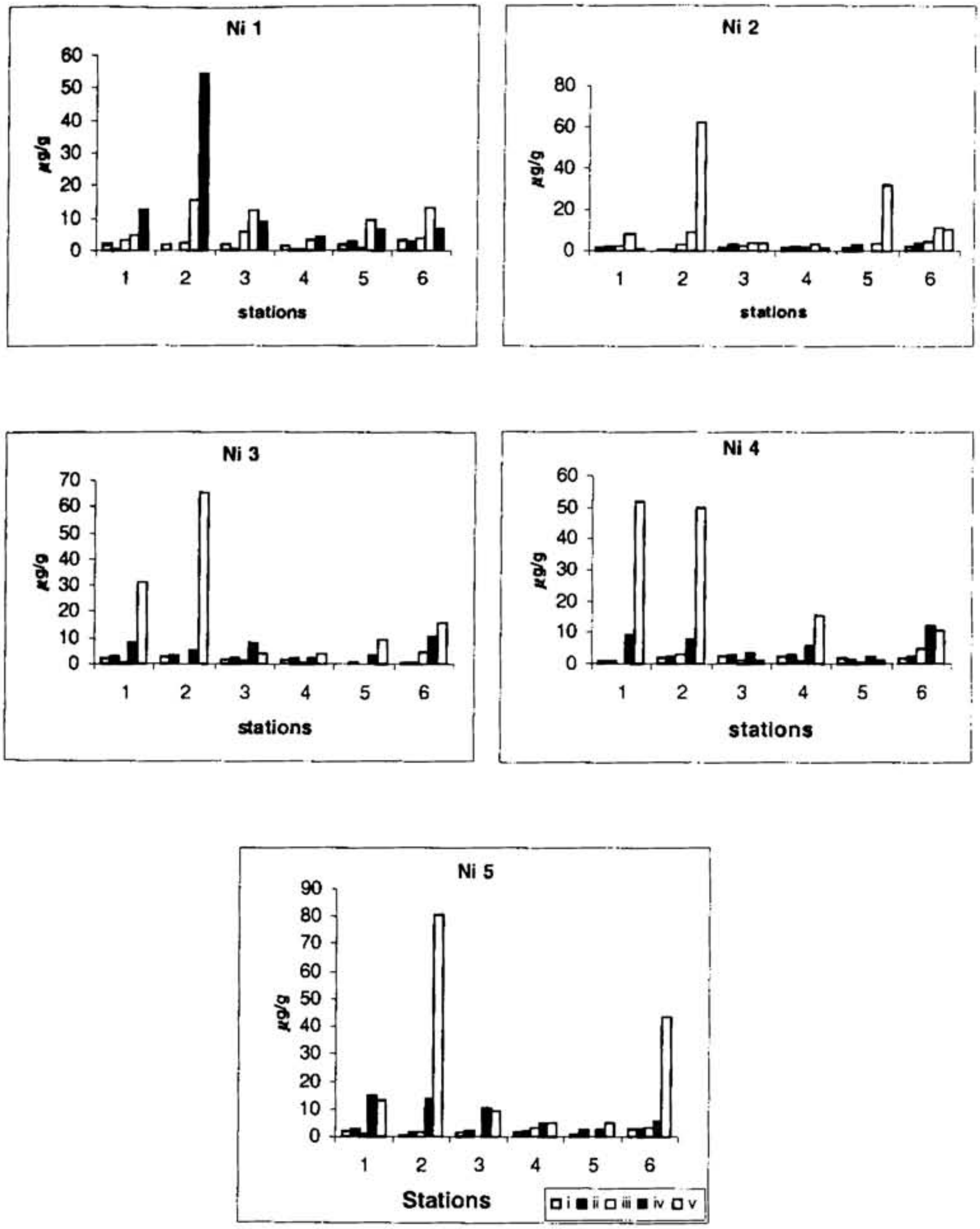

Fig 4.1.5 Distributions of nickel in different fractions of the sediment

For easily reducing fraction nickel content (Ni_2) varied from BDL (station 2) to 3.59 μg/g (station 6). General seasonal trend was noticed for stations 1,2 and 3.

Nickel concentrations in the moderately reducing component (Ni_3) were below the detectable limit at stations 1and 2. The observed maximum concentration was 5.60 μg/g (station 3). Stations 1, 3 and 5 showed general seasonal pattern.

Organic fraction of nickel (Ni_4) exhibited values between 2.29 µg/g (station 4) and 15.27 µg/g (station 2). The residual nickel content (Ni_5) was between 0.88µg/g(station 3) and 80.74 µg/g (station 2). General seasonal distribution pattern was noticed for stations 2 and 6.

Higher nickel concentrations were noticed in the residual fraction.

Zinc:

For most samples, major contributing component was the residual fraction. Exchangeable zinc concentrations were significant only at station 6. Moderately and easily reducible components made only a little contribution to total zinc.

The maximum value of zinc in the exchangeable fraction (Zn_1) was observed at station 6 (144.39 µg/g). Values were below the detectable limit at stations 4 and 5. Station wise mean concentrations varied from 0.06 μg/g (station 5) to 79.54 μg/g (station 6). General seasonal trend was noticed for stations 3, 4, 5 and 6.

Zinc content in the easily reducing component (Zn_2) was below the detectable limit for stations 3 and 5.The highest Zn_2 concentration was noticed at station 6 (19.86 µg/g - post monsoon). The highest and the lowest station wise average values were noticed at station 6 (11.83 μg/g) and station 3 (0.09 μg/g) respectively. The general seasonal pattern was observed at stations 1, 3 and 4.

The concentrations of zinc in the moderately reducing fraction (Zn3) ranged from 0.02 µg/g (station 2) to 83.96 µg/g (station 6). The highest and the lowest station wise average concentrations were 36.30μg/g (station 6) and 2.06 μg/g (station 1) respectively. Stations 1, 2, 3, 4 and 6 exhibited a reverse seasonal trend for Zn_3.

Table 4.1.6 Concentrations of zinc in different fractions of sediments extracted using modified Tessier's Procedure (µg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
Zn_1	1	0	0.10	0.02	Zn_2	1	0.01	0.14	0.09
	2	0.168	1.92	0.62		2	0.005	3.55	1.13
	3	0.289	2.21	0.83		3	0	0.21	0.09
	4	0	1.15	0.30		4	0.16	6.31	1.61
	5	0	0.13	0.06		5	0	2.31	0.62
	6	37.394	144.39	79.54		6	0.883	19.86	11.83
Zn_3	1	0.132	5.23	2.06	Zn_4	1	0.516	14.30	6.05
	2	0.015	5.29	2.89		2	0	25.50	14.98
	3	0.955	39.29	18.53		3	7.232	97.43	52.09
	4	3.773	7.15	5.41		4	2.24	8.46	4.42
	5	2.291	4.19	2.95		5	1.254	10.02	3.31
	6	2.763	83.96	36.30		6	22.69	63.38	40.93
Zn_5	1	14.35	57.34	32.28					
	2	47.734	112.95	88.46					
	3	13.349	115.65	65.46					
	4	0.147	54.65	21.14					
	5	2.905	7.64	5.13					
	6	3.163	99.60	31.17					

For Organic fraction including sulphides zinc content (Zn_4) fluctuated from BDL (station 2) to 97.43 µg/g (station 3). The station wise average concentrations varied from 3.31 µg/g (station 5) to 52.09 µg/g (station 3). For stations 2, 5 and 6, Zn_4 values showed the general seasonal behavior.

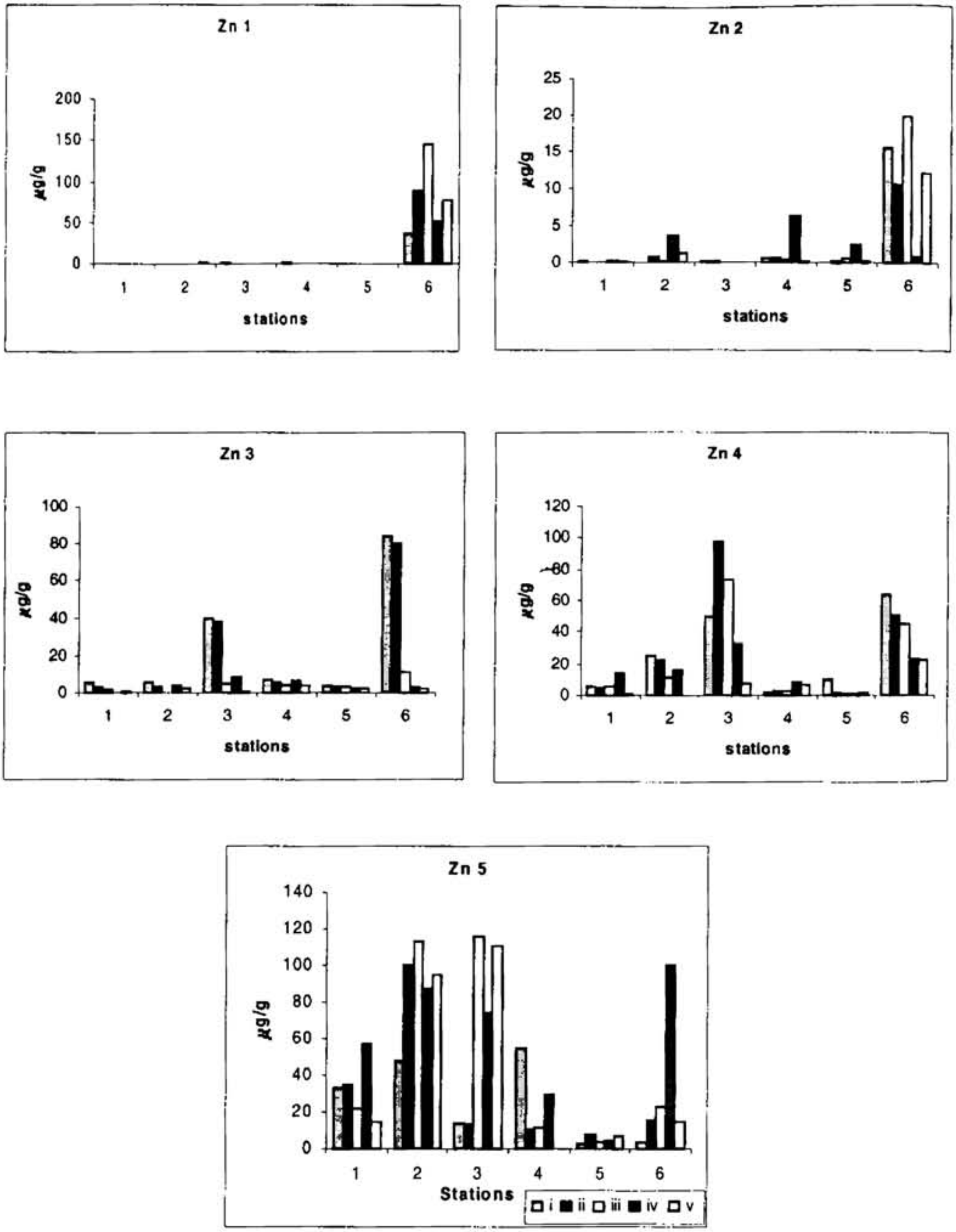

Fig 4.1.6 Distributions of zinc in different fractions of the sediment

Residual Zn concentrations (Zn_5) varied between 0.15µg/g (station 5) and 115.65 µg/g (station 3). The station wise average concentration was highest at station 2 (88.46 µg/g) and the lowest at station 5 (5.13 µg/g). A reverse seasonal trend was noticed for stations 2 and 6.

At station 6, higher concentrations were noticed in the exchangeable fraction. The speciation pattern of zinc was found to be similar to that of iron and manganese.

Discussion:

The metal concentrations in non – lithogenous fractions follows the order Cu > Ni > Pb > Zn > Mn > Fe. Exchangeable fraction indicates the form of the metals that are most available for plant uptake (Li *et al.,*, 1995). The sequence of leaching metals in the exchangeable fraction follows the order Ni > Pb > Zn > Mn > Cu > Fe.

Considering the mean concentration of heavy metals, the metals were found to concentrate in operationally defined fractions in the following order:

Copper	$Cu_4 > Cu_5 > Cu_3 > Cu_1 > Cu_2$.
Manganese	$Mn_5 > Mn_4 > Mn_3 > Mn_1 > Mn_2$.
Nickel	$Ni_5 > Ni_4 > Ni_2 > Ni_1 > Ni_2$.
Iron	$Fe_5 > Fe_4 > Fe_2 > Fe_1 > Fe_2$
Lead	$Pb_5 > Pb_4 > Pb_1 >$ Pb 3 $> Pb_2$
Zinc	$Zn_5 > Zn_4 > Zn_3 > Zn_1 > Zn_2$.

Higher values of Mn, Fe, Ni, Pb and Zn in the residual fraction indicate the locked nature of these elements. For all the six metals studied, the moderately reducing fraction made the lowest contribution to the total metal content. The contributions of exchangeable cations and easily reducing fractions (individually) to the total metal content were always less than 10 %. Copper behaves in a different manner in sediments. For copper, the organic fraction including sulphides made the largest contribution. This fraction is an effective scavenger for copper (Zhou *et al.*, 1998; Li *et al.*, 2000; Kotoky *et al.,*, 2003).

Many researchers reported distributions of metals in different fractions. Residual fraction is the major host for nickel (Tessier *et al.*, 1979; Adamo *et al.*, 1996; Zhou *et al.*, 1998) lead (Zhou *et al.*, 1998) and zinc (Gupta and Chen, 1975; Ma and Rao, 1997;Li *et al.*, 2000). Copper was mainly associated with organic matter for which it has a high affinity (Alloway, 1990). Majority of nickel was detrital in nature (Tessier *et al.*, 1979). Copper is an important trace element for nutrition to the plants and animals including human beings (Dash and Sahu, 1999). Copper can easily form complexes with organic compounds, which makes it rather stable in the environment (Stumm and Morgan, 1996). In aqueous systems natural organic matter markedly affects the distribution of copper as humic materials and amino acids. Predominance of copper in the organic phase has also been observed in fresh water and marine sediments (Baruh *et al.*, 1996; Chen *et al.*, 1996,Wong, 1996; Zhou *et al.*, 1998).

Speciation of trace metals is condition specific. It varies with the anoxic condition of the sediment, the character of the metal and the redoxtion of the overlying water column. Compiling the observations with these considerations, the six metals studied has been grouped into three.

Group A: Cu and Pb

Group B: Fe

Group C: Mn, Ni and Zn.

In sediments, storage of metals occur in the form of organic complexes and as stable mineral forms. Sulphide foration is predominant in anoxic sediments, rich in sulphides. In mangrove sediments the retention of copper and lead in sediments is in form sulphides. The contribution of copper to the organic/ sulphide fraction is greater than that of lead. Organic fraction was the major contributof for Copper. This might be due to the solubility differences of the compounds of lead and copper. Stumm and Morgan (1996) also reported that Cu(II) is more sensitive to complex formation than other metals. Inorganic and biomethylated compounds of lead are highly stable and therefore remains associated with the residual fraction. Oxidation of organic matter releases the metals bound to the organic complexes into the overlying water column. Easily oxidizable complexes are rare for lead. For copper, a slight contribution from easily oxidizable components also adds to higher

Cu_4 values. For iron, higher values were found in the residual fraction; this forms a separate class.The sulphidic sediments the storage of iron is through mineralization as pyrite. Pyrite is the most thermodynamically stable form of iron. Amorphous iron sulphides and gregite are meta stable with respect to pyrite (Berner, 1967; Rosily, 2002). The retention and distribution pattern of Group C metals are similar. Mn, Ni and Zn are found to be essential to plants. These metals may be reaching the sediments, through plant detritus. The slight variations observed in the distribution pattern of these metals might be due to the solubility differences of the metal complexes.

Correlations:

Significant correlations were obtained between different fractions of the same metal. (Table 4.2)

Table 4.2 Correlation coefficients between the metal concentrations in different fractions of the sediment

Correlations - Copper

		F1	F2	F3	F4	F5	T
Pearson Correlation	F1	1.000	.847**	.055	.279	.610**	.627**
	F2	.847**	1.000	.049	.157	.539**	.532**
	F3	.055	.049	1.000	.779**	.036	.485**
	F4	.279	.157	.779**	1.000	.352*	.750**
	F5	.610**	.539**	.036	.352*	1.000	.868**
	T	.627**	.532**	.485**	.750**	.868**	1.000

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

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

Correlations - Iron

		F1	F2	F3	F4	F5	T
Pearson Correlation	F1	1.000	.419*	.093	.359	.389*	.399*
	F2	.419*	1.000	.255	.088	.329	.335
	F3	.093	.255	1.000	.177	.043	.058
	F4	.359	.088	.177	1.000	.054	.085
	F5	.389*	.329	.043	.054	1.000	.999**
	T	.399*	.335	.058	.085	.999**	1.000

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

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

Table 4.2 Contd...

Correlations - Manganese

		F1	F2	F3	F4	F5	T
Pearson Correlation	F1	1.000	.772**	.149	.450*	.429*	.564**
	F2	.772**	1.000	.068	.398*	.585**	.669**
	F3	.149	.068	1.000	.072	.051	.114
	F4	.450*	.398*	.072	1.000	.502**	.669**
	F5	.429*	.585**	.051	.502**	1.000	.971**
	T	.564**	.669**	.114	.669**	.971**	1.000

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

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

Correlations - Nickel

		F1	F2	F3	F4	F5	T
Pearson Correlation	F1	1.000	.746**	.302*	.524**	.506**	.638**
	F2	.746**	1.000	.174	.172	.354*	.430**
	F3	.302*	.174	1.000	.325*	.233	.337*
	F4	.524**	.172	.325*	1.000	.605**	.746**
	F5	.506**	.354*	.233	.605**	1.000	.972**
	T	.638**	.430**	.337*	.746**	.972**	1.000

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

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

Correlations - Lead

		F1	F2	F3	F4	F5	T
Pearson Correlation	F1	1.000	.820**	.250	.431**	.548**	.665**
	F2	.820**	1.000	.244	.217	.520**	.579**
	F3	.250	.244	1.000	.417**	.197	.360*
	F4	.431**	.217	.417**	1.000	.459**	.684**
	F5	.548**	.520**	.197	.459**	1.000	.952**
	T	.665**	.579**	.360*	.684**	.952**	1.000

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

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

Table 4.2 Contd...

Correlations - Zinc

		F1	F2	F3	F4	F5	T
Pearson Correlation	F1	1.000	.860**	.371*	.339	-.129	.682**
	F2	.860**	1.000	.518**	.359	-.238	.618**
	F3	.371*	.518**	1.000	.648**	-.295	.566**
	F4	.339	.359	.648**	1.000	.052	.745**
	F5	-.129	-.238	-.295	.052	1.000	.398*
	T	.682**	.618**	.566**	.745**	.398*	1.000

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

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

4.2 Speciation based on pH

The results (mean and range) of the metal concentrations in the fractions extracted at pH values varying from 8 to 2 are presented in Table **4.3(Figures 4.3.1** to **4.3.6**)

In the speciation of trace metals in sediments, the values showed a tendency to decrease from pre monsoon to post monsoon through monsoon season.

Copper

Copper content in the fraction extracted at pH 8, varied between BDL to 2.07 µg/g. The maximum and the minimum concentrations at station 1 were 0.01 µg/g (monsoon) and 0.32 µg/g (pre monsoon) respectively. Pre monsoon and monsoon values of station 2 and monsoon and post monsoon values of station 3 were below detectable limit. Station 2 recorded a value of 0.40 µg/g in post monsoon season. Pre monsoon value at station 3 was 0.45 µg/g. At station 4, copper concentration decreased from pre monsoon to post monsoon. A reverse behavior was noticed at station 6. The values varied from 0.09 µg/g (monsoon) to 0.24 µg/g (post monsoon) at station 5.

At pH 7, copper concentrations ranged from 0.09 µg/g (station 5 - pre monsoon) to 5.19 µg/g (station 6 – post monsoon). The values increased from pre monsoon to post monsoon for stations 1,2,4,5 and 6. The observed maximum and minimum concentrations for station 3 were 1.01 µg/g (pre monsoon) to 0.30µg/g (monsoon).

Table 4.3.1 Concentrations of copper in different fractions of sediment extracted using a pH based speciation scheme (μg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
f 2	1	0.14	0.79	0.39	f 3	1	0.00	0.61	0.30
	2	0.14	0.63	0.36		2	0.30	0.56	0.42
	3	0.26	0.75	0.42		3	0.35	0.65	0.52
	4	0.10	1.83	0.71		4	0.31	2.15	0.99
	5	0.05	0.85	0.41		5	0.09	0.74	0.42
	6	0.12	6.58	1.79		6	0.08	3.36	1.08
f 4	1	0.15	1.11	0.52	f 5	1	0.07	1.73	0.91
	2	0.00	1.71	0.39		2	0.00	1.13	0.28
	3	0.00	1.11	0.24		3	0.00	5.01	1.39
	4	0.45	2.48	1.27		4	0.15	4.01	1.27
	5	0.02	0.51	0.26		5	0.16	1.21	0.44
	6	0.42	10.57	3.37		6	0.45	16.37	9.15
f 6	1	0.22	0.99	0.49	f 7	1	0.12	0.72	0.30
	2	0.00	1.06	0.27		2	0.17	0.33	0.26
	3	0.13	1.55	0.76		3	0.13	1.01	0.44
	4	0.18	1.79	0.85		4	0.10	0.92	0.31
	5	0.11	1.03	0.43		5	0.09	0.40	0.23
	6	0.31	64.29	23.72		6	0.19	5.19	1.76
f 8	1	0.01	0.37	0.25	R	1	8.26	21.65	12.84
	2	0.00	0.40	0.19		2	25.33	33.27	28.58
	3	0.00	0.45	0.22		3	0.26	18.87	10.67
	4	0.15	1.69	0.49		4	0.55	4.92	2.09
	5	0.09	0.67	0.27		5	0.10	2.31	0.98
	6	0.23	3.73	1.34		6	62.00	146.69	106.61

The fraction at pH 6, recorded values between BDL (station 2 – monsoon) to 64.29 μg/g (station6 – monsoon). The highest and the lowest values were noticed in pre monsoon and monsoon seasons for stations 1, 2 and 3. Cu concentrations varied from 0.18 μg/g (monsoon) to 1.06 μg/g (post monsoon) for station 4. For station 5, values decreased from pre monsoon to post monsoon season. At station 6, the maximum (64.29 µg/g) and the minimum (0.91 µg/g) values were observed in monsoon and pre monsoon seasons respectively.

At p H 5, the values of copper ranged from 0.04 µg/g (station 2 – monsoon) to 16.37 (station 6 – post monsoon). Cu concentrations decreased from pre monsoon to post monsoon at stations 1 and 3. A reverse behavior was noticed at station 6. The highest and the lowest values were noticed in pre monsoon and in monsoon seasons for stations 2 and 4. The values of copper at station 5 were between 0.16 µg/g (monsoon) and 0.35 µg/g (post monsoon).

The observed maximum copper content in the fraction extracted at pH 4 was 3.02 µg/g (station 6 – monsoon). Monsoon values at stations 2 and 3 were not detectable using AAS. The values decreased from pre monsoon to post monsoon at station 1. The maximum and the minimum copper content at stations 2, 3 and 4 were observed in pre monsoon and monsoon seasons respectively. The lowest value at station 4-was 0.45 µg/g (monsoon). For station 5, pre monsoon concentration (0.24µg/g) was the highest and post monsoon concentration (0.02 µg/g) the lowest.

For the fraction extracted at pH 3, the copper concentrations varied from BDL (station 1 – pre monsoon) to 1.41µg/g (station 4 – pre monsoon). The values increased from pre monsoon to post monsoon at station 1. The values at station 2 were between 0.332µg/g and 0.46 µg/g. The maximum and the minimum concentrations at stations 3 and 4 were notied in pre monsoon and monsoon seasons. For stations 5 and 6, monsoon concentrations were the highest The lowest values for these stations were respectively 0.19 1µg/g (pre monsoon) and 0.39 µg/g (post monsoon).

At pH 2, copper concentrations were observed to be between 0.05 µg/g (station 5 – pre monsoon) and 1.22 µg/g (station 5 – monsoon). The values varied from 0.33 µg/g (monsoon) to 0.79 µg/g (post monsoon for station 1. Copper content increased from pre monsoon to post monsoon at station 2. The lowest and the highest values were noticed in pre monsoon and monsoon seasons for stations 3, 4, 5 and 6.Residual copper values varied from 0.26 µg/g (station 3 – pre monsoon) to 101.88 µg/g (station 6 – monsoon). For all the six stations the highest seasonal values were noticed in monsoon. For stations 3,4 and 5 pre monsoon concentrations were the lowest. The minimum values for stations 1, 2 and 6 were observed in post monsoon season.

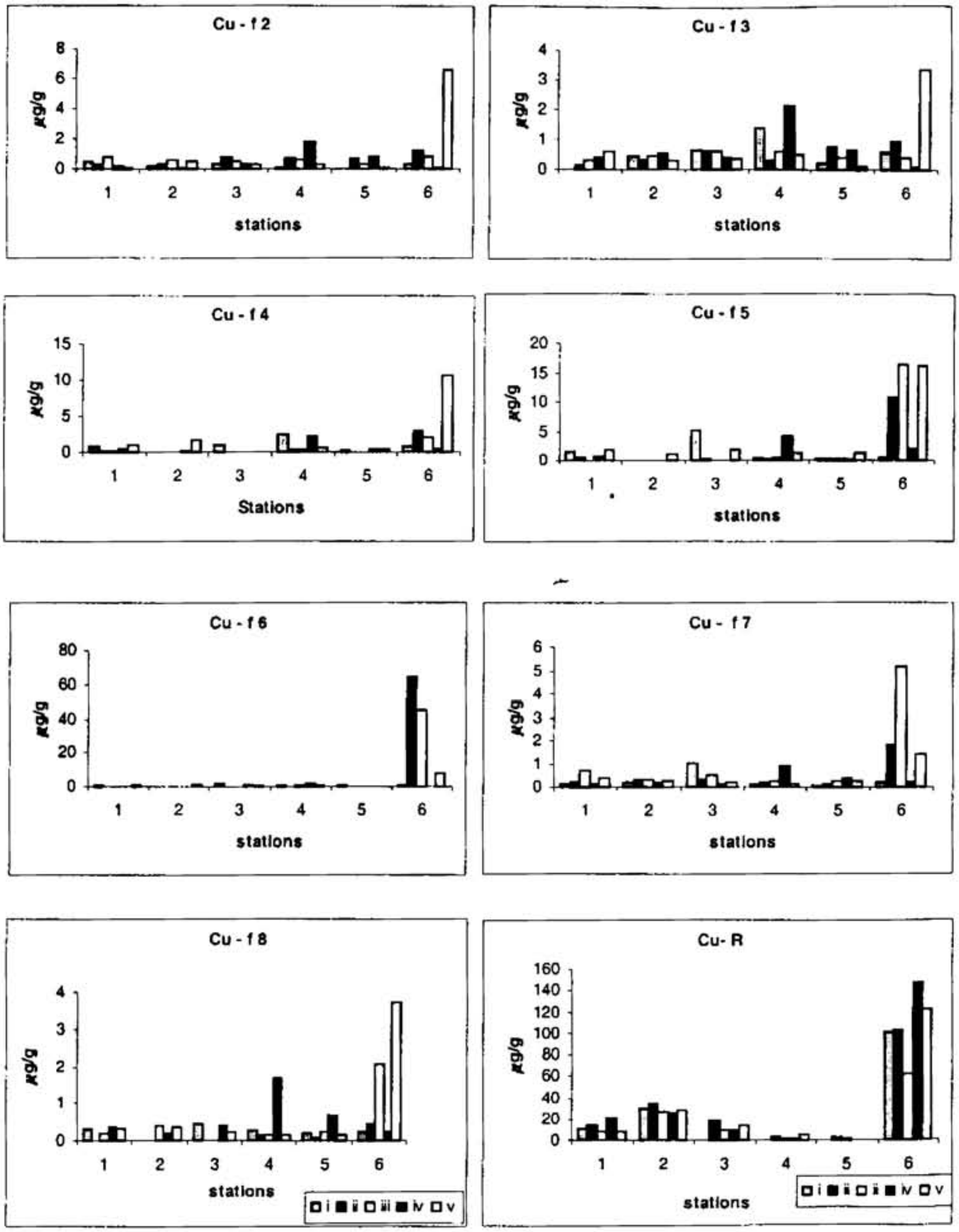

Fig 4.3.1 Distribution of copper in different fractions of the sediment

Bioaccumulation of copper in biota is dependent on the chemical forms in which it occurs (Crecelius *et al.*, 1982; Sanders *et al.*, 1984; Wright and Samuda, 1987). Uptake of copper by marine organisms depends mainly on the availability of Cu 2+. Redox conditions, organic complexing capacity of water, amount of suspended particulates, salinity and alkalinity are important abiotic factors that can influence copper accumulation by biota. Organic ligand and pH are the most important factors in deciding the bioavailabilty of copper. Copper forms complexes with carbonates and chlorides in seawater. Cupric ion is the most biotoxic form of copper followed by Cu-OH complexes. Complexation with sulphides is also important in anoxic conditions. Copper forms relatively insoluble complexes with sulphides. In anoxic waters, the possible forms are chlorides and sulphides. The adsorption and precipitation of copper on oxides and hydroxides are also important in understanding copper speciation (Sadiq, 1992)

In aquatic systems, the dominant copper species are $CuCO_3$, $CuOH^+$, and Cu^{2+}. Copper concentrations in the fractions leached at pH 6, 7 and 8 were comparatively low. Effective retention of copper occurs in sediments at pH 8.This might be due to the formation of carbonates (94%), which becomes soluble at pH values less than 5. For natural waters at pH 8, the main species was copper carbonate; the percentage of Cu^{2+} is s very small at this pH. In fresh waters at pH 8, 1.6 % of copper exists as $Cu (CO3)_2{}^{2-}$(Chester, 2000). Copper shows a very high tendency to form inorganic and organic complexes. All these factors lead to decrease in bioavailable concentrations. Almost all inorganic salts of copper will be leached at pH 2.For copper; the exchangeable copper values were lower than the labile copper concentrations.

Iron:

The fraction extracted at pH 8, showed values between BDL to 37.56 µg/g. At stations 2, 4, 5 and 6 iron concentrations increased from pre monsoon to post monsoon. The highest values at station 1 (5.14 µg/g) and station 3 (3.03 µg/g) were noticed in monsoon season. Pre monsoon values at stations 1, 2 and 5 were the highest. The monsoon value at station 2 and pre monsoon value at station 3 were observed to be below the detectable limit of AAS. Most observed values were in the range of BDL to 5.14 µg/g.

Table 4.3.2 Concentrations of iron in different fractions of sediment extracted using a pH based speciation scheme (μg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
f2	1	159.16	3005.85	1015.90	f3	1	11.70	1321.14	557.12
	2	88.08	2216.13	939.20		2	696.25	3500.07	1374.44
	3	290.40	1273.26	515.81		3	6.56	759.28	406.91
	4	208.35	755.37	430.99		4	40.28	1041.90	506.45
	5	52.49	167.09	94.58		5	78.62	2005.05	741.01
	6	85.63	635.82	274.05		6	179.84	964.37	644.92
f4	1	80.57	1854.07	756.47	f5	1	0.06	1.03	0.39
	2	35.94	955.24	419.83		2	0.03	1.09	0.38
	3	32.96	1136.38	271.77		3	0.01	1.92	0.40
	4	93.24	1164.39	613.11		4	0.04	3.99	1.48
	5	53.23	550.88	353.00		5	0.24	1.60	0.68
	6	218.35	1449.41	579.70		6	0.17	1.89	1.04
f6	1	117.08	3075.46	1326.11	f7	1	0.00	9.54	2.28
	2	11.16	2573.70	539.48		2	0.00	2.36	0.47
	3	13.79	826.70	245.82		3	0.00	3.52	0.81
	4	93.03	661.62	380.59		4	0.00	0.30	0.06
	5	41.13	589.17	311.30		5	0.00	48.04	12.23
	6	20.43	3222.07	1424.72		6	0.00	10.48	4.83
f8	1	0.00	5.14	1.40	R	1	1252.92	31854.96	14241.74
	2	0.00	7.12	2.83		2	1945.99	89748.42	46953.16
	3	0.00	8.41	2.96		3	11.35	21027.88	11191.93
	4	1.13	37.56	16.17		4	1130.24	15314.21	10174.75
	5	0.00	33.00	7.87		5	354.05	34449.18	8741.33
	6	1.45	7.51	3.61		6	2001.83	38064.88	19280.35

At pH 7, iron concentrations were below the detectable limit for most of the samples. The Observed maximum values for this fraction were 10.48 go/g (station 6 – monsoon). Post monsoon values of station 1 to 4, monsoon values of stations 2 to 5 and the pre monsoon values of stations 4 and 5 were below the detectable limit. The maximum values at station 1 (9.54 µg/g), station 2 (2.36 µg/g) and station 6 (10.48 µg/g) were noticed in pre monsoon.

The fraction leached at p H 6 showed values between 11.16 µg/g (station 2) and 3222.07 µg/g (station 6). Both the lowest and the highest values were noticed in monsoon season. For stations 3 and 4, iron content decreased from pre monsoon to post monsoon. The lowest values for stations 1 (117.08 µg/g) and station 2 (11.16 µg/g) were observed in monsoon. The maximum Fe concentrations for these stations were 3075.46 µg/g (pre monsoon) and 27.05 µg/g (post monsoon).

At pH 5, the iron concentrations varied from 0.01 µg/g (station 3) to 1.92 µg/g (station 3). The values increased from pre monsoon to post monsoon for stations 1 and 4. A reverse behavior was noticed for stations 3 and 5. At station 2,observed values ranged from 0.03 µg/g (monsoon) to 0.66 µg/g (pre monsoon). At station 6, the maximum iron concentration was 1.89 µg/g (monsoon). The lowest value for this station was 0.43 µg/g (post monsoon).

For the component extracted at pH 4, iron concentrations varied from 35.94 µg/g (station 2) to 1164.39 µg/g (station 4), both the lowest and the highest concentrations were noticed in monsoon. At station 1, the highest and the lowest observed values were 80.57 µg/g (pre monsoon) and 557.17 µg/g (monsoon). At stations 2,3,4 and 6 the lowest values were noticed in monsoon season. The maximum values for station 2 (475.22 µg/g) station 3 (1136.38 µg/g) were observed in pre monsoon. Maximum values observed for stations 4 and 6 were 350.90µg/g and 1449.41 µg/g, both in post monsoon.

At pH 3, iron concentrations varied from 161.01 µg/g (station 4) to 3500.07 µg/g (station 2). For stations 1 and 4 Fe concentrations increased from pre monsoon to post monsoon. An opposite behavior was noticed at station 5. The maximum Fe values for station 2 (3500.07 µg/g) station 3 (759.328 µg/g) and station 6 (964. 37 µg/g) were noticed in monsoon season. The lowest values for stations 3 (374.37 µg/g) and station 6 (179.84 µg/g) were noticed in pre monsoon season. The minimum value at station 2 was f 6, 96.25 µg/g (post monsoon).

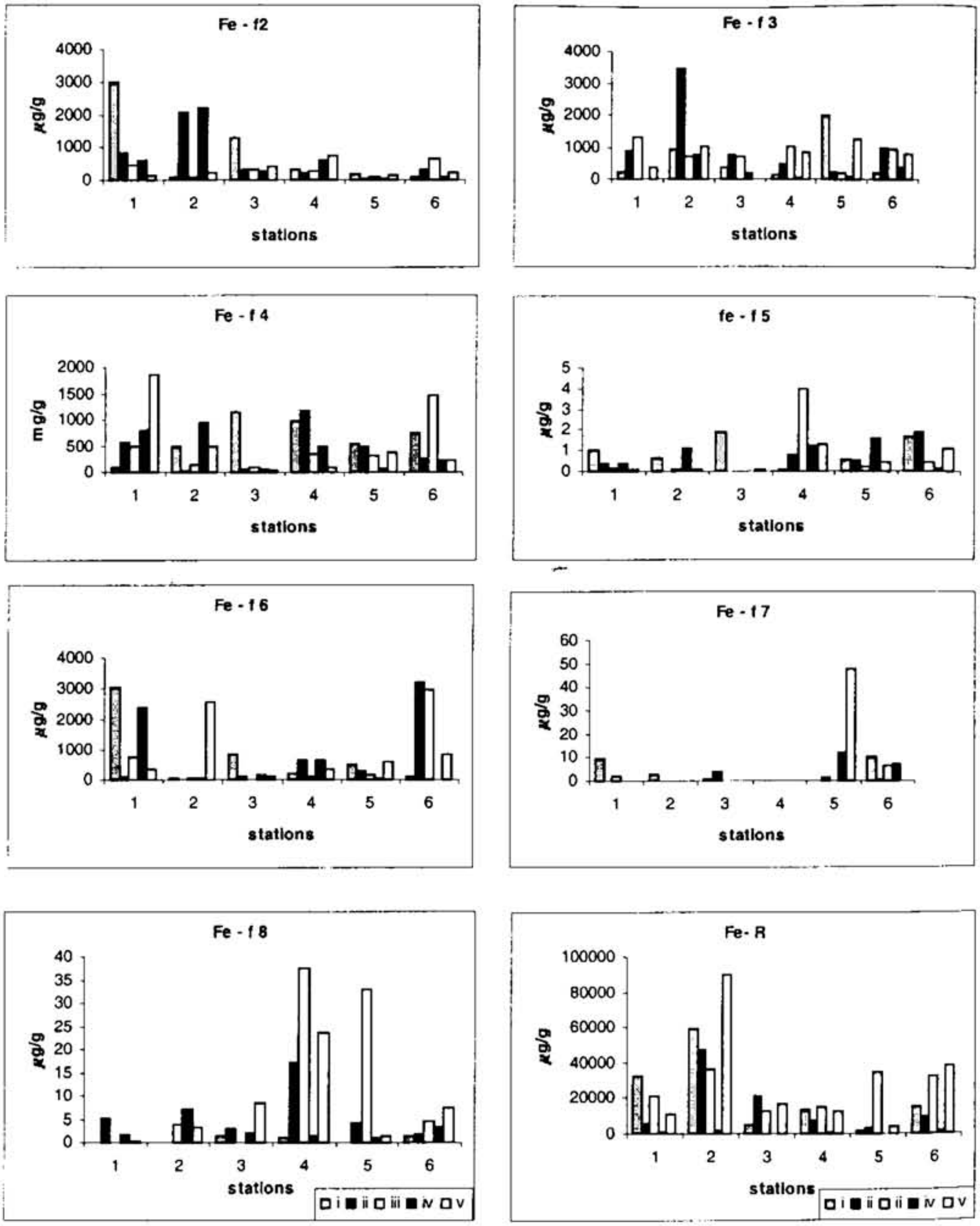

Fig 4.3.2 Distribution of iron in different fractions of the sediment

At pH 2, observed iron concentrations ranged between 63.98 µg/g (station 5) to 3005.8 µg/g (station 1). The values decreased from pre monsoon to monsoon for stations 1 and 3. A reverse trend was noticed at station 6. At station 2, the maximum and the minimum values were 2056.50µg/g (monsoon) and 88. 08 µg/g (post monsoon). For stations 4 and 5 the maximum and the minimum concentrations were noticed in monsoon and pre monsoon seasons. The values were in the range of (208.35 µg/g – 338.48 µg/g) and (63.98 µg/g – 167.09 µg/g).

Residual iron concentrations fluctuated from 1.368 µg/g (station 5) to 59.710 µg/g (station 2). Stations 1 and 2 showed a decrease in values from pre monsoon to post monsoon. Station 5 showed a reverse behavior. For stations 4 and 6 monsoon values were the lowest, the values were 7.395 µg/g and 9.330 µg/g. The observed maximum concentrations for these stations were 14.953 µg/g (pre monsoon) and 15.314 µg/g (post monsoon). At station 3, the values varied from 5.425 µg/g (pre monsoon) to 7.395 µg/g (monsoon).

Fe^{3+} is insoluble in anoxic waters. Soluble form of iron is Fe^{2+}. Fe is present largely as iron oxides and oxyhydroxides. Soluble Fe^{2+} is supplied by the reduction in sediments. Complexation of iron is important in controlling the toxicity. Complexation of iron with sulphides is important in controlling the toxicity. Digenetic sulphides are important sinks for trace metals in reduced sulphidic sediments, and during reduction oxyhydroxides of iron/ manganese favors the precipitation of arsenic, copper and zinc sulphides.

In the pH based speciation scheme, f6 showed higher iron values than f 5, f 7 and f 8. Dissolution of iron hydroxides starts at pH 5. $Fe(OH)_3$ is soluble at alkaline pH.

Lead

For the fraction extracted at pH 8, lead concentrations varied from 0.13 µg/g (station 1) to 1.80 µg/g (station 6), both in monsoon. At station 1, pre monsoon value (1.26 µg/g) was the highest and the monsoon value (0.13 µg/g) the lowest. General seasonal trend was observed at station 2. For stations 3,4,5 and 6 monsoon concentrations were the highest. The minimum values for station 3 (0.14 µg/g) and station 5 (0.18 µg/g) were noticed in pre monsoon season. The lowest lead concentrations in post monsoon seasons were noticed for stations 4 (0.59 µg/g)

Table 4.3.3 Concentrations of lead in different fractions of sediment extracted using a pH based speciation scheme (μg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
f2	1	0.33	2.39	1.43	f3	1	0.26	2.28	1.39
	2	0.00	4.18	1.71		2	0.80	5.68	2.36
	3	0.59	1.55	1.09		3	0.96	1.87	1.49
	4	0.13	3.99	1.14		4	0.81	2.52	1.54
	5	0.00	2.88	1.00		5	0.25	1.22	0.77
	6	0.00	3.54	2.02		6	1.11	8.36	4.75
F4	1	1.17	2.70	1.87	f5	1	0.10	0.95	0.63
	2	0.34	2.73	1.38		2	0.33	3.11	1.32
	3	0.05	2.79	1.34		3	0.05	2.59	1.11
	4	0.04	3.97	1.67		4	0.00	1.76	0.72
	5	0.00	3.31	1.69		5	0.14	2.25	0.79
	6	0.19	12.19	3.48		6	0.79	9.03	3.26
f6	1	0.00	1.13	0.56	f7	1	0.00	0.41	0.14
	2	0.61	2.78	1.48		2	0.00	2.46	0.74
	3	0.51	2.73	1.50		3	0.00	1.15	0.52
	4	0.25	3.53	1.26		4	0.00	1.24	0.41
	5	0.48	2.25	1.41		5	0.00	1.91	0.45
	6	0.00	3.16	1.19		6	0.00	1.17	0.34
f8	1	0.13	1.26	0.81	R	1	13.36	54.60	27.63
	2	0.57	3.71	1.52		2	13.75	38.93	28.40
	3	0.14	1.60	0.81		3	2.00	20.44	8.32
	4	0.59	1.36	0.97		4	0.60	23.02	7.10
	5	0.18	0.72	0.50		5	0.58	18.85	8.78
	6	0.49	1.81	0.99		6	21.69	106.03	64.88

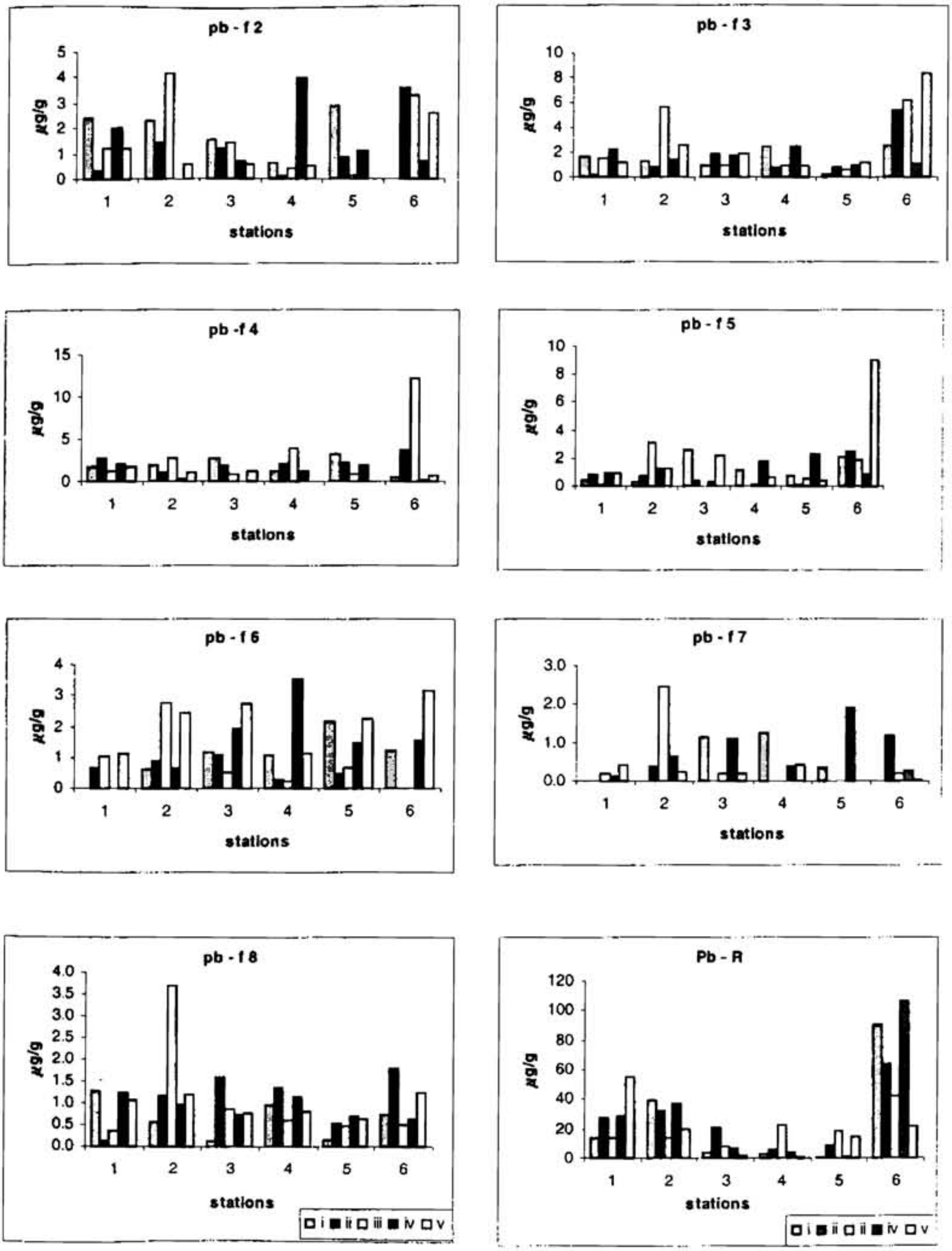

Fig 4.3.3 Distribution of lead in different fractions of the sediment

and 6 (0.49 μg/g). At station 6, post monsoon value (0.49 μg/g) was the lowest and the monsoon value the highest.

The observed maximum concentration for the fraction extracted at pH 7 was 2.46 μg/g (post monsoon). Pre monsoon values at stations 1 and 2, monsoon values at stations 1, 3,4 and 5 and post monsoon values for stations 4 and 5 were below the detectable limit. At station 2, Pb content for this fraction exhibited the general seasonal pattern of distribution. Pre monsoon values were highest for stations 3, 4 and 5. At station 6 the values varied from BDL (pre monsoon) to 1.17 μg/g (monsoon).

Pb concentrations for the fraction at pH 6, varied from BDL to 2.78 μg/g. General seasonal pattern were noticed at stations 3,4 and 5. A reverse trend was noticed for stations 1 and 2. The maximum concentration noticed for station 6 was 1.22 μg/g (pre monsoon).

The component extracted at pH 5, showed lead content varying between BDL (station 4 – monsoon) to 3.11μg/g (station 2 – post monsoon). At station 1 the values were between 0.10 μg/g (post monsoon) to 0.78 μg/g (monsoon). General seasonal trend was noticed at station 3. An opposite seasonal pattern was observed at station 2. The highest and the lowest values for stations 4 and 5 were observed in pre monsoon and monsoon seasons respectively. At station 6 post monsoon value was the lowest (1.89 μg/g) and the monsoon value (2.54 μg/g) the highest.

At pH 4, lead values varied between 0.52 μg/g (pre monsoon) to 12.19 μg/g (post monsoon), station 6. The observed maximum and the minimum concentrations were for station 6.At station 1 monsoon value (2.70 μg/g) was the highest and the post monsoon value (1.17 μg/g) the lowest. For station 2, the maximum (2.73 μg/g) and the minimum (1.01 μg/g) values were noticed in post monsoon and monsoon seasons respectively. General seasonal pattern was noticed for stations 3 and 5. An opposite trend was observed at stations 4 and 6.

For the component extracted at pH 3, lead content varied from 0.25 μg/g (station 5 -pre monsoon) to 6.22 μg/g (station 6 – post monsoon). For stations 1 and 4 pre monsoon value was the highest and the pre monsoon value the lowest. The highest (0.86 μg/g) and the lowest (0.25 μg/g) values for station 5 were noticed in monsoon and pre monsoon seasons respectively. For the stations 2 and 3, the values were in the range of 0.80 μg/g – 5.68 μg/g and 0.96 μg/g – 1.87 μg/g respectively. The values increased from pre monsoon to post monsoon for station 6.

Lead content in the fraction extracted at pH 2, varied from BDL (station 6 - pre monsoon) to 4.18 μg/g (station 2 – post monsoon). For stations 1,3 and 4,the maximum and the minimum values were noticed at monsoon and pre monsoon seasons respectively. At station 2, the post monsoon value (4.18 μg/g) was the highest and the monsoon value (1.46 μg/g) the lowest. The general seasonal trend was noticed at station 5. Observed maximum concentration at station 6 was 3.54 μg/g (monsoon).

Residual lead content varied from 7.05 μg/g (station 6) to 97.48 μg/g (station 2), both in pre monsoon season. The values ranged between 72.44 μg/g (monsoon) and 87.52μg/g (post monsoon) at station 1.For stations 3,5 and 6 the values increased from pre monsoon to post monsoon through monsoon season. At station 2, pre monsoon value (97.48 μg/g) was the highest and the monsoon value (89.40 μg/g) the lowest. Lead concentrations varied from 74.75 μg/g (monsoon) to 89.47 μg/g (post monsoon) at station 4.

In seawater, most probable species were $Pb\ (CO_3)$, $Pb\ (CO_3)_2\ ^{2-}$, and $PbCl^+$(Chester, 2000). Lead forms a number of complexes with many of the major anions including hydroxides, carbonates and sulphates. In anoxic systems, sulphide species (HS^-, $S\ ^{2-}$, $S_2\ ^{2-}$) are dominant than sulphate. Lead complexes with sulphides and Fe-Mn hydrous oxides in sediments. Sorption sulphides play a key role in determining the fate of lead complexes. $Pb\ ^{2+}$ complexes with sulphide minerals and precipitates onto pyrites. Stable form of lead in the anoxic form is PbS. The most toxic form of lead in the environment is $Pb\ ^{2+}$. Lead undergoes methylation in the environment to form several toxic organic derivatives (Sadiq, 1992). Lead sulphide formations also add to lower available lead values.

Lead forms a number of complexes with many of the anions including hydroxides, carbonates and sulphates. Complexation with organic and inorganic ligands leads to higher values in the lead concentration in the residual fraction. Affinities for the formation of organic complexes were greater than that for inorganic complexes. Lead also complexes with humic and fulvic acids forming moderately strong chelates.

Manganese

Observed maximum manganese values in the fraction extracted at pH 8, varied from BDL to 17.46 µg/g. At station 1, the values decreased from pre

Table 4.3.4 Concentrations of manganese in different fractions of sediment extracted using a pH based speciation scheme (µg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
f2	1	2.52	9.67	4.85	f3	1	5.08	11.92	7.43
	2	0.50	9.96	4.54		2	0.91	23.43	11.33
	3	4.09	14.92	9.98		3	8.37	17.43	12.94
	4	0.62	2.27	1.43		4	0.99	4.06	2.41
	5	0.32	0.62	0.44		5	0.50	0.98	0.74
	6	0.53	1.88	1.36		6	0.39	3.59	2.48
f4	1	1.38	14.79	7.38	f5	1	2.09	9.31	5.41
	2	0.03	13.81	4.09		2	0.61	10.27	4.90
	3	0.20	6.12	1.68		3	0.00	5.19	1.69
	4	0.38	10.45	3.46		4	0.71	2.99	1.39
	5	0.16	6.52	1.79		5	0.24	3.02	0.94
	6	0.00	4.09	2.53		6	0.20	2.98	1.85
f6	1	0.75	25.51	14.98	f7	1	0.30	2.87	1.65
	2	0.65	20.09	10.00		2	0.00	5.20	2.35
	3	0.00	13.94	4.04		3	0.00	0.28	0.08
	4	1.84	6.25	4.08		4	0.11	12.45	2.85
	5	0.98	12.19	3.56		5	0.01	0.72	0.35
	6	0.68	5.62	2.92		6	0.00	4.59	2.37
f8	1	0.00	4.69	1.93	R	1	14.20	334.76	104.90
	2	0.29	11.81	4.05		2	36.62	268.64	135.29
	3	0.00	2.02	0.58		3	5.90	95.29	38.33
	4	0.00	5.17	1.96		4	3.47	36.28	15.86
	5	0.00	2.06	0.79		5	9.51	27.14	16.79
	6	0.21	17.46	5.44		6	88.46	164.70	127.35

monsoon to post monsoon. A reverse trend was noticed at station 6. The values ranged from 0.29 µg/g (monsoon) to 3.64 µg/g (post monsoon) at station 2. For station 3, Mn concentrations at all the three seasons were below the detectable limit. The maximum values for stations 4 (5.17 µg/g) and station 5 (2.06 µg/g) were noticed in pre monsoon seasons. Post monsoon and monsoon values for these stations were below the detectable limit of AAS.

The component leached at pH 7, showed Mn values varying between BDL (staion 3 – pre monsoon) to 5.20 µg/g (station 2 – post monsoon). At stations 1 and 2 Mn concentrations increased from pre monsoon to post monsoon. For the other four stations monsoon values were the highest and the pre monsoon value the lowest.

For the fraction at pH 6, Mn concentrations varied from BDL (post monsoon) to 13.94 µg/g (pre monsoon); both at station 3. At station 3, the values decreased from pre monsoon to post monsoon. The highest and the lowest values were noticed in post monsoon and monsoon seasons for stations 1, 2 and 5.At station4 the values ranged from 1.84 µg/g (monsoon) to 6.25 µg/g (pre monsoon). The maximum and the minimum concentrations at station 6 were 5.62 µg/g (monsoon) and 1.43 µg/g (pre monsoon).

At pH 5, Mn concentrations ranged between BDL to 10.27 µg/g. The observed minimum value at station 2 was 0.61 µg/g (pre monsoon). For stations 1,5 and 6 the values decreased from pre monsoon to post monsoon. Stations 2 and 4 showed an opposite seasonal trend. Monsoon and post monsoon values at station 3 were below the detectable limit. Observed maximum Mn concentration at this station was 5.19 µg/g. Station 3 recorded a value of 5.19 µg/g in pre monsoon.

For the fraction at pH 4, Mn concentrations fluctuated from BDL (station 6) to 14.79 µg/g (station 1). At station 1 the lowest observed concentration was 5.41 µg/g (pre monsoon). The maximum and minimum values were noticed in the monsoon season. Mn values increased from pre monsoon to post monsoon at station 2. The highest and the lowest values were noticed in pre monsoon and monsoon seasons for stations 3, 4 and 5. The values at station 6 ranged from BDL (monsoon) to 3.32 µg/g (post monsoon).

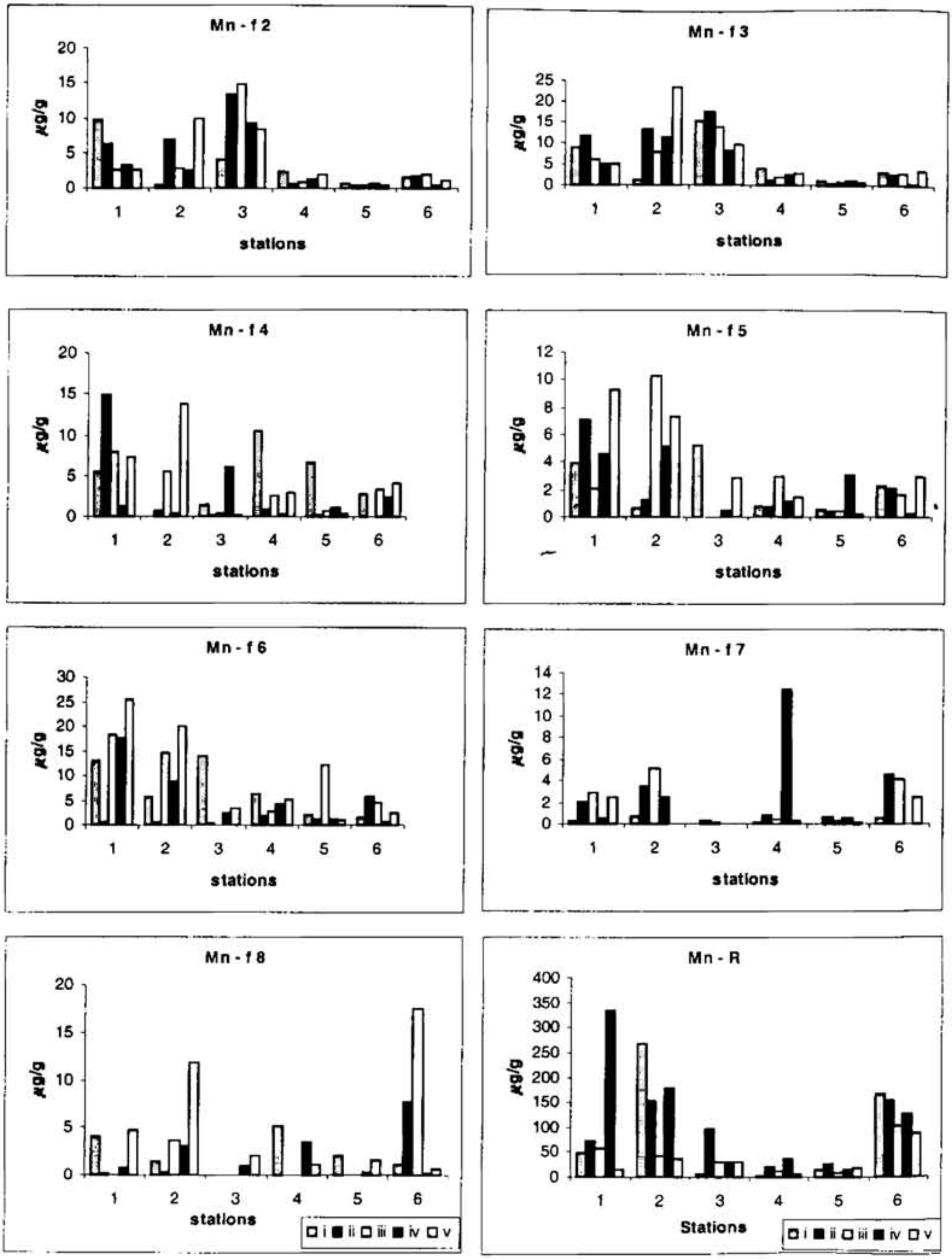

Fig 4.3.4 Distribution of manganese in different fractions of the sediment

For the component extracted at pH 3, Mn values varied between 0.50 μg/g (station 5) to 17.43 μg/g (station 3). The highest values at stations 1 and 2 were noticed in monsoon, the values were 11.92 μg/g and 13.05 μg/g. The minimum values for these stations were observed to be 6.06 μg/g (post monsoon) and 0.91 μg/g (pre monsoon) respectively. The maximum and the minimum concentrations were noticed in pre monsoon and monsoon seasons for stations 5 and 6.At station 4, the values ranged from 0.50 μg/g (monsoon) to 0.94 μg/g (pre monsoon).

For the fraction at pH 2, manganese values varied from 0.33 μg/g (station 5) to 14.92 μg/g (station 3), both in pre monsoon. At stations 1 and 5 the values decreased from pre monsoon to post monsoon season. A reverse seasonal behavior was noticed for stations 3 and 6. At station2 the values ranged from 0.50μg/g (pre monsoon) to 6.81 μg/g (monsoon). The maximum (2.27μg/g) and the minimum (0.62 μg/g) were noticed in pre monsoon and monsoon seasons respectively for station 4.

For manganese, hydroxide formation occurs at alkaline pH. The behavior of Mn is similar to that of Fe. Both are redox sensitive elements. Higher residual metal concentrations were noticed in the pH based speciation scheme. The fractions leached at pH values less than 5 are also small. This is attributed to the formation of stable oxides and hydroxides at alkaline pH along with other sparingly soluble inorganic salts. Mn^{2+} and Mn^{4+} are the dominant species in aquatic systems. The nitrate, chloride and sulfate salts of manganese are soluble in water whereas the corresponding hydroxides, sulfides, carbonates and oxides are sparingly soluble.

The chemistry of manganese is linked to the oxidation and reduction conditions. Redox reactions occur in sediments with high organic matter content and in systems with restricted water flow. In anoxic conditions, reduction of Mn 4+ to Mn 2+ occurs. Mn 2+ is soluble and is transported by diffusion and advection. The oxygenated waters results in the reoxidation of Mn 2+ to Mn 4+, which settles in the bottom. At higher redox potentials, Mn 4+ are reduced to dissolved Mn 2+.

Nickel

At pH 8, the observed maximum nickel concentration was 2.56 μg/g (post monsoon). Ni concentrations were not detected at pre monsoon samples of station 5 and 6. Nickel content varied between 0.44 μg/g (monsoon) to 0.51 μg/g (pre monsoon) for station 1.General seasonal pattern was noticed at stations 2 and 6. A reverse pattern was observed at station 3. The highest values for stations 4 and 5 were noticed in monsoon, the values were 1.02 µg/g and 0.36 µg/g respectively. At station 4, the lowest copper content was 0.04 µg/g (pre monsoon).

Table 4.3.5 Concentrations of nickel in different fractions of sediment extracted using a pH based speciation scheme (µg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
f2	1	0.05	1.23	0.53	f3	1	0.41	1.31	0.78
	2	0.79	1.74	1.19		2	0.22	2.11	1.14
	3	0.18	1.47	0.79		3	0.12	1.09	0.60
	4	0.40	1.04	0.63		4	0.15	1.36	0.66
	5	0.00	0.79	0.44		5	0.00	1.26	0.44
	6	0.00	0.80	0.43		6	0.05	1.72	0.79
f4	1	0.08	1.37	0.79	f5	1	0.17	2.48	1.31
	2	0.35	2.66	1.16		2	0.56	3.13	1.73
	3	0.00	1.62	0.48		3	0.22	1.88	1.01
	4	0.65	2.78	1.29		4	0.64	1.96	1.34
	5	0.00	1.78	0.99		5	0.54	1.37	0.92
	6	0.00	2.01	1.15		6	0.78	2.13	1.48
f6	1	0.00	2.34	1.61	f7	1	0.18	0.60	0.36
	2	0.00	2.92	1.20		2	0.40	1.60	0.71
	3	0.00	1.35	0.76		3	0.00	0.59	0.43
	4	0.00	2.71	1.24		4	0.16	1.96	0.72
	5	0.00	3.17	1.27		5	0.29	0.90	0.56
	6	0.27	4.21	1.81		6	0.34	1.21	0.75
f8	1	0.00	0.51	0.36	R	1	11.62	57.89	30.46
	2	0.03	1.55	0.60		2	59.68	87.05	69.96
	3	0.17	1.15	0.62		3	4.95	24.89	14.31
	4	0.00	1.02	0.32		4	1.93	18.55	8.82
	5	0.00	0.36	0.13		5	1.98	35.84	14.23
	6	0.00	2.56	0.64		6	21.76	49.33	29.52

For the fraction at pH 7, nickel content varied from BDL (station 3) to 1.60 µg/g (station 2), both in post monsoon season. At station 1 monsoon value (0.35 µg/g) was the highest and the pre monsoon value the lowest (0.18 µg/g). For station 2 the values varied between 0.40 µg/g (monsoon) to 1.60µg/g (post monsoon). At stations 3 and 4 the general seasonal behavior was observed. Lowest values for stations 5 and 6 were noticed in monsoon season. The maximum values for these stations were 0.64 µg/g (post monsoon) and 0.78 µg/g (pre monsoon).

The component extracted at pH 6 showed a maximum nickel concentration of 4.21 µg/g at station 6 in monsoon. Monsoon values were below the detectable limit at stations 1, 2 and 3. General trend was observed at stations 1 and 3. A reverse tend was noticed at station 2. For stations 4 and monsoon values were the lowest and the pre monsoon values the highest. For station 5, monsoon value (0.29 µg/g) was the lowest and the post monsoon value the highest. At station 6, Ni content ranged from 1.01 µg/g (pre monsoon) to 4.21 µg/g (monsoon).

Nickel content in the fraction extracted at pH 5 varied from 0.17µg/g (station 1) to 3.13µg/g (station 2), both in post monsoon season. At station 1 general seasonal behavior was noticed. At stations 2, 3 and 6 a reverse trend was observed. Monsoon concentrations were the lowest for stations 4 and 5. The observed maximum concentrations for these stations were 1.96 µg/g (pre monsoon) and 1.37 µg/g (post monsoon).

At pH 4, the maximum Ni content was observed at station 4 (2.78µg/g – post monsoon). Post monsoon values at stations 3 and 5 were not detected using AAS. The monsoon concentrations were highest for these stations. At station 1, the maximum and the minimum values were 1.28 lg/g (monsoon) and 0.08 µg/g (post monsoon). General seasonal pattern was observed at station 5. A reverse seasonal trend was noticed at station 2. For stations 3 and 6the highest and the lowest values were noticed in monsoon and post monsoon seasons respectively. At station 4, observed values varied from 0.80 µg/g (monsoon) to 2.78 µg/g (post monsoon).

The observed maximum concentrations for the fraction extracted at pH 3, were between BDL (station 5 – monsoon) and 2.11µg/g (station 2 – post monsoon). General seasonal behavior was noticed at station 4. Stations 1,2,3 and 6 exhibited a reverse trend in seasonal distribution. At station5 nickel content varied from BDL (monsoon) to 1.26 µg/g (pre monsoon).

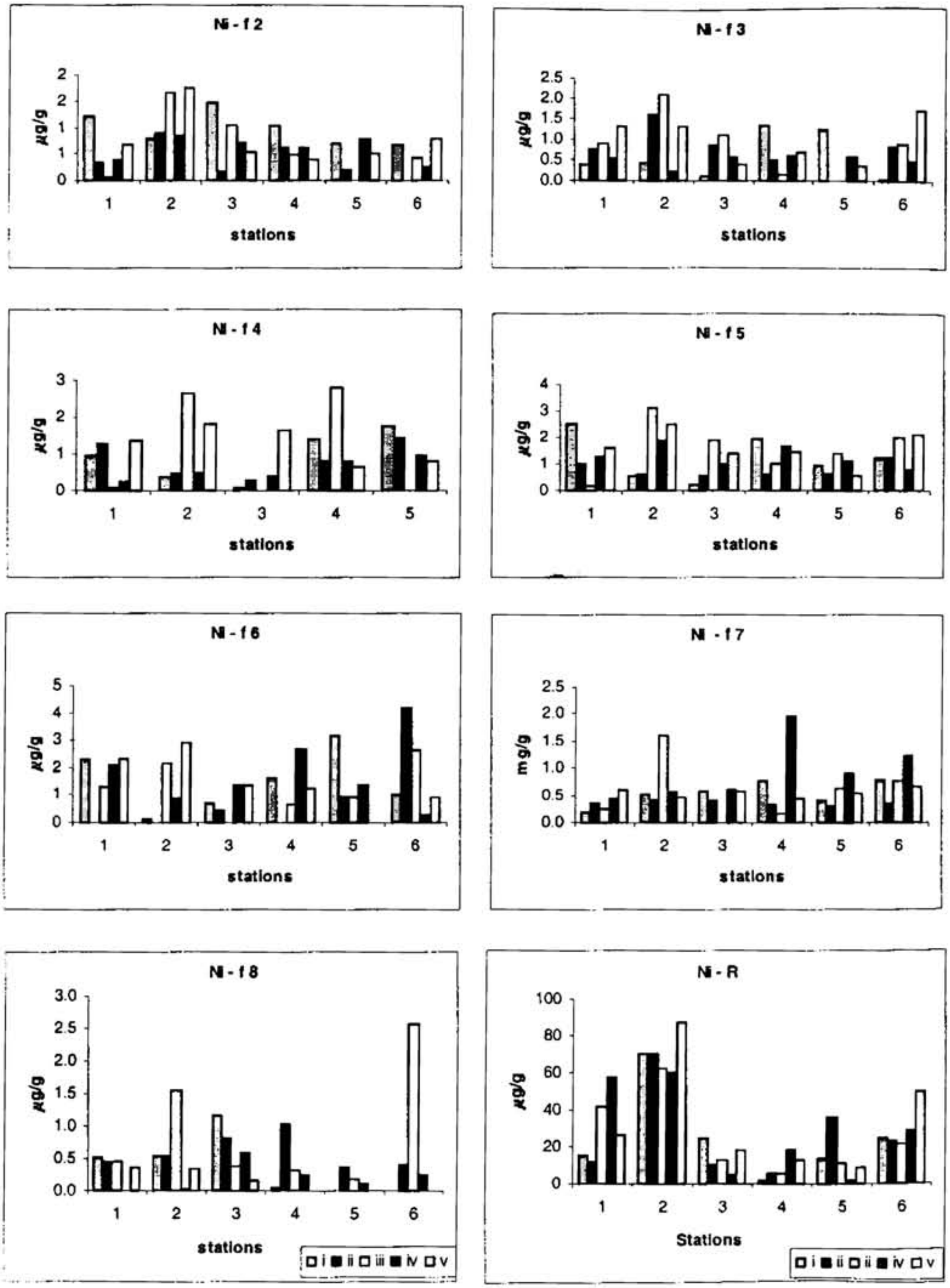

Fig 4.3.5 Distribution of Nickel in different fractions of the sediment

At pH 2, the maximum nickel content was noticed at station 2 in post monsoon (1.66 μg/g). Monsoon values at station 5 and post monsoon values at station 6 were low the detectable limit. General seasonal pattern was noticed for stations 1, 4 and 5. An opposite behavior was observed at station 2. For stations 3 and 4, the highest and the lowest values were noticed in pre monsoon and monsoon seasons.

The residual nickel content varied from 1.93 μg/g (station 4) to 70.52μg/g (station 2), both in pre monsoon. A trend opposite to the general seasonal pattern was noticed at station 1. Stations 2 and 6 followed general seasonal pattern. For station 3, pre monsoon value (24.89 μg/g) was the highest and the monsoon value the lowest. At station 4, the values varied between 10.56 μg/g (monsoon) to 24.89 μg/g (pre monsoon). Monsoon concentrations were highest for stations 4 and 5. The observed minimum concentrations for these stations were 1.93 μg/g (pre monsoon) and 10.88 μg/g (post monsoon).

Ni^{2+} complexes with organic and inorganic ligands. Inorganic complexes include halides, sulfates, phosphates, carbonates and carbonyls. Nickel tends to form insoluble complexes between pH 8 to 9 (Moore and Ramamoorthy, 1984). Under reducing conditions, metals form insoluble sulphides. At pH greater than 9, nickel complexes with hydroxides, carbonates, sulfates and naturally occurring organic ligands. Organic ligands having oxygen, nitrogen and sulfur forms donor atoms forms strong complexes with Ni. Among the organic complexes, the humic and fulvic acids complexes are important.

Lower Ni concentrations in f8 might be due to the formation of insoluble complexes between pH 8 and 9.For Ni the probable main species for Ni are Ni^{2+}, $NiCO_3$ and $NiCl^+$(Chester, 2000).

Zinc

The component extracted at pH 8, showed values between 0.02 μg/g to 84.20μg/g. At station 6, the values ranged from 1.13 μg/g (pre monsoon) to 84.02 μg/g (post monsoon). All other stations recorded the lowest seasonal values in post monsoon season. The general seasonal trend was noticed for stations 3,4 and 5. An opposite behavior was observed at station 6. For stations 1 and 2 the maximum and the minimum values were noticed in monsoon.

Zinc content in the fraction leached at pH 7, were below the detectable limit for majority of the samples. Only station 6 recorded higher values, ranging from 0.86 µg/g (post monsoon) to 9.70 µg/g (monsoon). Post monsoon value at station 2 was 0.60 µg/g. Station 3 recorded a value of 0.01 µg/g in monsoon.

Table 4.3.6 Concentrations of zinc in different fractions of sediment extracted using a pH based speciation scheme (µg/g)

	Stations	Min	Max	Mean		Stations	Min	Max	Mean
f2	1	0.52	3.76	1.47	f3	1	0.55	2.68	1.87
	2	3.56	4.83	4.09		2	0.00	15.91	8.75
	3	2.89	16.61	9.23		3	5.36	21.06	13.34
	4	0.98	5.92	2.72		4	1.18	11.87	4.30
	5	0.20	0.65	0.44		5	0.18	0.81	0.52
	6	0.35	19.46	7.98		6	0.34	12.46	4.43
f4	1	0.80	1.34	1.07	f5	1	0.00	1.33	0.45
	2	0.00	5.82	2.00		2	0.00	11.89	2.91
	3	0.00	4.13	0.84		3	0.00	10.06	3.10
	4	0.47	1.60	0.94		4	0.68	17.32	5.10
	5	0.35	1.15	0.61		5	0.25	2.36	1.02
	6	0.50	13.48	4.37		6	0.55	36.07	16.43
f6	1	0.00	3.73	0.99	f7	1	0.00	0.00	0.00
	2	0.00	7.65	1.75		2	0.00	0.60	0.12
	3	0.00	13.48	3.22		3	0.00	0.01	0.00
	4	0.62	3.37	1.79		4	0.00	0.65	0.13
	5	0.00	2.91	1.03		5	0.00	0.70	0.14
	6	0.19	101.25	38.54		6	0.00	9.70	3.46
f8	1	0.14	1.49	0.63	R	1	11.54	62.76	34.02
	2	0.07	6.40	1.54		2	61.47	99.31	86.91
	3	0.11	0.83	0.53		3	73.49	156.43	106.73
	4	0.02	1.52	0.47		4	0.46	46.68	17.42
	5	0.02	0.89	0.41		5	4.17	12.35	7.90
	6	0.17	84.02	22.21		6	39.59	176.12	102.33

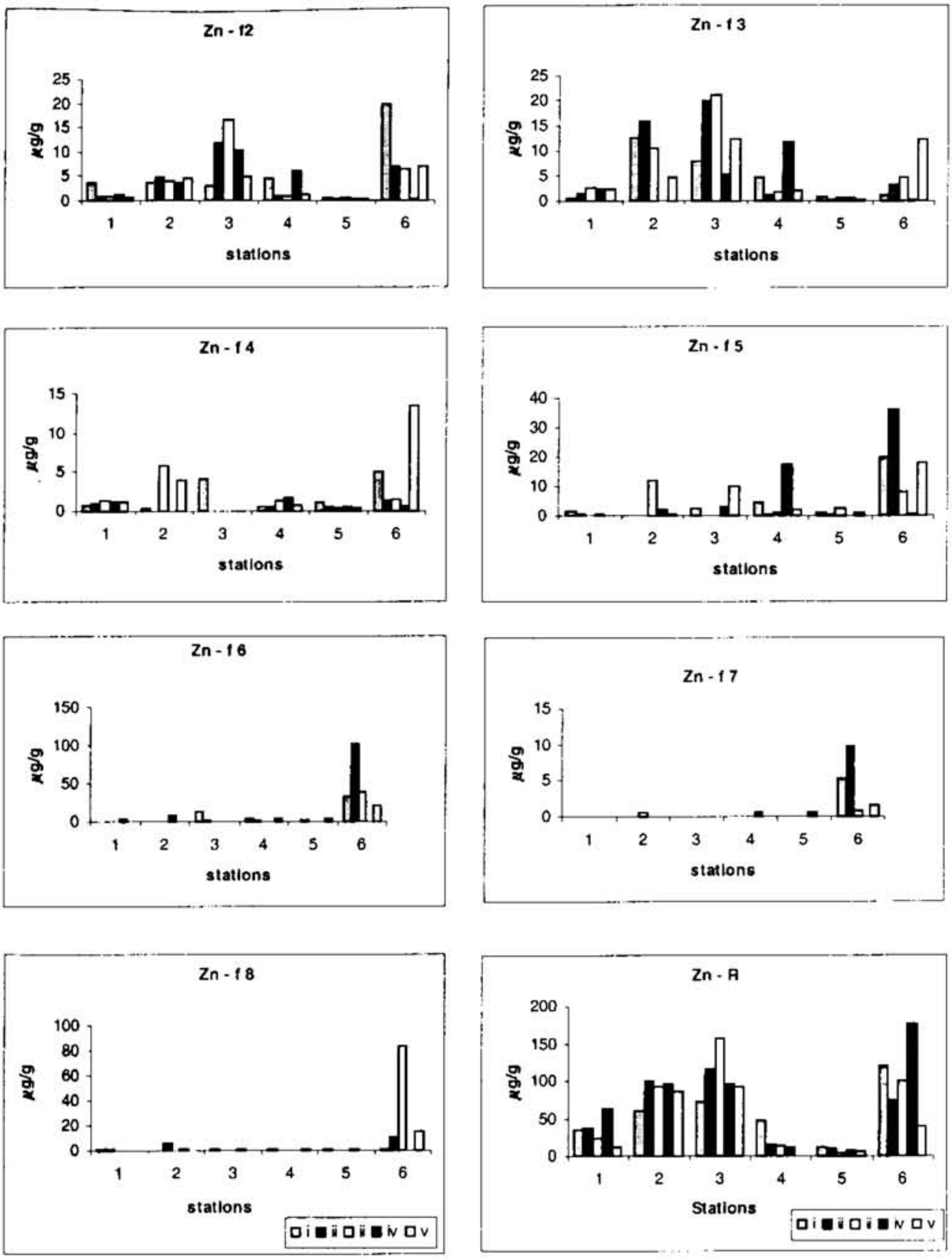

Fig 4.3.6 Distribution of zinc in different fractions of the sediment

At pH 6, zinc concentrations varied from BDL to 101.25 µg/g. General seasonal behavior were noticed at stations 1, 3 and 4. The highest values for stations 5 (1.26 µg/g) and 6 (101.25 µg/g) were noticed in monsoon. Lowest value observed at station 6 was 31.78 µg/g (pre monsoon). The post monsoon value at station 1 and the monsoon value at station 2 were below the detectable limit of AAS. At these stations the maximum values were noticed in the pre monsoon season; the values were 0.87 µg/g and 0.62 µg/g. At station 5 the values ranged from BDL (post monsoon) to 1.26 µg/g (monsoon).

The component extracted at pH 5 showed values from BDL to 36.07 µg/g. The maximum Zn concentration for this fraction was noticed at station 6; the values were in the range, 7.85 µg/g (post monsoon) to 36.07 µg/g (monsoon). Post monsoon value of station 1, pre monsoon and monsoon values of station 2 and post monsoon concentration of station 3 were below the detectable limit of AAS.

The fraction at pH 4, showed values varying between BDL to 5.08 µg/g. At station the values were in the range of 0.80 µg/g (pre monsoon) and 1.34 µg/g (post monsoon). Monsoon values for stations 2 and 3 and the post monsoon values at station 3 were not detected using AAS. General seasonal behavior was noticed for stations 3 and 5. A reverse trend was observed at station 4. The highest concentration noticed at station 6 was 5.08 µg/g (pre monsoon). At station 6, the values fluctuated between 1.30 µg/g (monsoon) and 5.08 µg/g (pre monsoon).

At pH 3, extractable zinc content varied from 0.38 µg/g (station 5 - monsoon) to 21.06 µg/g (station 3 – post monsoon). Station 4 showed the general seasonal trend. A reverse trend was noticed at stations 1, 3 and 6.The maximum and the minimum values at station 2 were 10.50 µg/g (post monsoon) and 15.91 µg/g (monsoon). At station 5, the values varied between 0.38 µg/g (monsoon) to 0.81 µg/g (pre monsoon).

The component extracted at pH 2 showed concentrations varying from 0.39 µg/g (station 5 – monsoon) to 19.46 µg/g (station 6 – pre monsoon). The maximum concentrations for station 1 (3.76 µg/g) and station 2 (4.83 µg/g) were noticed in pre monsoon and monsoon seasons. Monsoon value (0.99 µg/g) was the lowest at station 1. Observed minimum concentration of zinc at station 2 was 3.56 µg/g (pre monsoon). General seasonal pattern was noticed at stations 4 and 6.Reverse trend was noticed at station 3. At station 6, the post monsoon value was the highest (0.65 µg/g) and monsoon value (0.39 µg/g) the lowest.

Residual zinc concentrations varied from 4.17 µg/g (station 6) to 156.43 µg/g (station 3), both in post monsoon. The maximum values at station 1(37.32 µg/g) and station 2 (99.31 µg/g) were noticed in monsoon season. The lowest values for these stations were 23.34 µg/g (post monsoon) and 61.47 µg/g (pre monsoon) respectively. General seasonal distribution pattern was noticed for stations 4 and 5, an opposite behavior was observed at station 3. At station 6, the monsoon concentration (75.45 µg/g) was the lowest and the pre monsoon value (119.96 µg/g) the highest.

Zinc is a border line element according to HSAB classification in binding to ligands. In aqueous solution, Zn 2+ binds to F- > Cl^- > Br^- > I^-. Stability of organic complexes is affected by the presence of N and S atoms. Zn begins to hydrolyse at pH 7 – 7.5, and forms relatively stable Zn (OH) 2 at Ph.>8.0.At pH 6.7, zinc is present as divalent Zn available for sorption on to suspended mineral colloids and complexation with organic matter. Under natural environmental conditions the hydroxide may even promote the mobilization of Zn due to reduction in the charge of then cation and increases in the solubility of sparingly soluble salts. The Zn-Cu complexes will be formed when the chloride concentration exceeds 0.4M (Moore and Ramamoorthy, 1984).

Zinc content in f7 were below the detectable limit of AAS for all stations except station 6. In the speciation of zinc retention in the form of hydroxides at pH 8 is also evident from lower concentrations in fractions f8, f7 and f6.

Correlations:

The results of correlation analysis is given in Table **4.4**. The basic assumption of speciation is proved by the correlation analysis.

Table : 4.4 Correlation between different fractions

Correlations - Copper

	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
f 2	1.000	.861**	.922**	.669**	.177	.277	.874**	.431*
f 3	.861**	1.000	.864**	.558**	.128	.197	.794**	.290
f 4	.922**	.864**	1.000	.774**	.314	.367*	.881**	.506**
f 5	.669**	.558**	.774**	1.000	.726**	.835**	.836**	.550**
f 6	.177	.128	.314	.726**	1.000	.749**	.315	.439*
f 7	.277	.197	.367*	.835**	.749**	1.000	.590**	.322
f 8	.874**	.794**	.881**	.836**	.315	.590**	1.000	.424*
R	.431*	.290	.506**	.550**	.439*	.322	.424*	1.000

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

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

Correlations - Iron

	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
f 2	1.000	.241	-.021	.079	.274	-.069	-.127	-.051
f 3	.241	1.000	-.163	-.068	-.040	.046	-.082	.109
f 4	-.021	-.163	1.000	.004	.167	-.089	-.088	-.008
f 5	.079	-.068	.004	1.000	.077	.006	.466**	.019
f 6	.274	-.040	.167	.077	1.000	.034	-.184	.081
f 7	-.069	.046	-.089	.006	.034	1.000	-.177	.022
f 8	-.127	-.082	-.088	.466**	-.184	-.177	1.000	-.050
R	-.051	.109	-.008	.019	.081	.022	-.050	1.000

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

Correlations - Lead

	f 2	f 3	f 4	f 5	f 6	f 7	VIII	R
f 2	1.000	.587**	.446*	.378*	.196	.338	.464**	-.044
f 3	.587**	1.000	.376*	.785**	.254	.249	.512**	.175
f 4	.446*	.376*	1.000	.048	-.353	.028	-.046	.067
f 5	.378*	.785**	.048	1.000	.479**	.233	.275	.057
f 6	.196	.254	-.353	.479**	1.000	.241	.213	-.219
f 7	.338	.249	.028	.233	.241	1.000	.508**	-.168
f 8	.464**	.512**	-.046	.275	.213	.508**	1.000	.022
R	-.044	.175	.067	.057	-.219	-.168	.022	1.000

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

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

Table ; 4.4 : Contd…

Correlations - Manganese

	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
f 2	1.000	.816**	.167	.057	.002	-.202	.020	-.074
f 3	.816**	1.000	.328	.381*	.255	-.114	.132	-.021
f 4	.167	.328	1.000	.489**	.359	-.088	.286	-.255
f 5	.057	.381*	.489**	1.000	.662**	.156	.233	-.003
f 6	.002	.255	.359	.662**	1.000	.063	.279	.042
f 7	-.202	-.114	-.088	.156	.063	1.000	.276	.057
f 8	.020	.132	.286	.233	.279	.276	1.000	.024
R	-.074	-.021	-.255	-.003	.042	.057	.024	1.000

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

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

Correlations - Nickel

	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
f 2	1.000	.411*	.228	.528**	.094	.179	.172	.381*
f 3	.411*	1.000	.391*	.479**	.274	.184	.193	.343
f 4	.228	.391*	1.000	.453*	.429*	.087	.041	.051
f 5	.528**	.479**	.453*	1.000	.472**	.313	.140	.215
f 6	.094	.274	.429*	.472**	1.000	.229	.101	.080
f 7	.179	.184	.087	.313	.229	1.000	.142	.079
f 8	.172	.193	.041	.140	.101	.142	1.000	.054
R	.381*	.343	.051	.215	.080	.079	.054	1.000

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

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

Correlations - Zinc

	f 2	f 3	f 4	f 4	f 5	f 6	f 8	R
f 2	1.000	.536**	.200	.402*	.294	.391*	.110	.616**
f 3	.536**	1.000	.142	.088	-.076	-.083	.024	.453*
f 4	.200	.142	1.000	.436*	.210	.225	.128	.009
f 5	.402*	.088	.436*	1.000	.820**	.874**	.198	.122
f 6	.294	-.076	.210	.820**	1.000	.928**	.402*	.169
f 7	.391*	-.083	.225	.874**	.928**	1.000	.135	.156
f 8	.110	.024	.128	.198	.402*	.135	1.000	.166
R	.616**	.453*	.009	.122	.169	.156	.166	1.000

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

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

Discussion:

The purpose of speciation is to get an understanding of the behavior of metals in varying natural conditions. Most natural waters have pH values ranging from 6.5 to 8. For sea water the pH values from open oceans range between 7.5-8.4(Chester, 2000).In mangroves due to the frequent conversion from anoxic to oxic character, the redox potential continuously changes and as a result pH also changes. pH values greater than 7 is not a rare situation in mangroves. At pH 6, free metal ions were released from carbonates; metal ions were also made available by ion exchange processes. Under normal conditions, pH values varying from 8 to 4 can better predict the fraction available for biological uptake. A pH value of 2 is an extreme situation, it is rarely encountered in aquatic systems. Almost all metal fractions (that can be released by natural changes) becomes available at a pH of 2.Thus the releasing pattern of metals from sediments to the water column will be more evident by considering their behavior at pH values varying from 8 to 2. In that way, our scheme mimics the natural conditions.

The mean and standard deviation of trace metal concentrations in different fractions separated using Tessier's modified Scheme and the one based on pH are given in Tables **4.5.1** and **4.5.2** respectively. In the conventional scheme, the first fraction is extracted using ammomium acetate at pH 7.The major defect of the scheme is that it does not consider pH values greater than 7. In our experiments measurable fractions were leached at pH 6, 7 and 8. All these fractions together made a higher contribution to the total metal content. The metal concentrations in the exchangeable fraction was lower than the sum of the metal content in fractions f 6, f 7 and f 8.

The character of each metal varies with the species and environmental conditions. Different metals have different distribution pattern as evidenced by the percentage of metal released in each step. For all fractions, the percentage of contribution was less than 10 %.

Table 4.5.1 Mean and Standard deviation of trace metal concentrations (%) in different fractions separated using Tessier's modified procedure.

	Mean	SD %		Mean	SD %
Cu$_1$	3.18	3.44	Mn$_1$	6.39	6.46
Cu$_2$	1.74	1.88	Mn$_2$	3.19	4.75
Cu$_3$	19.88	15.95	Mn$_3$	4.08	3.5
Cu$_4$	45.37	20.65	Mn$_4$	21.8	17.14
R	29.82	24.77	Mn$_5$	64.57	66.06
Fe$_1$	0.05	0.08	Ni$_1$	8.11	6.2
Fe$_2$	0.19	0.37	Ni$_2$	9.85	8.01
Fe$_3$	4.97	8.91	Ni$_3$	7.49	6.19
Fe$_4$	5.89	7.52	Ni$_4$	27.75	12.79
R	88.9	13.12	R	46.8	25.03
Pb$_1$	7.23	6.07	Zn$_1$	7.14	16.58
Pb$_2$	3.33	3.05	Zn$_2$	2.9	4.79
Pb$_3$	7.15	6.83	Zn$_3$	14.57	13.31
Pb$_4$	29.47	19.16	Zn$_4$	21.66	16.83
R	52.47	25.76	R	53.73	30.85

Significant spatial variations were noticed in the distribution of metals in different fractions. Stations 1,4 and 5 are sandy in nature. For these stations the average organic carbon content were 0.89 %, 0.59 % and 1.50 % respectively. The zinc content in sediments was higher than the values noticed for average shale. Enriched zinc concentrations in sediments were noticed at stations2, 3 and 6. Higher Fe concentration was noticed in sediments at station 2. Copper values were the highest at station 6.

For all the six metals studied, the fraction leached at pH values of 7 and 8 made the lowest contribution to the labile metal content.

The copper content in different fractions decreases in the order f 5 > f 6 > f 4 > f 3 > f 2 > f 7 > f 8. The major contributing component for copper at stations 1 and 2 was the fraction f 5. F 6 showed the largest average (%) values for stations 5 and 6. At station 3, the maximum and the minimum contributors were the fractions extracted at pH 5 and 8 respectively.

Iron concentrations associated with different fractions were in the order of f 3 > f 6 > f 2 > f 4 > f 7 > f 8 > f 5.Among the different fractions f 5 was the lowest contributor for iron. On the basis of mean (%) values f 6 was the highest contributing fraction for station 1, f 2 for stations 2 and 3 and f 3 for stations 4 and 5.

For lead the overall mean (%) concentrations varied from f 4 to f 7 in the order f4 > f 3 > f 6 > f 2 > f 5> f 8 > f 7. Lead was mainly associated with f 4 at stations 1 and 5; f 3 for stations 2, 4 and 6.

The mean percentage values for manganese in different fractions decreases in the order: f 6 > f 3 > f 4 > f 2 > f 5 > f 8 > f 7. The fraction leached at pH 3 is the major contributor for stations 2 and 3.f 6 dominated the manganese distribution at stations 1, 4 and 5.

The nickel content in the component extracted at different ph values were in the order f 5> f6> f 4> f 3> f 2 > f 7 > f 8. F 5 was the major contributor for stations 1, 2 and 3.For stations 5 and 6 pH 5. For stations 5 and 6, nickel concentration was mainly associated with f 6.The maximum and the minimum contributions at station 4 were from the fractions at pH 3 and pH 8 respectively. The fractions at pH values of 7 and 8 made the lowest contribution.

The percentage average concentration of zinc varied between different fractions in the order f 3 > f 6 > f 5 > f 2 > f 8 > f 4 > f 7. The highest contributor of zinc at stations 1,2 and 3 was f 3.

Bio transfer of metals varies with the metal concentration in different fractions. In pH based speciation scheme, the total labile metal concentrations were in the order Fe < Mn < Zn < Ni < Cu < Pb. The sum of metal content at pH values 6, 7 and 8 gives the metal concentration available without any external modifications to the system, the values were in the decreasing order of Fe > Zn > Mn > Cu > Ni > Pb. The metal concentrations in the exchangeable fraction (Tessier's modified scheme) were in the order of Ni> Pb> Zn> Mn> Cu > Fe.

Table 4.5.2 Mean and standard deviation of trace metal concentrations (%) in different fractions separated using pH based speciation scheme

	Mean	SD %		Mean	SD %
Copper			Manganese		
f 2	4.65	5.64	f 2	5.1	5.75
f 3	5.26	5.98	f 3	8.06	7.64
f 4	5.67	8.28	f 4	5.85	7.49
f 5	8.52	11.69	f 5	3.89	4.24
f 6	8.48	10.92	f 6	10.17	11.95
f 7	3.04	3.06	f 7	2.02	3.7
f 8	2.92	3.8	f 8	3.11	4.16
R	61.46	32.78	R	61.79	25.27
Iron			Nickel		
f 2	6.36	10.09	f 2	2.96	2.77
f 3	6.86	9.12	f 3	3.09	2.85
f 4	5.8	5.79	f 4	4.59	5.32
f 5	0.02	0.05	f 5	5.71	4.34
f 6	6.69	10.23	f 6	5.38	5.21
f 7	0.11	0.39	f 7	2.67	2.56
f 8	0.06	0.39	f 8	1.93	2.58
R	71.25	25.45	R	73.68	18.73
Lead			Zinc		
f 2	6.16	6.28	f 2	5	2.9
f 3	7.85	5.63	f 3	7.42	5.93
f 4	7.91	7.59	f 4	3.02	2.83
f 5	5.32	6.29	f 5	6.35	8.51
f 6	6.67	7.1	f 6	7.05	10.48
f 7	2.48	4.08	f 7	0.54	1.42
f 8	4.3	3.74	f 8	3.09	6.51
R	59.32	27.71	R	67.52	21.74

On the basis of these considerations, Fe was the most bio available metal followed by Zn and Mn. Pb has a very little tendency to get transported to the biota. The mean concentration of iron was the highest in most of the fractions analysed. Cu; Ni or Pb showed the lowest mean values at all pH. For all the fractions from f 8 to f2, the second highest average concentration was noticed for Zn or Mn.

Our Scheme considers only the effects of pH variations on metal mobility. The residual component in pH based speciation scheme, showed values higher than that obtained by Tessier's procedure. Metals released by chemical reactions (oxidation and reduction) were not detected using a pH based speciation scheme. Mild oxidizing and reducing conditions occurring in nature are not taken into consideration. Although the oxidizing conditions are rare, the mildly reducing conditions operating in these systems mobilizes the metals. Reduction processes occurring in nature are microbial reductions. The metals released by ordinary chemical reactions are not comparable with that made available by microbial action. This attributes to the differences in the metal content in the residual fraction by both the schemes.

In all the speciation schemes the sequential extraction begins at pH 7. In natural water bodies pH values greater than 7 is not a rare observation. In our speciation scheme, the first extraction was done at pH 8.The fraction f 7 has metal concentrations lower than that extracted at the same pH by the modified Tessier's scheme. Slight alkaline modifications (pH > 7) might lead to the stabilization and storage of metals in sediments. These metals are released to the water column only at a lower pH (pH≤ 2).In mangroves, even though the sediment is having a lower pH, the surface sediment exposed to water is at a higher pH. Overlying water is always observed to have a pH higher than 7.Dissolution and retention of metals occur at the sediment- water interface. So a fraction scheme starting with a pH > 7 could better predict the possible speciation and behaviour of metals in these sediments.

Table 4.6 Distribution of metal species in estuarine/coastal sediments of Kerala (μg/g)

Fraction	COPPER			IRON			MANGANESE		
	1	2	3	1	2	3	1	2	3
EF	2.08	BDL	1.08-1.90		< 0.05	< 0.05	7.52	0.34-5.4	0.63-4.3
CF	2.72	< 9.07	< 2.5	0.07	.01-5.3	0.3-4.06	11.16	0.85-29.13	23-26
ERF	0.74	< 2.9	< 1	1.27	.007-3.42	1.17-1.93	8.91	0.94-8.3	1.02-12.03
MRF		5.4-35.7	13.5-34.1		30-60	31 53		3-11.41	12-19
OSF	20.34	16.5-55	34.1	1.16	0.09-36.49	17.33-36.44	26.11	11.4-43	4.8-38.3
R	71.21	21.2-54.5	34-45	97.44		16-50	46.3	30-76.36	4.78-66.5

Fraction	LEAD			ZINC		
	1	2	3	1	2	3
EF	2.86	BDL	< 7.08	1.75	BDL	0.07-1.8
CF	4.32	BDL-11.7	1.81-13.4	6.43	0.29-2.36	1.4-9.6
ERF	5.68	BDL-9.7	BDL	9.37	BDL	1.98-4.47
MRF		2.3-23	BDL-29.1		2.78 -19.45	20.2-34.3
OSF	10.37	BDL-60	16.2-32.6	24.28	20-67	23-54
R	76.78	14-100	32.6-75.4	58.22	26.4-63	13-52

1. Cochin estuary, Nair, 1992 2 & 3. Rajammani Amma, 1994

EF – Exchangeable frcation, CF- Carbonate Fraction, ERF- Easily Reducible Fraction,
MRF – Moderately Reducible Fraction, OSF- Organic and sulphide Fraction
R- Residual Fraction

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Chapter 5

STATISTICAL ANALYSIS

5.1 Factor Analysis:

Element associations and the factors controlling metal variability have been assessed using principal component analysis (PCA). The main aim of PCA is to reduce the number of variables that needed to be considered into a smaller number of indices, principal components (PCs), which can be more easily interpreted (Szfer *et al.*, 1995; Manly, 1997; Panigrahy *et al.*, 1999; Spencer, 2002). Factor analysis was employed to reduce the large number of variables to a smaller number of orthogonal factors (Szfer *et al.*, 1995). The parameter with factor loadings of greater than 0.4 and factors with eigen values greater than 1 are considered for interpretation in this study.

The factor analysis technique deals with the establishment of a correlation coefficient matrix (N, M) of normalised variables, from the data matrix having dimensions of N and M, denoting number of samples and number of variables M. This steps followed by the calculation of eigen vector matrix (V), which represents the magnitudes, and directions of variables in space and eigen values (E) represent their corresponding variance. The final step includes the rotation of the principal factor to achieve a simple structure leading to the rotated factor matrix (Panigrahy *et al.*, 1999).

In the present study, factor analysis is attempted using the data on sedimentary parameters that are supposed to be associated with the distribution and cycling of metals. System characteristics as a whole are not considered in the present investigation. Since we consider only the sediment, additions into the sediment and removal from the sediment is our major concern. Dominant processes contributing to the incorporation of metals in sediments are lateral additions, precipitation and adsorption processes. Diagenetic processes play a dominant role in deciding the fate of metals. Diagenesis can be diagenetic additions or diagenetic removal. Water circulation and tidal activity are also important in the study of metals in sediments. Diagenetic decomposition can result in positive loadings for organic nitrogen and organic carbon. Lateral addition lead to positive loadings of metals. The positive loading of sand/ silt might be due to lateral additions or mineralization processes.

5.1.1 System characteristics:

System characteristics have a major role in determining the processes responsible for different factors and also in deciding the dominance of one factor over others. Since, the system characteristics vary widely between stations; a general factor analysis has a little meaning. So a station wise analysis is done on sediment parameters. Since organic carbon and grain size are identified as the major contributors in the retention and removal of metals from sediments, the contributions of organic nitrogen, protein and carbohydrate in the distribution of metals are assed only for stations 2 and 3. For all the other four stations, the hydrographical parameters and sedimentary characteristics only are included in the factor analysis. For all the six stations, the principal component analysis was also done between the nine metals.

Factor analysis was done using the programme (SPSS-7.5, Version 2.4). The results of the analysis are presented in Table **5. 1**and **5.2**

Station 1: Varimax rotation resulted in two dominant factors with a total variance of 55.74%. Factor 1(37.42 % of the variance) has positive loadings for clay, Co, Cr, Cu, Fe, organic carbon, lead, silt and zinc and the negative loadings for sand and alkalinity. Positive loadings of clay, silt and organic carbon with metals could be the result of riverine additions. This is a common character observed in estuarine and marine aquatic systems (Katz and Kaplan, 1981: Seidemann, 1991; Croudace and Cundy, 1995; Senthilnathan and Subramanian, 1997; Fang and Hong, 1999). Factor 2 with positive loadings for Cd, Cr, Mn, Ni, organic carbon and zinc accounts for 18.32 % of the variance. It can be considered as the geochemical factor. Processes such as precipitation, adsorption and complexation with metals occur at the river mouth.

Table 5.1. 1 Varimax rotated factor matrix for trace metals, hydrographical and sedimentary parameters - Station 1

Variables	Station 1	
	Factor 1	Factor 2
Cd	0.368	0.426
Clay	0.535	0.076
Co	0.796	0.051
Cr	0.72	0.657
Cu	0.88	0.36
Fe	0.647	-0.241
Mn	0.304	0.951
Ni	-0.011	0.503
OC %	0.586	0.631
Pb	0.807	0.233
pH	-0.012	0.367
Salinity	0.271	0.113
Sand	-0.657	-0.05
Silt	0.66	0.378
Zn	0.892	0.408
Alkalinity	-0.62	0.219
Variance %	37.42	18.3

Station 2: Principal component analysis of the data results in four factors, which accounts for 50.41 % of the variance. Factor 1(28.65 % of the variance) displays large positive loadings for clay, Fe and Mn and negative loadings for organic carbon and nitrogen. As has been pointed out earlier, this represents the dominance of diagenetic processes. Associations of Fe and Mn with clay are a general observation in marine sediments (Fang and Hong, 1999; Streckemann, 1999). Negative loadings for organic carbon and nitrogen in factor 1 may also support diagenesis. The observed negative loadings for Zn might be due to the relatively low retention of zinc in sediments. Zinc easily forms soluble complexes in alkaline and acidic conditions. Factor 2 (17.89 % of the variance) represents positive loadings for pH, cobalt and negative loadings for sand and silt. Comparatively high

negative loadings for silt and sand signify the outflow of materials from the system through tidal flushing. Negative loadings of sand and silt could be the result of

Table 5.1.2 Varimax rotated factor matrix for trace metals, hydrographical and sedimentary parameters - Station 2

Variables	Station 2		
	Factor 1	Factor 2	Factor 3
Alkalinity	-0.355	-0.63	0.056
Carbohydrate	0.656	0.124	0.058
Cd	0.897	0.435	0.014
Clay %	-0.127	0.096	-0.933
Co	0.861	-0.226	0.171
Cr	0.926	0.085	-0.218
Cu	0.736	0.223	-0.076
Fe	0.87	0.263	0.086
Mn	0.955	0.263	-0.092
Ni	-0.009	-0.066	-0.751
OC %	0.832	0.183	0.381
Organic Nitrogen	0.704	0.058	0.281
Pb	0.600	0.658	0.022
pH	0.348	0.22	-0.213
Protein	0.443	0.614	0.364
Salinity	-0.391	0.714	-0.202
Sand %	-0.098	-0.300	0.08
Silt %	-0.008	-0.135	957
Zn	0.143	0.985	0.098
Variance %	38.08	17.63	15.35

decreased loading or removal through tidal flushing. Factor 3(3.15 % of the variance) has relatively high positive loadings for carbohydrate, Cr, Cu, Ni and organic nitrogen and negative loadings for Cr and salinity. From the loadings of various parameters, factor 3 is recognised to be linked with inflow to the system. Input can be either from plants or from in situ productivity. From the negative loadings of organic carbon, organic nitrogen and protein in factor 1 and the positive loading of carbohydrate in factor 3, the processes leading to factor 3 is expected to be complimentary to the processes resulting in factor 1. Inputs from land (terrestrial) and organic detritus (by decomposition of litter) are the major contributing processes for factor 3. Negative loading of salinity points to out flow into adjacent coastal waters.

Station 3: Varimax rotation resulted in three factors accounting for 71.06 % of the total variance. Factor 1 (38.08 %of the variance) has positive loadings for carbohydrate, organic nitrogen, protein, pH, Cd, Co, Cr, Fe, Mn, Pb and organic carbon. Mangalavanam is a closed mangrove area, with low tidal action. Even though reducing conditions exists, oxygen is available to the surface sediment. Undecomposed litter is often noticed in sediments from Mangalavanam. Benthic productivity is also high. This results in positive loadings for organic carbon, organic nitrogen, carbohydrate and metals. Factor 2(17.63 % of the variance) has positive loadings for Cd, Pb, Zn, protein and salinity and negative loadings for carbohydrate. This points to microbial decomposition processes, which are condition specific. Retention of metals as a part of organic matter is also expected here. Contribution from bird droppings have also a major role in deciding the fate of contaminants. Behavior of organic matter in this mangrove area is widely different from that of other mangroves. Decomposition path of organic matter is different. Major portion of the system is in direct contact with the atmosphere. Possibility for a mixed decomposition path with intermittent aerobic and anaerobic conditions is comparatively high. Diagenetic products in these sediments will be different from that in normal anoxic sediments. Factor 3(15.35 %of the variance) has strong positive loadings for silt and negative loadings for clay and Ni. Undecayed organic detritus can also result in positive loading of silt.

Table 5.1.3. Varimax rotated factor matrix for trace metals, hydrographical and sedimentary parameters - Station 3

Variables	Station 3			
	Factor 1	Factor 2	Factor 3	Factor 4
Alkalinity	0.583	0.395	-0.494	0.149
Carbohydrate	-0.156	0.14	0.631	-0.381
Cd	0.356	0.063	-0.361	0.208
Clay %	0.725	0.429	-0.005	-0.091
Co	0.084	0.763	0.146	0.44
Cr	-0.005	0.037	0.988	-0.121
Cu	-0.09	0.238	0.752	0.28
Fe	0.528	0.266	-0.164	-0.278
Mn	0.991	-0.085	0.074	0.061
Ni	-0.307	-0.083	0.431	-0.257
OC %	0.944	-0.051	0.197	0.076
Organic Nirogen	-0.86	0.076	0.44	0.054
Pb	0.58	-0.415	-0.155	0.399
pH	0.087	0.95	0.243	-0.123
Protein	-0.894	-0.298	-0.114	0.226
Salinity	0.06	-0.011	-0.503	0.035
Sand %	0.007	-0.716	0.077	0.244
Silt %	-0.231	-0.791	0.078	-0.132
Zn	-0.476	0.008	-0.052	0.874
Variance %	28.65	17.88	16.58	9.10

From PCA, sediments of Mangalavanam are observed to be deviating from the normal aquatic character. A micro level characterization only can better predict the exact system characteristics.

Table 5.1.4. Varimax rotated factor matrix for trace metals, hydrographical and sedimentary parameters - Station 4

Variables	Station 4		
	Factor 1	Factor 2	Factor 3
Cd	0.358	0.26	0.128
Clay	0.004	-0.776	-0.048
Co	0.179	0.175	0.351
Cr	0.92	0.208	0.097
Cu	0.79	0.008	0.005
Fe	-0.05	337	0.491
Mn	0.92	-0.098	0.021
Ni	0.599	-0.03	0.238
OC %	0.714	0.076	0.095
Pb	-0.088	0.379	0.511
pH	-0.623	0.428	0.289
Salinity	0.467	0.384	-0.169
Sand	0.018	0.906	0.08
Silt	-0.1	0.0203	-0.631
Zn	-0.064	0.314	-0.946
Alkalinity	0.361	-0.054	0.011
Variance %	25.67	14.20	13.32

Station 4 : Varimax rotation resulted in three factors with 53.09 % of the variance. Nettor is an open mangrove area. Mangrove waters are saline in all seasons except in monsoon.. The impact of salinity intrusion associated with riverine systems is dominantt here. Factor 1, with positive loadings of salinity, organic carbon and metals and negative loading for pH, accounts for 25.67 % of the total variance. This factor indicates the contribution from river run off and mixing processes. Mixing processes leads to the deposition of organic carbon and other easily precipitable materials. As a result there is a scavenging tendency for metals from water into the sediment. Positive loadings for metals is expected in such a situation and it is the observation. Factor 2 with positive loadings for pH and sand and negative loading for clay has a variance of 14.2 %. It may point to the depositional character of sand in riverine sediments. Factor 3(13.32 % of the variance) has positive loadings for Fe and Pb and negative loadings for silt and zinc. This factor is associated with sedimentation processes during mixing. Precipitation of iron can occur as a result of mixing. In estuaries behavior of zinc is complex. Negative loading of zinc was also noticed earlier for the sediments of station 2 in factor 1.

Station 5: This a cultivated mangrove area. It's behaviour is entirely different from that of natural mangroves. No factor shows dominance here. Different factors contribute almost equally to the system characteristics. All the three factors together have a total variance of 47.96 %. Factor 1(18.06% of the variance) has positive loadings for Cd, Cr, Cu and Fe and negative loadings for salinity and zinc. This is associated with out flow to adjacent water bodies. Factor 2 (16.21 % of variance), with positive loadings for Fe, organic carbon and sand and negative loadings for clay and silt account for riverine additions. The third factor (13.69 % of the variance) with positive loadings of Mn, Ni and organic carbon indicates the contribution of plant litter to organic detritus.

Table 5.1.5. Varimax rotated factor matrix for trace metals, hydrographical and sedimentary parameters - Station 5

Variables	Station 5		
	Factor 1	Factor 2	Factor 3
Cd	0.477	-0.003	0.01
Clay	-0.054	-0.478	0.322
Co	-0.001	0.012	-0.221
Cr	0.858	-0.113	-0.011
Cu	0.451	0.076	0.134
Fe	0.756	0.633	0.148
Mn	-0.199	0.283	0.669
Ni	-0.016	-0.154	0.985
OC %	0.002	0.500	0.594
Pb	0.157	-0.049	-0.094
pH	-0.361	0.119	-0.271
Salinity	-0.65	0.241	0.228
Sand	-0.252	0.868	0.079
Silt	0.296	-0.815	-0.109
Zn	-0.543	0.292	0.232
Alakalinity	-0.124	-0.124	-0.141
Variance %	18.06	16.21	13.69

Station 6: Three factors with a total variance of 53.65% were extracted using varimax rotation. Factor 1(29.27 % of the variance) has positive loadings for clay, organic carbon, Cd, Co, Cr, Mn, Ni, and Zn and negative loading for sand. Riverine additions may be the major process responsible for this factor. Evethough, in the river mouth, stagnant nature is observed in the mangroves of this area. Municipal waste dumping is also evident from this factor. This generates an organic rich condition favorable for loading of metals. Organic matter also promotes the deposition of clay. In natural aquatic water bodies, clay is usually found to be associated with organic matter. The second factor with positive

loadings for Cd, pH, salinity and negative loading for copper has a variance of 13.43 %. Mixing is the major criteria governing this factor. Removal of copper as soluble sulfates is evident from the negative loading of copper in this factor. Factor 3(10.95 % of the variance) has positive loading for lead and negative loading for sand. Factor 3 is almost complimentary to factor 1. The major source of lead in the sediment is atmospheric precipitation (Nriagu, 1979;Moore and Ramoorthy, 1984), but it has no localized nature. So the observed positive loading of lead might be the result of municipal waste dumping at this station.

Table 5.1.6. Varimax rotated factor matrix for trace metals, hydrographical and sedimentary parameters - Station 6

Variables	Station 6		
	Factor 1	Factor 2	Factor 3
Cd	0.445	0.402	-0.008
Clay	0.663	-0.299	0.203
Co	0.499	-0.153	0.376
Cr	0.797	0.13	0.186
Cu	0.381	-0.888	0.198
Fe	-0.027	0.141	-0.352
Mn	0.887	0.254	-0.103
Ni	0.601	-0.272	0.221
OC %	0.575	-0.141	-0.027
Pb	0.383	0.03	0.917
pH	-0.032	0.589	-0.115
Salinity	-0.083	0.617	0.039
Sand	0.676	0.075	-0.444
Silt	0.219	0.208	0.382
Zn	0.94	-0.330	-0.039
Alkalinity	-0.114	-0.063	0.334
Variance %	29.27	13.43	10.95

5.1.2 Trace metals

A number of geochemical processes determine the fate of metals in sediments. Different processes that contribute to the storage in sediments are inorganic/organic complexation, precipitation, adsorption, mixed oxide formation etc. A number of sub processes govern these major processes. The contributions of these sub processes to different factors varies with the priority of one process over others. We get only the cumulative effect of different processes operating in sediments. The contribution of each individual processes is not evident from factor analysis. In principal component analysis, the positive loadings represent the retention to the sediment and negative loadings the removal from the sediment. The results of the principal component analysis for all the six stations are as follows:

For all the stations, the analysis results in two factors. The analysis results in two factors at all the six stations. Both the factors have positive loadings for metals at all stations except station 4.At station 4, factor 2 had a negative loading for zinc; negative loading of zinc might be due to the complex estuarine behavior of this metal. At station 1, the varimax rotation leads to two factors with a total variance of 69.68 %. Factor 1 with 43.67 % of variance has positive loadings for Co, Cr, Cu, Fe and Pb. The second factor (26.01 % of the variance) accounts for positive loadings of Cd, Cr, Cu, Mn, Ni and Zn. At station 2, two relatively lower contributing factors are obtained. The total variance obtained for these two factors together was only 37.55 %. Factor 1(20.83 % of the variance) has positive loadings for Mn and Pb and factor 2(16.72 % of the variance) has positive loadings for Cr and Fe. At station 3, the total variance obtained for both the factors was 58.85 %. Factor 1 (43.09 % of the variance) accounts for positive loadings of Cd, Co, Co, Cr, Cu, Fe, Mn and Pb. Factor 2 with positive loadings of Mn and Zn has a variance of 15.76 %. At station 4, factor 1 has positive loadings of Cd, Cr, Cu, Mn and Ni and Factor 2 has negative loading of Zn. The percentages of variance for these factors were 31.81 % and 15.68 % respectively. At station 5, two factors obtained have lower percentages of variance. Factor 1 has a percentage of variance of 19.78 % and for factor 2 the percentage of variance was 17.09 %. The total variance for these two factors together was 36.87 %. Factor 1 has positive loadings for Cr, Cu and Fe. Factor 2 accounts for positive loadings of Mn and Ni. At station 6, both the factors have almost equal contribution to the total percentage of variance. Factor 1 (27.5 % of the variance) accounts for the positive loadings of Cd, Cr, Mn and Ni. Factor 2 (17.09 %) has positive loadings for Co, Cu, Ni, Pb and Zn.

Table 5.2 Varimax rotated factor matrix for trace metals in sediments

Variables	Station 1		Station 2		Station 3	
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
Cd	0.398	0.424	0.301	0.395	0.536	-0.096
Co	0.834	0.078	0.038	-0.171	0.578	0.074
Cr	0.716	0.684	-0.059	0.987	0.959	0.248
Cu	0.876	0.400	-0.175	-0.353	0.817	-0.197
Fe	0.668	-0.209	0.112	0.420	0.545	0.264
Mn	0.246	0.968	0.991	0.117	0.867	0.484
Ni	-0.033	0.500	-0.407	-0.028	0.001	-0.072
Pb	0.713	0.306	0.661	-0.064	0.784	-0.029
Zn	0.883	0.450	-0.338	-0.161	0.075	0.997
% Variance	43.67	26.01	20.83	16.72	43.09	15.76

Variables	Station 4		Station 5		Station 6	
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
Cd	0.415	0.048	0.392	-0.024	0.529	-0.167
Co	0.174	0.287	-0.018	-0.225	0.306	0.469
Cr	0.948	0.029	-0.624	-0.051	0.709	0.277
Cu	0.774	0.002	0.422	0.099	0.021	0.971
Fe	0.034	0.363	0.994	0.029	104.000	-0.256
Mn	0.907	0.045	0.078	0.647	0.907	0.092
Ni	0.578	0.239	0.011	0.995	0.401	0.554
Pb	-0.025	0.375	0.091	-0.104	0.111	0.467
Zn	-0.065	-0.997	-0.238	0.233	0.768	0.632
% Variance	31.81	15.68	19.78	17.09	27.50	25.20

At stations 2 and 5, factor 1 and factor 2 are having relatively lower percentages of variance. Here, the factors 1 and 2 together have a total variance of less than 40 %. These factors have a lower contribution in deciding the behaviour of metals in sediments. A number of other processes are important in deciding the fate of metals.

For all the other three stations, the first factor with higher percentage of variance has positive loadings of Fe and other metals. Sulphide formation is predicted by this factor. Sedimentary retention of metals as insoluble sulphides can occur in anoxic sediments. Sulphur cycle gives enough sulfates for this process. In organic rich anoxic sediments, a portion of the organic materials is converted to inorganic minerals during diagenesis. In oxic conditions, the pore water can function as a removal media. But, the anoxic conditions of the mangrove sediments favor precipitation and storage of metals. Both these result in the retention of metals in sediments. The first factor at stations 1, 3 and the second factor at station 6 predicts the possibility of sulphide formation in sediments. The second factor at stations 1 and 3 and the first factor at station 6 points to organic contributions from plants as litter.

Principal component analysis identifies different processes governing the distribution of metals in sediments. The contributions of different species in the distribution pattern of different metals was obtained by sequential extraction studies. When the metals concentrations were considered, factor analysis identifies two factors. Factor 1 is expected to be due to sulphide formation in sediments. The second factor might be expected to be due to organic contributions from plant litter and mangrove detritus. In anoxic conditions, when sulphide formation predominates, the free metal ion concentration in pore water is expected to be lower. Lower labile metal concentrations metal content in f7 and f8) in the pH based fractionation scheme also supports the results of factor analysis.

On considering, the metal concentrations and the station characteristics together, PCA identifies lateral additions as the principal component at stations 2, 3, 5 and 6. In the fractionation based on pH, higher residual metal concentrations were noticed. If mineralisation was the major process, labile metal concentrations are expected to be higher. Lower labile metal concentrations and the higher residual metal concentrations also support addition process. The principal component analysis, agrees with the results of speciation analysis.

5.2 The model:

Modelling is considered to be an approach or tool to recognize the system behaviour and to predict, if possible, the magnitude of modification in the system characteristics in similar systems. Models can be used for the prediction of the changes that will be brought in by changes in the processes that define the system also. Models can be represented in three ways – either as 1) a physical organization or representation of the characters and processes or 2) by a mathematical (now a days more often as a computer programme of the mathematical expression) expression which contains contributions from processes and the state functions or 3) a combination of both when the system is too complex and cannot be possible to express by any one of the other two. Selection of the model depends on the availability or possibility of obtaining data. In general modelling has the following steps.

1. Identification of all the system characteristics and processes
2. Verification and establishment of the relations between the observable parameters.
3. Development of the physical picture of the system in terms of observables and derivation of the mathematical expressions, development of computer programme if intended.
4. Testing of the model

Generally when a process based model is under consideration it can be done on two ways based on the following two basic approaches

1. The Steady State approach
2. The mass balance approach

The mass conservation under equilibrium conditions is the basis of mass balance approach. In this study the mass balance approach is used to define the model and the modeling is limited to two typical stations - the stations 2 and 3. Being a process based model, the behaviour and transport of metals in the sedimentary compartment has been used for modelling. Since the Sediment functioning as a sink and a source is our major consideration, transfer processes involving the sediments are important. Modelling is done by balancing the inflows and out flows of metals in sediments.

System Characteristics:

Station 2: It is an open mangrove site closer to the sea. Anthropogenic influences are maximum in this area. Vegetation and aqua cultural practices influences the inflow of contaminants. Salinity is observed to be maximum in pre monsoon and the minimum in monsoon. Water depth varies between 0 to 3m. The seasonal average values of the finer fraction varied from 52.71 %(monsoon) to 92.81% (post monsoon).

Station 3: It is not in direct contact with the costal waters. This protected mangrove forest is close to the centers of urbanization and industrialization. The maximum and the minimum salinity values were observed in pre monsoon and monsoon seasons respectively. In summer months, water depth is very low (<0.5m). Tidal influence is minimum in this area. Undecomposed litter is commonly noticed in mangrove sediments. Productivity is also comparatively higher in this area. Seasonal mean values of (silt +clay)% varied between 30.83 %(post monsoon) to 47.41%(pre monsoon).

Factor analysis between the metals has identified diagenesis, tidal action and lateral additions as the major processes controlling the distribution of metals. Diagenesis of organic matter only makes the metals available for other geochemical processes. Diagenesis can result in either positive (storage) or negative (releases) loading. The fate and behavior of metals also depends on the conditions available to the system. The following processes control the distribution of metals in sediments.

In flow

- Lateral additions (restricted to monsoon period)
- Plant litter
- Sea water
- Atmospheric precipitation

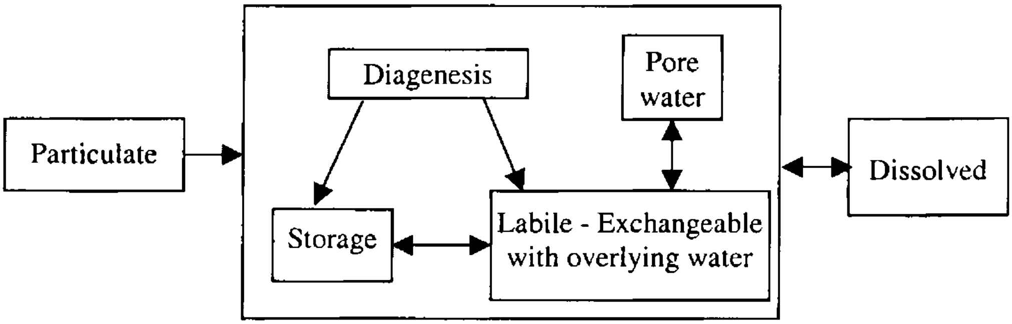
Out flow

- Sea water
- Biological uptake
- Storage

The input is through sea water. The out put is through, the dissolved metals or storage in sediments. Bioturbation is also important in the sedimentary compartment, but it is reflected in the dissolved and storage.

The physical representation of the model can be given as

Sediment Compartment



The analysis of the metal content in the different compartments indicates that major source of metal in the sediment is particulate. It is observed that the particulate metal concentrations were always higher than that in sediments (Table **5.3**)

Table 5.3.1 Loading character of metals – Station 2

Metal	Season	PM	SM	P M - S M	PM / SM
Cu	Pre mon	1024.1997	26.53	997.67	38.604
	Mon	241.46982	33.56	207.91	7.196
Fe	Pre mon	4234.9467	5.92	4229.02	714.88
	Mon	32978.373	94.04	32884.33	350.692
Mn	Pre mon	45.731707	211.64	-165.91	0.216
	Mon	268.55643	126.25	142.31	2.127
Zn	Pre mon	620.23628	110.19	510.04	5.629
	Mon	268.55643	100.45	168.1	2.673

Table 5.3.2 Loading character of metals – Station 3

Metal	Season	PM	SM	P M - S M	PM / SM
Cu	Pre mon	1085.13	12.52	1072.61	86.69
	Mon	420.07	17.33	402.74	24.23
Fe	Pre mon	6153.85	0.71	6153.14	8655.2
	Mon	809.52	17.39	792.13	46.56
Mn	Pre mon	385.98	56.73	329.25	6.8
	Mon	113.38	58.03	55.35	1.95
Zn	Pre mon	517.95	116.33	401.62	4.45
	Mon	231.45	119.24	112.21	1.94

The concentrations of metals in the core samples also indicate a geochemical loss of the metals during diagenesis. Such geochemical losses from the particulate matter also can lead to such an observation. But here the depth of the water column is too low (range: 0 – 3 m) that the possibility of geochemical loss during sedimentation will not be significant. Moreover, the benthic microbial population indicates a significantly high microbial activity and to a resultant high diagenesis which can lead to a heavy loss of the metals either through the direct transfer between the overlying water column and the sediment or through the pore water to the water column. Low water depth also results in faster sedimentation rate. The above considerations were found to be valid for both the stations and so in the present model consideration the input is limited to the addition through particulate matter. The difference between the sediment level and particulate matter is the out flow. The geochemical loss during the conversion of particulate metal to the sedimentary metal is quantified as percentage loss. Geo chemical loss = 100 – (SM/PM)*100. Geochemical loss is given in the table 5.4

When we go through the sediment depth, the variation from the surface level was found to be low. The analyses of the core data for geochemical reactivity (which can be obtained by the ratios in the different depths to the surface level) indicate that below the surface level the geochemical loss is very low. The values are given in Table **5.5** as the ratio to the surface value.

Table 5.4 Geochemical loss from the sediment

Geochemical Loss from surface sediment			
Metal	Season	Station 2	Station 3
Cu	Pre mon	97.41	98.85
	Mon	86.1	95.87
Fe	Pre mon	99.86	99.99
	Mon	99.71	97.85
Mn	Pre mon	-362.79	85.3
	Mon	52.99	48.82
Zn	Pre mon	82.23	77.54
	Mon	62.6	48.48

Table 5.5.1 Geo chemical reactivity - Station 2

Metal	Season	5-10/ 0-5	5-15/ 0-5	15-25/ 0-5	20-25/ 0-5
Fe	mon	0.986	0.947	0.875	0.579
	post mon	0.843	0.889	0.976	0.899
	pre mon	1.921	1.957	1.506	1.422
Cu	mon	0.913	0.913	0.755	0.607
	post mon	0.880	0.942	1.041	1.057
	pre mon	0.985	0.974	0.996	0.996
Mn	mon	0.913	0.913	0.755	0.607
	post mon	0.880	0.942	1.041	1.057
	pre mon	0.985	0.974	0.996	0.996
Zn	mon	1.185	1.187	0.820	0.686
	post mon	0.813	0.846	0.879	0.890
	pre mon	0.897	0.906	0.905	0.970

Table 5.5.2 Geo chemical reactivity - Station 3

Metal	Season	5 -10 / 0 - 5	5 -15 / 0 - 5	15 - 25 / 0 - 5	20 - 25 / 0 - 5
Fe	mon	1.023	1.185	0.710	0.569
	post mon	0.732	1.560	2.048	1.752
	pre mon	2.615	3.212	2.842	2.118
Cu	mon	1.108	1.104	0.600	0.499
	post mon	1.000	1.457	1.069	1.258
	pre mon	0.844	0.804	0.711	0.659
Mn	mon	0.671	0.802	0.542	0.474
	post mon	0.769	1.043	0.660	0.785
	pre mon	0.747	0.759	0.662	0.642
Zn	mon	0.735	0.701	0.416	0.280
	post mon	0.700	0.897	0.475	0.587
	pre mon	0.532	0.499	0.457	0.441

This is quite expected because the removal of metals from the sediment depths can take place only through pore water and the diffusion through pore water will generally be very low. Also the rate of diagenesis will not have significant impact on the removal of metals from the sediment depths. In other words the variation observed in the different depths of the sediments can only be due to the rate of metal transport through the pore water and the normal expressions of geochemical reactivity will not have much significance. The movement of the system that can be transported in the present systems can be represented as geochemical loss.

Though the geochemical loss indicates close similarity between the stations, significant seasonal variability is an issue that has to be considered seriously. The dynamicity of the environmental parameters has not been given due consideration while working out the geochemical loss. The dynamics of the chemical speciation within the sedimentary compartment along with the transport mechanisms at the sediment - water interface has to be examined in detail to apply this concept and model to other systems.

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Summary

Mangrove ecosystems act as a buffer between the land and the sea. Mangroves are ecologically important as they function as nutrient filters and recyclers, aid in flood water mitigation and help to protect coastal areas from sea water intrusion. Mangroves create unique ecological environments that support rich assemblages of species. They act as a nursery and breeding ground for fishes and prawns. Mangroves serve as natural sinks and filtration systems. Mangrove sediments are usually water logged and anoxic. High sulphate ion content and organic matter favour diagenesis and sulphide formation. Pyrite is the stabilized form of iron. Metals other than iron can also form insoluble sulphides or they can substitute for some of the iron in iron sulphides. Redox situations prevailing in the system has a major role in deciding the behavior and fate of metals in these coastal ecosystems. The thesis is an attempt to study the geochemical role of mangroves in retaining pollutants.

The system characters were identified only to understand the hydrographic and sedimentological parameters. Distribution of trace metals in different compartments of mangroves – plant tissues, water and sediment were determined. An investigation on the metal cycling helps to identify the biogeochemical processes controlling the accumulation and distribution of metals in mangroves. Metal concentrations in the sediment showed marked spatial variations. In sediments and plant tissues, iron was the most abundant metal and cadmium the least abundant. Between the stations, station 2 recorded the highest annual mean concentrations of Mn, Ni, Cr, Co and Fe. The highest annual mean values of Cu, Pb and Zn were noticed at station 6. Station 3 recorded the highest annual average concentration of cadmium. Variability in the heavy metal concentrations between mangrove sites could be due to the natural variability of the sediments or due to anthropogenic contamination. All the six stations exhibited elevated cadmium concentrations when compared with the black shale value. A well defined seasonal character is not observed in the distribution of trace metals in sediments. The metal content in sediment was well within the range reported for metals from other

mangroves of the world. They are also comparable with the metal content in adjacent estuarine sediments.

Metal content in plant tissues also showed spatial and interspecies variations. In the common plant species (*A. ilicifolious, A. officinalis and R.mucronata*) the distribution of metals follows the order: Fe > Mn > Zn > Co > Pb > Ni > Cr > Cd. The comparison of the metal content in plant tissues with that in sediment and water indicated that, generally the metal content in plant tissues are reflections of the metal concentration in sediments and water. But, this consideration can not be applied to all cases. Plants differ in their ability to accumulate trace metals. Growth conditions, nutrient status and respiration rate determine elemental uptake. The plant parts also show varying abilities to accumulate metals.

Pearson correlations among the metals were determined in different compartments of the system. In sediments, the correlations of trace metals with iron, organic carbon (%) and grain size were also determined. Only a few correlations are found for metals with Fe, silt and clay. This is against the conventional behavior observed in marine sediments. The variation from the normal expected character is attributed to the dynamic and fluctuating character of mangroves. Statistical significance of the observed variations in metal concentrations was also estimated.

Knowledge of how elements are combined with the sediment phase is of a great concern in understanding their biogeochemical transformations and ultimate fate. Metals bound to different phases will behave differently in the sedimentary and diagenetic environment. The speciation studies help to identify the different forms of metals in the environment. The environmental impact of a particular species is more important than the total metal concentration. The results of the modified Tessier's scheme showed that the residual fraction composed of detrital silicate minerals, resistant sulphides and refractory organics is an important carrier for all metals except copper. For copper, the major contributor was the organic fraction including sulphides. Copper showed a very high tendency to form organic complexes. Moderately reducing fraction made the lowest contribution to the total metal content. The contributions of the exchangeable and moderately reducing components were always less than 10 % of the total. The metals bound to the residual phase are unlikely to be reactive during sedimentation and diagenesis and thus pose little environmental nuisance. Therefore the labile metal concentrations are important in predicting bioavailability. Considering the labile and the non – labile metal content the six metals studied are grouped in to three. Group A (Cu, Pb) metals are retained as sulphides in anoxic sediments. Group B (Fe) metal is stabilized through mineralization as pyrite. Group C (Mn, Ni and Zn) metals are essential to plants and are found in higher concentrations in plant tissues. The source of these metals to sediments may be plant litter.

In natural aquatic systems, pH > 7 is not a rare situation. The releasing pattern of metals from sediments will be more evident if we consider the extractability at pH values varying from 8 to 2.The fractions leached at pH values of 6, 7 and 8 predicts the metal concentration available without any external modifications in the system. Measurable concentrations were leached at pH 6, 7 and 8. The sum of the metal content in f 6, f 7 and f 8 were in the order of Fe > Zn > Mn > Cu > Ni > Pb. The metal content in plant tissues also follows a similar distribution pattern. The exchangeable metal content in Tessier's scheme was in the order. Ni > Pb > Zn > Mn > Cu > Fe. The character of each metal varies with the species and the environmental conditions. Distribution pattern of each metal is different. For the metals Fe and Zn f 3 was the major contributor and f 5 made the highest contribution for Cu and Ni.The lowest contributing component for all the six metals studied were f 7 or f 8. The sum of the metal content in f 6, f 7 and f 8 was higher than the metal content in the exchangeable fraction of the Tessier's scheme. The residual metal concentrations in this scheme were also higher than that suggested by sequential extraction by the conventional Tessier's protocol. The difference might be due to the microbial nature of the redox reactions occurring in mangrove ecosystem, which can not be predicted by laboratory oxidation and reduction reactions.

Principal component analysis was attempted to identify the different processes operating in the system. For this we considered only the sedimentary compartment. The data on biogeoorganics and trace metals were subjected to factor analysis at stations 2 and 3 to understand their role in determining the system characteristics. Since organic carbon and grain size were identified as the major controls on system characteristics, monthly data on these parameters and metal concentrations are included in the factor analysis at stations 1, 4, 5 and 6. Factor analysis identifies diagenesis and lateral additions as the major processes occurring in mangrove sediments. Combination of these results with the speciation data suggests the dominance of lateral additions over diagenetic mineralization. Factor analysis between metals indicated sulphide formation and additions through organic detritus as major processes resulting in the storage of metals in mangrove sediments. Speciation data also supports this observation.

APPENDIX I A

STATION WISE MONTHLY DATA OF GENERAL HYDROGRAPHICAL PARAMETERS AND SEDIMENT CHARACTERISTICS

Parameter	stations	FEB'01	MARCH"01	APRIL"01	MAY'01	JUNE'01	JULY'01	SEPT'01	OCT'01	NOV'01	JAN'01	APR '03	SEPT' 03
Salinity (ppt)	1	22.90	17.65	15.42	14.20	0.32	1.40	12.27	5.17	6.45	24.65	23.61	14.14
	2	18.70	21.90	22.70	4.80	2.10	3.20	17.24	3.19	13.62	17.52	24.85	10.83
	3	19.60	17.97	14.80	3.50	3.20	2.30	9.63	3.21	25.67	16.96	15.53	12.81
	4	18.20	16.09	17.40	4.80	2.60	1.30	8.37	1.29	28.30	19.31	21.74	18.44
	5	22.70	21.20	19.90	12.50	6.90	11.96	21.19	8.10	4.99	21.80	11.80	22.13
	6	27.80	26.00	22.90	15.20	4.50	3.30	11.44	5.08	3.81	26.05	24.23	17.86
Alkalinity (m mol/l)	1	3.25	2.28	3.22	2.38	3.64	3.76	1.88	3.40	3.96	3.69	3.84	3.64
	2	3.64	2.04	2.21	2.38	1.28	1.36	1.72	0.20	1.56	1.89	2.66	1.56
	3	3.74	2.44	3.36	2.74	2.36	2.24	1.04	1.20	0.88	1.76	2.02	2.72
	4	3.00	3.56	4.40	1.48	4.36	3.80	2.96	3.72	3.18	3.52	4.00	3.18
	5	3.11	1.16	2.25	2.85	2.96	3.36	1.96	3.20	3.16	2.87	3.53	4.72
	6	1.75	1.60	2.18	1.91	2.76	2.60	1.24	1.60	1.76	0.48	1.92	2.88
pH	1	7.28	7.49	7.38	7.55	7.52	7.26	6.91	7.12	7.64	7.56	7.87	7.63
	2	7.90	7.80	7.90	7.85	7.80	7.75	7.60	7.01	7.36	7.42	7.92	8.12
	3	7.65	7.42	7.95	7.63	7.55	7.81	7.39	7.91	7.93	7.39	7.61	7.75
	4	7.67	7.72	7.43	7.58	7.46	7.65	7.48	8.07	7.76	7.68	7.2	7.92
	5	7.96	8.12	7.89	7.81	7.93	7.85	7.07	7.56	7.37	7.26	8.33	8.37
	6	8.61	8.50	8.50	8.30	8.25	7.46	7.69	7.52	7.63	7.82	8.29	7.89
Temperature °C	1	30	30.1	31	30	24	27.2	28.2	27.9	29.1	30.2	33.5	31.3
	2	30	30.1	30.8	30.5	23.8	27.6	28.5	29.4	30.1	29.7	32.1	30.8
	3	30.5	30.5	28.3	30	24.3	26	28.3	29.2	28.9	30.1	33.5	32.6
	4	30.5	30.5	28.7	23.5	26	24.2	28.3	30	30.1	32.5	33.5	33.2
	5	30.1	30	30.5	31	28.4	26.5	23.5	32	30	30.4	35.6	34.5
	6	30.3	31	31.5	31.1	32.1	26	28.5	29.3	30.3	30.2	33.4	32.3

APPENDIX I A Contd ...

Parameter	Stations	FEB'01	MARCH"01	APRIL"01	MAY'01	JUNE'01	JULY'01	SEPT'01	OCT'01	NOV'01	JAN'01	APR '03	SEPT' 03
Sand %	1	89.78	20.42	22.30	58.44	14.31	64.65	38.79	75.91	69.93	52.17	25.42	74.16
	2	49.78	30.87	18.73	8.62	46.75	65.33	29.80	11.71		2.67	25.28	7.90
	3	60.63	35.48	88.61	35.48	50.00	80.67	70.41	61.75		76.60	87.10	19.79
	4	87.22	87.22	86.31	90.52	58.98	82.25	49.31	89.74		82.89	74.86	91.80
	5	94.65	93.04	96.18	72.73	88.14	87.50	74.78	96.48	80.28	96.48	70.93	90.34
	6	59.09	72.12	22.63	47.42	88.66	48.98	31.90	26.11	83.14	37.30	48.33	51.63
Silt %	1	2.00	35.08	29.45	28.49	2.80	14.51	42.19	16.27	8.77	15.24	35.45	10.21
	2	0.68	45.37	31.79	48.28	22.02	24.30	31.01	21.47		47.86	33.90	64.85
	3	41.65	52.69	3.68	52.69	45.14	8.53	9.02	4.58		14.94	9.92	61.58
	4	31.79	13.15	4.30	6.72	37.15	6.88	1.72	2.82		7.33	12.07	2.00
	5	0.85	1.48	0.96	12.65	7.63	4.82	13.93	1.10	10.57	1.10	25.70	2.79
	6	33.72	13.15	60.65	24.44	3.28	27.55	23.09	17.38	10.26	38.06	13.22	40.56
Clay %	1	7.54	44.50	48.26	3.08	40.64	20.84	19.02	7.82	21.30	32.59	39.13	15.63
	2	8.58	23.77	49.48	43.04	31.24	10.37	39.19	66.82		49.47	40.82	27.26
	3	7.58	11.83	7.72	11.83	4.87	10.80	20.58	33.67		8.47	2.98	28.64
	4	5.54	14.73	9.33	2.76	3.87	10.87	48.96	7.45		9.78	13.07	6.20
	5	4.50	5.50	2.86	4.63	4.24	7.68	11.29	2.42	9.15	2.42	3.38	6.87
	6	7.19	14.73	16.72	28.14	8.07	23.47	45.01	56.51	6.60	24.65	38.44	7.81
OC %	1	0.23	1.41	1.01	0.72	0.51	0.96	1.61	0.55	0.85	1.04	1.98	1.12
	2	1.98	1.55	2.24	1.51	1.74	2.61	2.70	2.86	2.66	2.88	1.05	1.06
	3	2.75	1.52	2.14	1.59	2.54	2.24	4.80	2.33	1.87	2.04	2.64	3.93
	4	0.32	0.73	1.02	0.80	0.61	0.46	0.29	0.61	0.73	0.29	1.45	0.93
	5	2.85	2.37	0.69	0.69	1.67	1.34	1.31	2.33	0.61	1.10	1.58	0.96
	6	5.11	6.63	5.26	4.92	6.62	5.46	7.40	8.62	3.64	6.01	6.15	6.58

APPENDIX I B
SEASONAL VARIATION OF HYDROGRAPHICAL PARAMETERS AND SEDIMENT CHARACTERISTICS

Parameter	Stations	Pre Mon	Mon	Post mon
pH	1	7.43	7.23	7.44
	2	7.86	7.72	7.26
	3	7.66	7.58	7.74
	4	7.60	7.53	7.84
	5	7.95	7.62	7.40
	6	8.48	7.80	7.66
Temperature0 c	1	30.3	26.5	29.1
	2	30.4	26.6	29.7
	3	29.8	26.2	29.4
	4	28.3	26.2	30.9
	5	30.4	26.1	30.8
	6	31.0	28.9	29.9
Salinity ppt	1	17.54	4.66	12.09
	2	17.03	7.51	11.44
	3	13.97	5.04	15.28
	4	14.12	4.09	16.30
	5	19.08	13.35	11.63
	6	22.98	6.41	11.65
Alkalinity m mol/l	1	2.78	3.09	3.68
	2	2.57	1.45	1.22
	3	3.07	1.88	1.28
	4	3.11	3.71	3.47
	5	2.34	2.76	3.08
	6	1.86	2.20	1.28

APPENDIX I B Contd....

stations	OC %			Stations	Sand %		
	pre Mon	Mon	Post Mon		Pre Mon	Mon	Post mon
1	0.84	1.03	0.82	1	47.73	39.25	66.00
2	1.82	2.35	2.80	2	27.00	47.29	7.19
3	2.00	3.19	2.08	3	55.05	67.02	69.17
4	0.72	0.46	0.54	4	87.82	63.52	86.32
5	1.65	1.44	1.35	5	89.15	83.47	91.08
6	5.48	6.50	6.09	6	50.32	56.51	48.85

stations	Silt %			stations	Clay %		
	Pre Mon	Mon	Post mon		Pre Mon	Mon	Post mon
1	23.75	19.83	13.42	1	25.84	26.84	20.57
2	31.53	25.78	34.67	2	31.22	26.93	58.15
3	37.68	20.90	9.76	3	9.74	12.08	21.07
4	13.99	15.25	5.07	4	8.09	21.23	8.61
5	3.99	8.79	4.26	5	4.37	7.74	4.67
6	32.99	17.97	21.90	6	16.70	25.52	29.25

APPENDIX II A

MONTHLY VARIATION OF TOTAL TRACE METAL CONCENTRATIONS IN SEDIMENTS (for most metals μg/g dry weight, for iron mg/g)

Metal	Stations	FEB'01	MARCH"01	APRIL"01	MAY'01	JUNE'01	JULY'01	SEPT'01	OCT'01	NOV'01	JAN'01	APR '03	SEPT' 03
Cadmium	1	2.68	3.69	2.42	1.70	0.00	1.09	4.77	4.02	2.97	4.24	3.61	0.29
	2	5.26	4.19	3.84	2.94	3.28	1.07	4.66	3.29	2.05	4.23	2.57	3.22
	3	2.73	1.60	2.24	2.99	12.82	2.97	4.81	0.10	3.33	1.69	1.22	1.81
	4	0.64	2.16	2.84	2.52	1.62	1.91	0.09	0.00	1.67	0.69	0.00	0.34
	5	0.17	1.81	1.94	1.67	0.27	2.02	3.64	2.99	2.62	1.56	0.94	0.00
	6	3.87	2.39	3.22	3.77	1.79	3.37	0.00	5.00	2.01	4.36	3.98	1.96
Chromium	1	58.71	163.72	45.86	57.08	39.48	79.62	145.16	77.84	69.57	69.79	174.06	57.50
	2	244.01	169.13	160.45	184.94	168.59	138.26	94.97	177.55	178.93	218.65	89.58	147.77
	3	44.86	31.74	31.55	44.04	105.10	56.62	176.55	37.60	98.58	1.91	36.83	45.75
	4	25.13	71.09	68.59	35.37	43.19	42.74	28.10	18.35	47.41	50.39	58.69	39.03
	5	38.31	32.67	29.77	46.32	44.91	60.93	49.26	67.39	58.02	48.44	51.05	37.64
	6	116.96	55.38	136.08	128.26	84.16	94.73	87.48	133.68	45.12	121.50	91.28	88.35
Cobalt	1	6.52	58.05	13.23	10.64	14.99	16.38	68.16	9.34	15.52	19.04	23.64	41.53
	2	58.41	35.21	37.15	37.34	26.78	50.91	60.28	27.61	31.19	40.37	42.64	36.03
	3	6.17	2.31	1.44	3.57	13.17	3.99	25.61	12.89	9.69	2.64	13.74	30.16
	4	0.00	5.44	7.26	1.88	0.26	2.46	1.84	1.79	4.59	6.44	6.38	25.14
	5	0.60	0.00	0.00	1.71	2.75	4.60	1.70	2.84	3.30	4.37	3.65	16.89
	6	16.23	3.98	15.76	19.50	19.21	23.13	16.08	19.13	4.01	16.17	21.68	20.05
Copper	1	6.50	34.94	11.80	8.16	6.03	9.22	32.38	10.26	11.09	11.29	24.09	13.80
	2	30.06	28.99	30.64	30.86	28.73	34.00	39.95	33.97	27.90	27.90	26.53	33.56
	3	15.30	8.05	6.36	11.48	16.99	10.89	34.49	13.88	0.13	0.13	12.52	17.33
	4	2.79	8.25	7.07	6.08	4.76	5.05	3.34	3.65	5.08	5.08	16.32	8.58
	5	3.31	2.88	1.16	2.66	3.81	6.69	3.06	5.12	2.64	2.64	3.70	2.81
	6	37.74	34.77	168.69	174.52	177.51	132.16	243.32	200.15	139.98	139.98	149.96	171.78

Metal	Stations	FEB'01	MARCH"01	APRIL"01	MAY'01	JUNE'01	JULY'01	SEPT'01	OCT'01	NOV'01	JAN'01	APR '03	SEPT' 03
Iron	1	15.07	92.54	25.61	19.79	17.55	7.91	0.59	24.74	32.05	15.83	5.05	13.32
	2	60.46	86.26	62.53	35.78	72.84	41.19	44.63	35.69	21.13	54.32	5.92	94.04
	3	9.15	7.05	6.50	13.46	30.97	13.96	21.89	7.57	18.24	15.50	0.71	17.39
	4	3.75	22.89	21.83	13.73	11.97	10.66	7.05	27.39	10.12	13.85	2.88	15.18
	5	10.18	3.73	1.69	2.68	3.48	1.20	7.82	95.44	4.09	6.00	0.59	6.80
	6	46.10	6.86	10.86	0.53	30.76	4.25	7.23	25.17	9.52	79.38	2.72	40.16
Lead	1	10.32	43.47	18.29	10.80	38.32	21.49	38.04	18.38	19.08	20.07	267.70	71.28
	2	41.86	47.06	46.37	48.57	47.16	19.08	50.39	26.77	44.27	44.14	211.64	126.25
	3	17.62	10.64	10.56	17.83	29.27	20.80	35.44	11.37	26.57	0.73	56.73	58.03
	4	5.11	13.94	14.00	12.04	11.40	9.55	9.46	18.13	11.78	58.21	61.97	21.30
	5	12.36	11.41	5.06	12.74	8.80	14.09	18.18	15.77	14.16	36.44	22.13	23.07
	6	107.68	42.27	114.12	125.38	11.69	121.90	114.77	144.36	40.98	13.69	131.97	105.82
Manganese	1	89.80	153.91	70.36	54.00	12.16	71.67	149.45	86.53	118.70	82.40	62.87	34.42
	2	241.38	318.16	229.36	325.98	223.18	110.29	203.86	118.71	152.04	112.17	64.56	98.10
	3	66.55	31.43	28.00	57.81	88.57	71.35	220.81	54.65	121.04	51.32	10.19	24.02
	4	12.44	43.62	39.63	34.24	28.06	30.02	23.56	18.85	31.89	21.98	27.18	17.36
	5	43.55	36.56	15.98	12.22	25.25	36.08	30.05	28.04	23.92	20.76	7.73	11.73
	6	174.42	171.95	186.35	177.56	180.24	166.13	191.13	216.18	46.57	148.22	32.04	57.57
Nickel	1	8.38	37.58	27.39	19.59	18.59	18.53	10.29	77.79	27.39	28.96	38.04	18.38
	2	70.39	70.60	75.64	78.52	66.23	81.67	77.31	89.97	69.26	71.49	50.39	26.77
	3	16.53	75.90	7.43	17.07	10.17	10.02	22.06	22.22	28.55	1.76	35.44	11.37
	4	5.20	6.65	16.23	12.30	10.74	8.75	8.70	8.03	10.60	14.50	9.46	18.13
	5	72.91	6.59	3.08	4.31	39.97	11.09	67.86	18.84	15.68	7.48	18.18	15.77
	6	10.32	15.87	45.92	45.39	36.35	37.61	21.46	51.28	2.99	41.87	114.77	144.36
Zinc	1	26.22	103.34	23.14	20.60	20.25	33.57	75.16	25.18	29.59	30.77	71.91	15.82
	2	102.90	72.95	35.55	103.39	125.45	101.27	152.66	102.60	121.70	149.39	110.19	100.45
	3	116.90	122.89	104.94	75.37	108.35	131.03	210.39	114.42	230.41	238.48	116.33	119.24
	4	153.43	61.24	29.53	19.30	21.88	21.37	14.71	19.08	21.69	14.02	50.54	10.42
	5	20.37	38.37	3.88	5.98	12.62	14.33	11.88	6.90	8.66	9.38	10.80	11.13
	6	86.69	121.19	301.96	304.51	254.63	219.96	258.28	439.70	61.17	229.72	178.22	129.21

APPENDIX II B

TRACE METAL CONCENTRATIONS IN DIFFERENT SPECIES OF MANGROVE PLANTS (μg/ g DRY WEIGHT)

Stations	Species	CADMIUM			CHROMIUM		
		L	S	R	L	S	R
1	Ac	0.61	0.43	0.47	0.06	1.7	5.61
	Av	0.31	ND	0.62	0.98	1.89	2.47
	R m	0.47	ND	0.83	1.17	14.37	4.54
	B c	0.64	0.65	0.39	2.66	0.69	2.23
	A co	0.87	0.28	3.51	2.07	2.08	2.26
2	Ac	0.54	0.38	1.63	0.12	1.53	10.21
	Av	2.87	1.59	0.02	2.17	0.88	1.9
	R m	0.53	1.5	1.08	0.05	2.86	8.37
	E a	2.52	3.22	3.51	0.02	2.17	2.26
	C i	0.78	0.8	0.36	0.67	2.19	2
3	Ac	0.39	ND	ND	0.41	1.27	1.61
	Av	0.35	0.34	1.45	0.05	1.7	4.41
	R m	ND	ND	0.63	1.8	0.68	0.85
4	Ac	0.83	0.25	0.29	1.41	0.59	11.43
	Av	0.98	0.94	0.42	1.26	0.48	2.54
	R m	0.57	0.51	0.43	1.72	3.47	7.54
	C i	0.13	0.94		3.7	9.6	
5	Ac	0.25	0.4	0.02	3.47	1.78	1.19
	Av	0.55	0.92	0.91	4.83	5.47	5.3
	R m	0.79	0.08	0.87	1.41	2.21	1.43
	B c	1.46	1.35	0.9	2.79	1.89	7.49
	E a	1.53	0.89	1.35	2.56	1.64	2.41
	A co	0.46	0.21	0.09	1.63	0.8	2.63
	C i	0.24	0.8	0.98	3.36	3.94	4.13
6	Ac	2.98	0.78	3.61	1.44	0.67	2
	Av	0.53	0.98	0.42	0.05	1.12	2.68
	R m	1.11	0.3	ND	0.61	2.24	3.97
	B g	0	0.58	ND	2.58	0.37	1.51
	E a	0.02	0.45	0.72	0.86	1.26	2.18

Stations	Species	COBALT			COPPER		
		L	S	R	L	S	R
1	Ac	12.97	5.89	41.27	8.44	6.92	9.35
	Av	13.6	32.21	6.36	4.03	10.36	11.84
	R m	9.26	40.2	5.44	1.21	2.09	2.85
	B c	3.74	ND	8.46	3.21	2.44	4.85
	A co	3.76	11.37	16.87	3.18	7.17	15.45
2	Ac	1.45	ND	7.22	5.19	3.61	3.98
	Av	0.92	5.57	37.44	2.49	2.06	6.38
	R m	0	8.11	1.36	1.73	1.21	4.82
	E a	4.01	2.33	6.87	6.18	17.71	21.364
	C i	4.49	7.27	4.26	13.43	16.56	22.21
3	Ac	5.34	7.38	10.22	10.06	9.28	10.51
	Av	10.97	10.71	21.31	6.85	5.74	7.27
	R m	7.75	26.76	3.55	2.33	5.96	6.65
4	Ac	9.7	7.95	27.45	8.01	12.45	6.41
	Av	35.53	26.21	38.55	9.59	5.91	6.15
	R m	11.96	0.36	1.52	1.7	1.96	2.91
	C i	3.83	6.31		11.02	9.23	
5	Ac	46.72	ND	36.39	6.21	7.29	20.8
	Av	0	2.77	5	4.76	8.05	8.39
	R m	5.04	7	2.97	1.53	7.61	8.21
	B c	1.31	0.45	4.04	8.76	3.11	4.53
	E a	32.74	11.78	12.53	8.11	3.58	9.83
	A co	1.25	8.63	19.7	3.53	3.71	2.96
	C i	ND	7.43	8.46	10.07	17.43	24.15
6	Ac	3.53	0.367	42.6	9.47	13.43	22.21
	Av	ND	2.93	42.92	1.73	9.36	13.97
	R m	4.11	2.62	9.12	4.91	2.72	2.71
	B g	34.62	5.89	13.09	4.16	4.35	24.7
	E a	5.59	12.56	50.23	6.57	8.69	10.65

Stations	Species	IRON			LEAD		
		L	S	R	L	S	R
1	Ac	213.2	294.83	2659.2	0.55	0.49	41.06
	Av	78.57	168.96	210.67	1.72	33.4	1.92
	R m	59.93	26.17	296.57	1.89	29.7	2.65
	B c	57.11	153.93	396.17	0.1	34.42	0.88
	A co	92.08	75.07	106.76	1.21	0.46	2.15
2	Ac	92.17	137.71	1385.88	3.77	1.11	8.16
	Av	9.61	190.67	301.93	2.93	1.66	0.98
	R m	20.35	35.23	19.15	1.21	2.22	5.73
	E a	61.76	80.55	295.54	1.47	3.43	2.15
	C i	58.21	212.59	266.66	1.91	3.11	1.03
3	Ac	196.54	30.79	66.35	12.19	6.81	20.68
	Av	79.19	55.1	196.81	18.08	8.99	14.49
	R m	28.96	96.53	947.41	14.05	4.35	20.1
4	Ac	256.51	50.68	1783.38	1.96	0.55	0.23
	Av	278.23	595.44	208.54	0.44	0.33	2.45
	R m	136.79	151	550.97	0.69	1.36	1.36
	C i	239.44	224.22		2.48	2.95	
5	Ac	296.72	188.48	71.83	36.75	4.39	3.12
	Av	15.87	1070.34	367.35	4.09	2.31	0.07
	R m	65.46	61.69	72.54	3.82	1.38	1.34
	B c	74.73	39.1	578.48	4.72	1.54	1.12
	E a	6.21	309.84	497.3	4.44	0.41	0.714
	A co	103.81	29.89	411.04	0.48	1.33	0.12
	C i	25.29	210.56	287.66	4.36	4.57	5.61
6	Ac	79.32	58.21	266.66	4.5	1.91	3.03
	Av	20.35	126.04	49.41	1.21	1.05	1.95
	R m	203.97	65.82	180.79	8.39	2.28	2.11
	B g	165.41	107.18	141.12	6.14	3.45	3.39
	E a	105.36	145.23	174.26	0.65	0.98	2.84

		MANGANESE			NICKEL		
Stations	Species	L	S	R	L	S	R
1	Ac	7.86	48.19	72.69	5.74	5.06	20.51
	Av	32.24	17.76	77.69	ND	9.84	4.9
	R m	91.96	43.11	21.67	0.91	10.48	3.26
	B c	86.87	8.38	75.63	6.42	29.85	7.01
	A co	35.68	6.94	96.91	5.65	5.09	9.73
2	Ac	86.78	31.14	39.77	3.65	2.7	7.74
	Av	71.34	41.76	75.89	3.24	1.21	1.89
	R m	36.44	34.88	9.15	2.87	2.83	4.38
	E a	86.84	40.44	96.91	4.86	5.76	9.73
	C i	6.61	19.9	4.84	0.57	5.94	16.73
3	Ac	25.91	14.42	19.92	4.83	2.16	0.18
	Av	39.88	17.07	36.83	3.41	1.93	7.3
	R m	30.29	51.51	12.24	3.73	3.73	1.24
4	Ac	6.32	38.54	97.85	5.65	7.54	3.84
	Av	125.97	17.39	23.08	6.71	6.22	7.36
	R m	5.41	5.29	10.74	6.3	9.08	4.44
	C i	12.98	119.04		12.71	2.8	
5	Ac	15.67	74.46	18.54	12.87	2.96	5.56
	Av	69.68	27.17	9.8	4.95	3.81	4.47
	R m	35.89	15.89	11.4	3.51	1.7	1.54
	B c	53.79	12.73	15.05	5.38	5.24	2.94
	E a	59.32	25.73	8.27	4.46	4.97	5.56
	A co	26	4.44	3.74	2.23	1.56	5.21
	C i	38.09	17.9	21.67	5.49	5.94	15.78
6	Ac	70.48	6.61	23.654	3.48	4.489	5.73
	Av	36.44	36.32	13.36	2.87	5.77	0.56
	R m	92.32	69.53	13.31	2.85	2.3	1.36
	B g	16.19	28.29	16.99	1.78	2.79	0.74
	E a	65.23	87.65	101.88	2.18	3.45	4.57

Stations	Species	ZINC		
		L	S	R
1	Ac	66.38	17.62	10.31
	Av	22.67	23.6	31.59
	R m	6.06	2.63	3.02
	B c	2.82	5.09	3.95
	A co	8.52	11.13	56.33
2	Ac	56.53	20.79	26.71
	Av	31.6	22.28	31.09
	R m	7.64	10.41	33.12
	E a	48.2	34.53	56.33
	C i	17.18	36.88	19.74
3	Ac	135.58	68.56	23.57
	Av	41.96	30.72	80.51
	R m	7.74	17.05	8.92
4	Ac	78.88	24.18	31.54
	Av	32.67	9.65	26.16
	R m	3.17	2.84	8.4
	C i	140.95	50.97	
5	Ac	10.41	64.2	25.31
	Av	25.55	26.95	20.92
	R m	12.09	11.17	16
	B c	14.87	7.09	20.73
	E a	61.12	11.77	14.99
	A co	13.22	13.78	7.21
	C i	20.29	32.88	36.89
6	Ac	30.38	17.18	19.74
	Av	7.64	25.05	21.09
	R m	12.59	4.61	5.77
	B g	5.16	6.48	26.66
	E a	33.41	11.25	65.36

APPENDIX II C
METAL CONCENTRATIONS IN WATER

Dissoved trace metal concentrations (μg/l)

metal	stations	pre mon	mon	metal	stations	pre mon	mon	metal	stations	pre mon	mon
Cd	1	0.01	0.31	Cu	1	0.57	27.93	Ni	1	12.34	3.76
	2	0.09	0.15		2	5.10	16.84		2	7.82	14.63
	3	0.14	1.04		3	3.22	14.40		3	1.35	6.41
	4	0.39	0.15		4	38.04	1.32		4	0.73	0.27
	5	0.18	0.69		5	5.21	12.48		5	1.73	9.15
	6	0.37	0.10		6	4.35	25.00		6	2.98	5.89
Co	1	0.10	0.14	Fe * 1000	1	57.25	17.25	Pb	1	0.91	4.25
	2	0.02	0.08		2	91.50	18.50		2	1.42	2.23
	3	0.11	0.06		3	21.75	75.63		3	3.69	8.44
	4	0.02	0.00		4	10.25	47.50		4	1.93	0.01
	5	0.01	0.10		5	99.25	35.00		5	0.24	0.56
	6	0.01	0.09		6	9.00	5.00		6	1.04	8.84
Cr	1	0.23	0.55	Mn	1	0.56	8.84	Zn	1	0.81	89.38
	2	0.32	0.07		2	5.16	1.89		2	16.51	11.15
	3	0.41	49.58		3	0.64	30.50		3	3.45	28.73
	4	0.28	0.24		4	1.64	3.38		4	12.69	2.47
	5	0.76	11.13		5	0.40	5.03		5	0.79	5.69
	6	0.20	13.09		6	1.74	1.05		6	15.23	0.69

Particulate trace metal concentrations(μg/l)

metal	stations	pre mon	mon	metal	stations	pre mon	mon	metal	stations	pre mon	mon
Cd	1	0.15	0.80	Cu	1	12.41	6.68	Ni	1	8.33	1.21
	2	0.23	0.41		2	26.88	4.60		2	20.15	1.24
	3	0.50	0.49		3	6.35	5.65		3	2.27	2.29
	4	0.53	0.82		4	13.79	4.07		4	10.43	0.34
	5	0.46	0.32		5	5.02	6.01		5	0.94	2.28
	6	0.70	0.90		6	5.41	5.53		6	1.20	2.16
Co	1	0.17	0.28	Fe * 1000	1	72.62	70.28	Pb	1	3.22	2.80
	2	1.12	0.09		2	111.13	628.24		2	4.15	2.31
	3	0.05	0.01		3	36.00	10.89		3	2.13	1.00
	4	0.21	0.17		4	88.58	35.08		4	1.44	2.57
	5	0.26	0.17		5	13.74	11.26		5	3.15	2.19
	6	0.34	0.06		6	2.81	12.36		6	1.14	2.73
Cr	1	2.64	2.60	Mn	1	4.73	4.63	Zn	1	5.82	5.67
	2	4.10	0.91		2	1.20	5.12		2	16.28	5.12
	3	0.77	0.58		3	2.26	1.53		3	3.03	3.11
	4	4.55	1.52		4	4.44	4.45		4	5.73	2.13
	5	0.73	1.32		5	9.62	6.54		5	1.27	0.89
	6	1.95	0.16		6	4.14	0.03		6	11.14	13.88

APPENDIX III A
METAL CONCENTRATIONS IN DIFFERENT FRACTIONS EXTRACTED USING CONVENTIONAL TESSIER'S PROCEDURE (μg/g)

MANGANESE

Seasons	Stations	Mn 1	Mn 2	Mn 3	Mn 4	Mn 5
Pre monsoon '01	1	3.586	1.900	6.257	6.591	73.682
	2	5.883	3.462	3.812	30.012	235.552
	3	1.805	0.035	3.900	28.146	12.062
	4	2.125	1.054	2.404	3.294	23.605
	5	0.538	0.099	7.022	12.507	6.910
	6	11.558	1.914	5.336	55.670	103.093
Monsoon '01	1	9.637	4.316	16.900	13.872	71.034
	2	21.185	16.646	2.817	22.794	115.669
	3	0.597	0.000	2.712	34.924	88.675
	4	2.975	1.433	3.488	6.505	12.812
	5	2.292	0.561	2.186	3.125	22.295
	6	19.447	5.194	5.855	49.494	99.171
Post Monsoon '01	1	8.648	6.759	12.674	17.989	49.810
	2	18.714	4.895	0.000	9.709	56.932
	3	0.506	0.000	1.785	24.592	32.120
	4	1.725	0.936	2.259	4.658	14.661
	5	3.663	1.054	1.470	3.954	14.101
	6	12.144	6.851	5.109	49.563	63.320
Pre Monsoon '03	1	14.120	18.961	2.092	52.246	280.278
	2	1.805	0.280	4.142	28.416	176.998
	3	0.321	0.148	1.796	14.074	40.389
	4	1.924	0.519	3.001	5.229	51.291
	5	0.392	0.370	1.569	2.229	17.569
	6	9.166	1.003	6.779	22.958	92.065
Monsoon '03	1	6.080	0.253	4.194	34.454	26.294
	2	15.901	8.920	0.976	21.471	75.733
	3	0.373	0.164	0.044	41.942	15.505
	4	0.821	0.283	3.962	5.188	11.050
	5	0.564	0.305	2.098	2.682	17.424
	6	10.115	7.357	5.663	45.699	36.985

COPPER

Seasons	Stations	Cu 1	Cu 2	Cu 3	Cu 4	Cu 5
Pre monsoon '01	1	0.148	0.181	2.4	10.753	1.868
	2	0.365	0.104	3.191	3.343	23.133
	3	0.291	0.128	2.961	6.146	0.767
	4	0.367	0.226	0.575	4.679	0.199
	5	0.317	0.145	0.785	0.769	0.486
	6	3.008	1.252	1.283	59.407	38.978
Monsoon '01	1	0.058	0.085	0.188	7.254	8.292
	2	0.313	0.342	0.543	10.71	22.317
	3	0.291	0.024	5.623	12.835	2.015
	4	0.075	0.007	0.369	3.618	0.313
	5	0.276	0.258	0.69	2.267	1.029
	6	3.008	1.403	68.06	104.268	7.639
Post Monsoon '01	1	0.321	0.238	4.973	4.973	0.373
	2	0.305	0.3	0	8.043	20.661
	3	0.215	0.219	2.688	8.501	0.766
	4	0.206	0.123	1.781	0.47	1.056
	5	0.1	0.226	0.825	0.814	1.607
	6	0.295	0.571	35.678	69.163	28.293
Pre Monsoon '03	1	0.305	0.3	0	8.043	15.439
	2	0.261	0.205	2.118	6.185	17.762
	3	0.245	0.158	4.832	6.44	0.842
	4	0.181	0.118	2.169	5.729	8.125
	5	0.174	0.174	1.792	1.382	0.18
	6	4.626	0.92	2.536	32.339	109.538
Monsoon '03	1	0.193	0.075	2.927	9.563	1.044
	2	0.463	0.154	1.366	16.601	14.973
	3	0.431	0.013	0.262	13.335	3.293
	4	0.585	0.019	2.816	4.49	0.669
	5	0.427	0.122	1.19	0.195	0.872
	6	2.979	0.616	53.086	70.095	45.007

NICKEL

Seasons	Stations	Ni 1	Ni 2	Ni 3	Ni 4	Ni 5
Pre monsoon '01	1	2.233	0.367	3.21	4.572	12.855
	2	2.056	0	2.249	15.267	54.213
	3	2.002	0.528	5.602	12.17	8.939
	4	1.598	0.589	0.478	3.267	4.164
	5	1.975	2.709	0.947	9.405	6.683
	6	3.236	2.76	3.712	13.206	6.459
Monsoon '01	1	1.467	2.433	2.54	8.264	1.098
	2	0.604	0.931	2.62	8.88	62.038
	3	1.819	2.894	1.934	3.463	3.972
	4	1.49	2.583	1.23	2.847	1.248
	5	1.148	2.764	0.276	3.783	31.668
	6	2.09	3.589	4.381	11.468	10.281
Post Monsoon '01	1	2.163	2.8	0.549	7.877	31.322
	2	2.958	3.294	0	5.181	65.474
	3	1.629	2.228	1.418	8.194	4.044
	4	1.818	2.044	0.789	2.294	4.099
	5	0.065	0.758	0.276	3.693	9.21
	6	0.648	0.779	4.616	10.538	15.466
Pre Monsoon '03	1	0.835	1.135	0	9.213	51.692
	2	1.814	2.356	2.673	7.706	50.015
	3	2.179	2.863	1.046	3.215	0.883
	4	2.345	2.742	1.018	5.719	15.356
	5	2.024	1.516	0.606	2.514	1.066
	6	2.042	2.497	4.838	11.966	10.699
Monsoon '03	1	2.069	2.932	1.224	14.825	13.37
	2	0.79	1.489	1.53	13.545	80.744
	3	1.915	2.048	0.262	10.554	9.245
	4	1.571	2.165	3.476	5.113	5.041
	5	0.909	2.921	0.025	2.936	4.943
	6	2.674	2.827	3.206	5.614	43.245

LEAD

Seasons	Stations	Pb 1	Pb 2	Pb 3	Pb 4	Pb 5
Pre monsoon '01	1	0.619	0	1.619	6.857	11.624
	2	1.43	1.085	0.69	8.482	34.281
	3	1.183	0.592	2.602	7.357	2.428
	4	0.974	1.151	2.524	4.25	2.374
	5	2.129	0	0.045	6.433	1.784
	6	4.81	1.503	8.918	53.807	28.326
Monsoon '01	1	1.342	1.744	0.581	6.172	22.776
	2	1.965	0.608	0.561	3.369	32.374
	3	0.86	0.86	1.194	4.68	20.91
	4	1.838	0.519	1.226	4.977	0.000
	5	1.469	1.291	1.959	3.739	5.232
	6	4.543	1.009	1.262	36.697	39.276
Post Monsoon '01	1	0.673	0.518	0.569	4.554	12.86
	2	1.581	0	0.816	1.53	34.464
	3	0.97	0.295	0.886	5.485	5.256
	4	0.245	0.735	1.617	3.038	23.739
	5	1.957	0.703	1.462	2.011	15.991
	6	1.403	1.016	16.643	40.254	7.025
Pre Monsoon '03	1	1.425	1.222	0.305	4.479	30.021
	2	1.586	0.606	0.653	5.411	34.287
	3	0.97	0.153	1.225	4.593	6.992
	4	1.812	0.832	0.196	4.7	10.672
	5	2.095	0.981	0.579	2.229	5.569
	6	1.518	2.575	2.759	15.452	89.027
Monsoon '03	1	1.97	0	1.173	42.249	16.925
	2	1.271	0.908	1.226	3.722	21.697
	3	1.51	1.111	1.199	7.111	0.551
	4	1.226	0.409	0.33	1.207	1.901
	5	0	0	1.321	2.845	15.108
	6	2.758	0.788	9.652	5.909	27.676

IRON

Seasons	Stations	Fe 1	Fe 2	Fe 3	Fe 4	Fe 5
Pre monsoon '01	1	6.514	21.835	18.875	371.211	37832.565
	2	8.317	11.818	712.764	963.371	59559.730
	3	6.322	8.486	450.197	841.815	7733.180
	4	4.332	2.078	368.173	213.307	14961.110
	5	5.111	15.21	391.711	674.779	3484.189
	6	10.717	8.408	275.546	2274.904	13518.425
Monsoon '01	1	2.16	13.98	696.576	568.674	7398.610
	2	15.016	39.685	72.565	402.452	52354.282
	3	3.01	2.417	268.403	1077.813	20922.357
	4	4.022	3.267	306.454	346.382	9232.875
	5	5.349	9.807	211.52	196.831	3742.493
	6	2.038	43.767	539.662	2078.698	11413.835
Post Monsoon '01	1	4.071	15.56	455.411	516.892	23213.066
	2	7.151	2.548	314.674	269.239	36453.388
	3	3.294	2.938	226.506	502.211	13034.051
	4	0.048	12.345	130.996	146.629	16825.982
	5	6.093	117.787	596.674	135.783	34319.663
	6	34.34	58.825	552.427	1705.179	35673.229
Pre Monsoon '03	1	7.851	48.452	345.472	556.562	4092.663
	2	1.741	9.029	120.063	585.947	5207.220
	3	1.172	3.828	551.041	153.801	1.158
	4	2.421	8.391	150.806	1951.86	765.522
	5	2.98	21.141	359.41	85.317	125.152
	6	3.363	5.034	399.137	442.137	1870.329
Monsoon '03	1	2.531	4.402	16.514	123.855	13172.698
	2	9.499	36.739	208.715	993.645	92789.402
	3	2.703	6.551	513.06	262.882	16602.804
	4	0.69	3.582	88.199	257.334	14831.195
	5	2.761	20.207	439.781	121.82	6218.431
	6	2.546	17.703	786.535	1190.636	38158.580

ZINC

Seasons	Stations	Zn 1	Zn 2	Zn 3	Zn 4	Zn 5
Pre monsoon '01	1	0.095	0.119	5.229	5.167	32.713
	2	0.168	0.005	5.286	25.504	47.734
	3	2.209	0.207	39.286	49.793	13.532
	4	1.151	0.677	7.154	2.24	54.654
	5	0.036	0	4.186	10.022	2.905
	6	37.394	15.696	83.961	63.375	3.163
Monsoon '01	1	0	0.063	2.826	5.036	35.067
	2	0.538	0.711	3.036	22.607	99.566
	3	0.482	0.196	38.467	97.426	13.349
	4	0.151	0.509	5.647	2.64	10.374
	5	0.067	0.107	2.844	2.288	7.636
	6	87.884	10.509	80.486	50.178	15.233
Post Monsoon '01	1	0	0.01	1.304	5.248	21.954
	2	0.229	0.209	0.015	11.157	112.953
	3	0.418	0.004	4.934	73.429	115.651
	4	0.064	0.397	4.063	2.431	11.31
	5	0	0.512	3.031	1.254	3.514
	6	144.392	19.856	11.458	45.131	22.694
Pre Monsoon '03	1	0	0.137	0.132	14.303	57.338
	2	0.243	3.545	3.643	15.607	87.154
	3	0.755	0	8.998	32.546	74.031
	4	0.157	6.311	6.414	8.461	29.194
	5	0.125	2.313	2.407	1.257	4.696
	6	51.599	0.883	2.848	23.289	99.603
Monsoon '03	1	0	0.131	0.826	0.516	14.35
	2	1.92	1.203	2.46	0	94.869
	3	0.289	0.049	0.955	7.232	110.712
	4	0	0.16	3.773	6.339	0.147
	5	0.061	0.173	2.291	1.707	6.902
	6	76.441	12.185	2.763	22.685	15.137

APPENDIX III B
METAL CONCENTRATIONS IN DIFFERENT FRACTIONS EXTRACTED USING pH BASED EXTRACTION SCHEME (μg/g)

Copper		Metal concentrations in different fractions							
Seasons	Stations	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
Pre monsoon '01	1	0.472	0.000	0.743	1.522	0.989	0.141	0.321	11.162
	2	0.226	0.455	0.075	0.127	0.151	0.203	0.000	28.898
	3	0.259	0.649	1.106	5.013	1.553	1.006	0.449	0.259
	4	0.102	1.405	2.480	0.584	0.527	0.119	0.280	0.549
	5	0.049	0.192	0.242	0.226	1.029	0.089	0.187	0.488
	6	0.262	0.611	0.735	0.445	0.908	0.211	0.229	100.528
Monsoon '01	1	0.327	0.163	0.270	0.449	0.274	0.166	0.009	14.219
	2	0.276	0.322	0.000	0.037	0.000	0.319	0.000	33.271
	3	0.754	0.597	0.000	0.138	0.132	0.303	0.000	18.865
	4	0.692	0.305	0.449	0.146	0.182	0.172	0.157	2.279
	5	0.657	0.740	0.095	0.162	0.348	0.124	0.086	2.309
	6	1.220	0.969	3.016	10.780	64.290	1.776	0.444	101.882
Post Monsoon '01	1	0.790	0.301	0.147	0.066	0.390	0.724	0.198	8.261
	2	0.628	0.456	0.065	0.104	0.126	0.327	0.404	27.200
	3	0.495	0.624	0.086	0.091	0.197	0.546	0.000	10.350
	4	0.645	0.588	0.492	0.394	1.063	0.246	0.148	1.060
	5	0.341	0.412	0.021	0.351	0.110	0.247	0.241	1.849
	6	0.782	0.391	2.117	16.374	45.083	5.186	2.069	61.998
Pre Monsoon '03	1	0.201	0.410	0.345	0.769	0.217	0.123	0.373	21.649
	2	0.136	0.562	0.123	0.000	0.008	0.170	0.199	25.334
	3	0.298	0.382	0.014	0.000	0.940	0.131	0.398	10.354
	4	1.834	2.145	2.289	4.005	1.786	0.917	1.685	1.661
	5	0.846	0.647	0.514	0.252	0.237	0.398	0.670	0.138
	6	0.116	0.076	0.422	1.928	0.306	0.190	0.227	146.694
Monsoon '03	1	0.144	0.613	1.113	1.728	0.580	0.359	0.333	8.932
	2	0.547	0.295	1.707	1.127	1.064	0.283	0.350	28.184
	3	0.301	0.351	0.000	1.718	1.002	0.207	0.240	13.515
	4	0.293	0.507	0.644	1.235	0.716	0.101	0.159	4.923
	5	0.137	0.091	0.421	1.214	0.426	0.269	0.152	0.097
	6	6.576	3.356	10.567	16.207	7.993	1.417	3.731	121.935

Iron		Metal concentrations in different fractions							
Seasons	Stations	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
Pre monsoon '01	1	3005.846	223.593	80.568	1.032	3075.455	9.542	0.000	31854.97
	2	109.443	932.000	475.220	0.661	25.751	2.358	0.000	59710.57
	3	1273.258	374.374	1136.377	1.917	826.703	0.504	1.375	5425.492
	4	338.484	161.011	964.648	0.038	183.131	0.000	1.127	13900.56
	5	167.088	2005.055	550.875	0.570	478.658	0.000	0.000	1368.754
	6	100.551	179.835	753.694	1.642	87.100	10.478	1.447	14953.25
Monsoon '01	1	836.934	875.808	557.172	0.362	117.079	0.000	5.140	6287.506
	2	2056.503	3500.074	35.939	0.031	11.165	0.000	0.000	47280.29
	3	314.921	759.278	49.793	0.008	115.567	3.522	3.027	21027.88
	4	208.346	445.320	1164.395	0.817	661.618	0.303	17.167	7395.036
	5	63.983	211.943	495.106	0.525	299.920	1.047	4.332	3089.143
	6	303.862	964.365	253.767	1.894	3222.066	0.586	1.464	9329.995
Post Monsoon '01	1	463.251	1321.143	487.549	0.114	746.733	1.874	0.000	21184.34
	2	88.077	696.248	151.284	0.084	27.048	0.000	3.711	36080.55
	3	309.298	718.866	80.034	0.011	13.794	0.000	0.000	12647
	4	274.428	1041.896	350.902	3.986	93.026	0.000	37.555	15314.21
	5	74.363	164.699	306.893	0.242	147.624	0.000	32.998	34449.18
	6	635.817	914.719	1449.410	0.428	2961.366	6.119	4.419	32051.72
Pre Monsoon '03	1	614.302	11.701	802.972	0.378	2367.110	0.000	1.616	1252.921
	2	2216.129	738.710	955.237	1.093	59.720	0.000	7.120	1945.993
	3	290.404	175.475	59.667	0.010	172.105	0.000	1.989	11.35021
	4	578.312	40.283	492.345	1.237	635.264	0.000	1.323	1130.236
	5	52.487	78.620	53.231	1.599	41.132	12.056	0.821	354.0541
	6	85.632	378.531	223.254	0.171	20.435	6.951	3.197	2001.829
Monsoon '03	1	159.161	353.356	1854.075	0.058	324.161	0.000	0.240	10628.95
	2	225.842	1005.168	481.475	0.046	2573.704	0.000	3.342	89748.42
	3	391.151	6.561	32.955	0.043	100.942	0.000	8.412	16847.94
	4	755.374	843.757	93.239	1.340	329.898	0.000	23.686	13133.71
	5	114.989	1244.722	358.909	0.457	589.168	48.039	1.185	4445.531
	6	244.398	787.151	218.351	1.069	832.645	0.000	7.507	38064.88

Manganese		Metal concentrations in different fractions							
Seasons	Stations	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
Pre monsoon '01	1	9.673	8.950	5.414	3.943	12.902	0.301	4.043	46.790
	2	0.496	0.908	0.028	0.608	5.888	0.674	1.474	268.644
	3	4.088	15.290	1.540	5.187	13.941	0.000	0.000	5.903
	4	2.273	4.062	10.445	0.713	6.248	0.105	5.168	3.469
	5	0.576	0.944	6.519	0.586	2.122	0.010	2.062	14.257
	6	1.502	3.119	2.844	2.330	1.432	0.519	1.123	164.702
Monsoon '01	1	6.198	11.917	14.792	7.135	0.749	2.047	0.196	72.726
	2	6.805	13.047	0.686	1.223	0.649	3.440	0.292	152.970
	3	13.318	17.429	0.231	0.000	0.363	0.281	0.000	95.287
	4	0.616	0.990	0.990	0.757	1.838	0.889	0.000	21.134
	5	0.371	0.495	0.157	0.424	1.157	0.719	0.000	27.135
	6	1.703	2.596	0.000	2.099	5.622	4.592	7.696	154.854
Post Monsoon '01	1	2.669	6.063	7.943	2.087	18.220	2.867	0.000	56.030
	2	2.838	7.712	5.496	10.266	14.463	5.196	3.640	40.642
	3	14.915	13.859	0.334	0.000	0.000	0.106	0.000	29.789
	4	0.852	1.644	2.589	2.988	2.860	0.473	0.000	12.835
	5	0.325	0.714	0.803	0.425	12.187	0.278	0.000	9.512
	6	1.884	2.690	3.317	1.671	4.550	4.220	17.462	101.194
Pre Monsoon '03	1	3.187	5.076	1.376	4.558	17.513	0.513	0.713	334.762
	2	2.590	11.541	0.420	5.115	8.917	2.454	3.047	177.558
	3	9.280	8.367	6.120	0.416	2.464	0.000	0.868	29.213
	4	1.354	2.527	0.384	1.133	4.361	12.449	3.475	36.283
	5	0.620	0.977	1.139	3.023	1.335	0.569	0.257	14.209
	6	0.533	0.394	2.400	0.199	0.681	0.000	0.213	127.549
Monsoon '03	1	2.524	5.129	7.381	9.314	25.508	2.523	4.693	14.204
	2	9.957	23.428	13.806	7.296	20.086	0.000	11.807	36.620
	3	8.288	9.775	0.198	2.847	3.441	0.000	2.024	31.456
	4	2.043	2.850	2.879	1.380	5.086	0.341	1.168	5.557
	5	0.323	0.592	0.323	0.235	0.984	0.171	1.620	18.825
	6	1.157	3.585	4.093	2.975	2.337	2.518	0.700	88.455

Nickel		Metal concentrations in different fractions							
Seasons	Stations	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
Pre monsoon '01	1	1.225	0.407	0.957	2.481	2.335	0.181	0.512	15.138
	2	0.792	0.415	0.347	0.561	0.104	0.509	0.542	70.515
	3	1.467	0.120	0.100	0.220	0.714	0.578	1.150	24.891
	4	1.036	1.357	1.414	1.961	1.604	0.756	0.037	1.932
	5	0.701	1.259	1.776	0.960	3.165	0.416	0.000	13.442
	6	0.674	0.047	0.775	1.203	1.006	0.777	0.000	24.893
Monsoon '01	1	0.327	0.758	1.278	1.024	0.000	0.348	0.444	11.623
	2	0.914	1.622	0.497	0.590	0.000	0.404	0.548	70.498
	3	0.176	0.847	0.294	0.567	0.435	0.396	0.809	10.557
	4	0.606	0.505	0.795	0.636	0.000	0.323	1.015	5.518
	5	0.190	0.000	1.421	0.614	0.919	0.290	0.362	35.843
	6	0.000	0.820	1.969	1.249	4.212	0.342	0.410	22.807
Post Monsoon '01	1	0.051	0.886	0.079	0.172	1.292	0.253	0.456	41.522
	2	1.659	2.107	2.655	3.127	2.128	1.599	1.550	62.081
	3	1.056	1.091	0.000	1.880	0.000	0.000	0.389	13.097
	4	0.477	0.153	2.783	0.999	0.655	0.158	0.310	5.509
	5	0.000	0.005	0.000	1.374	0.934	0.635	0.178	10.875
	6	0.422	0.893	0.998	2.015	2.637	0.758	2.559	21.764
Pre Monsoon '03	1	0.407	0.540	0.259	1.265	2.084	0.435	0.000	57.885
	2	0.856	0.216	0.490	1.882	0.839	0.572	0.030	59.679
	3	0.714	0.561	0.405	1.022	1.347	0.588	0.597	4.954
	4	0.626	0.617	0.787	1.667	2.712	1.962	0.260	18.549
	5	0.791	0.562	0.962	1.100	1.325	0.896	0.107	1.983
	6	0.259	0.473	0.000	0.778	0.269	1.214	0.250	28.798
Monsoon '03	1	0.662	1.313	1.367	1.626	2.333	0.600	0.364	26.156
	2	1.735	1.323	1.786	2.488	2.924	0.460	0.336	87.046
	3	0.527	0.395	1.621	1.365	1.323	0.574	0.169	18.049
	4	0.399	0.683	0.647	1.418	1.221	0.423	0.000	12.575
	5	0.499	0.357	0.800	0.543	0.000	0.538	0.000	8.997
	6	0.802	1.716	2.007	2.134	0.931	0.644	0.000	49.332

Lead		Metal concentrations in different fractions							
Seasons	Stations	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
Pre monsoon '01	1	2.386	1.657	1.657	0.402	0.000	0.000	1.256	13.362
	2	2.317	1.321	1.887	0.330	0.613	0.000	0.566	38.934
	3	1.545	0.996	2.790	2.593	1.195	1.146	0.138	3.759
	4	0.619	2.521	1.146	1.100	1.100	1.237	0.962	2.588
	5	2.875	0.250	3.314	0.686	2.171	0.343	0.175	0.579
	6	0.000	2.621	0.515	2.059	1.217	0.000	0.749	90.202
Monsoon '01	1	0.327	0.261	2.700	0.784	0.653	0.000	0.131	27.758
	2	1.462	0.797	1.010	0.691	0.904	0.372	1.170	32.471
	3	1.183	1.871	1.871	0.440	1.101	0.000	1.596	20.440
	4	0.126	0.808	2.020	0.000	0.303	0.000	1.363	5.518
	5	0.881	0.857	2.285	0.143	0.476	0.000	0.524	8.524
	6	3.538	5.466	3.855	2.538	0.000	1.171	1.806	64.413
Post Monsoon '01	1	1.190	1.520	1.165	0.101	1.013	0.203	0.355	13.627
	2	4.175	5.676	2.729	3.111	2.783	2.456	3.711	13.750
	3	1.440	0.960	0.808	0.051	0.505	0.202	0.859	8.069
	4	0.418	0.984	3.974	0.140	0.246	0.000	0.591	23.021
	5	0.131	0.577	0.944	0.472	0.682	0.000	0.472	18.845
	6	3.278	6.216	12.188	1.894	0.000	0.194	0.486	42.086
Pre Monsoon '03	1	2.034	2.284	2.062	0.947	0.000	0.111	1.226	28.789
	2	0.000	1.441	0.339	1.271	0.678	0.636	0.975	37.203
	3	0.701	1.808	0.045	0.271	1.944	1.085	0.723	7.355
	4	3.991	2.469	1.147	1.764	3.528	0.397	1.147	3.770
	5	1.102	0.934	1.914	2.245	1.445	1.914	0.716	1.182
	6	0.718	1.112	0.185	0.788	1.575	0.278	0.649	106.026
Monsoon '03	1	1.205	1.231	1.744	0.923	1.128	0.410	1.077	54.599
	2	0.599	2.541	0.959	1.198	2.445	0.240	1.198	19.644
	3	0.588	1.836	1.177	2.212	2.730	0.188	0.753	1.998
	4	0.545	0.923	0.044	0.613	1.115	0.429	0.801	0.603
	5	0.000	1.223	0.000	0.392	2.251	0.000	0.636	14.772
	6	2.568	8.355	0.677	9.032	3.161	0.056	1.242	21.691

Zinc		Metal concentrations in different fractions							
Seasons	Stations	f 2	f 3	f 4	f 5	f 6	f 7	f 8	R
Pre monsoon '01	1	3.762	0.547	0.801	1.334	0.874	0.000	0.848	35.157
	2	3.562	12.631	0.321	0.000	0.623	0.000	0.089	61.472
	3	2.888	7.926	4.128	2.283	13.475	0.000	0.834	73.494
	4	4.648	4.647	0.471	4.569	3.344	0.000	1.522	46.675
	5	0.552	0.805	1.145	1.138	0.267	0.000	0.889	12.353
	6	19.460	1.193	5.075	19.814	31.779	5.184	1.127	119.957
Monsoon '01	1	0.989	1.616	0.895	0.327	0.362	0.000	1.485	37.319
	2	4.833	15.912	0.000	0.000	0.000	0.000	6.401	99.312
	3	11.615	20.051	0.000	0.160	1.695	0.011	0.314	116.075
	4	0.985	1.182	0.588	0.677	0.997	0.000	0.096	14.797
	5	0.386	0.376	0.574	0.276	1.257	0.000	0.138	9.935
	6	6.876	3.382	1.301	36.074	101.253	9.702	10.253	75.449
Post Monsoon '01	1	1.023	2.675	1.340	0.000	0.000	0.000	0.142	23.337
	2	3.837	10.500	5.815	11.887	0.491	0.600	0.067	91.367
	3	16.606	21.062	0.000	0.000	0.238	0.000	0.106	156.425
	4	0.984	1.674	1.327	0.881	0.620	0.000	0.020	12.759
	5	0.645	0.708	0.412	2.356	0.000	0.000	0.016	4.174
	6	6.211	4.793	1.515	7.852	37.731	0.855	84.023	100.552
Pre Monsoon '03	1	1.070	2.285	1.101	0.552	3.732	0.000	0.412	62.760
	2	3.725	0.000	0.000	2.246	7.648	0.000	0.882	95.691
	3	10.204	5.363	0.011	3.011	0.685	0.000	0.827	96.228
	4	5.918	11.867	1.602	17.316	0.626	0.652	0.130	12.427
	5	0.428	0.514	0.564	0.247	0.695	0.695	0.680	6.974
	6	0.348	0.338	0.503	0.551	0.187	0.000	0.171	176.124
Monsoon '03	1	0.518	2.221	1.218	0.041	0.000	0.000	0.282	11.543
	2	4.501	4.703	3.871	0.393	0.000	0.000	0.269	86.715
	3	4.843	12.305	0.040	10.063	0.000	0.000	0.560	91.426
	4	1.057	2.139	0.733	2.067	3.369	0.000	0.596	0.458
	5	0.201	0.176	0.346	1.096	2.910	0.000	0.318	6.087
	6	6.983	12.458	13.475	17.883	21.758	1.575	15.487	39.592

APPENDIX IV

METAL CONCENTRATIONS IN SEDIMENT CORE (μg/g) - STATION 2

Depth	Copper			Iron $\times 10^3$		
	Mon	Post Mon	PRE MON	MON	POST MON	PRE MON
0 - 5	40.29	35.56	33.54	34.63	33.2	32.06
5 -10	36.77	31.3	35.01	34.16	27.98	61.6
10 - 15	36.83	35.72	34.24	31.42	31.08	63.86
15 - 20	36.4	36.44	35.43	40.55	34.98	5.93
20- 25	24.46	37.59	35.4	20.05	29.85	45.6
25 - 30		33.63	35.01		23.15	101.56

Depth	Manganese			Zinc		
	Mon	Post mon	Pre mon	Mon	Post mon	Pre mon
0 - 5	4.29	35.56	35.54	96.87	104.96	99.44
5 - 10	36.77	31.3	35.01	114.76	85.36	89.18
10 - 15	36.83	35.72	34.24	115.24	92.19	91.1
15 - 20	36.4	36.44	35.43	92.51	91.2	83.56
20- 25	24.46	37.59	35.4	66.43	93.37	96.49
25 - 30		33.63	35.01		73.61	86.25

METAL CONCENTRATIONS IN SEDIMENT CORE (μg/g) - STATION 3

Depth	Copper			Iron $\times 10^3$		
	Mon	Post Mon	Pre Mon	Mon	Post Mon	Pre Mon
0 - 5	39.25	13.58	21.66	21.22	6.55	3.17
5 - 10	43.5	13.58	18.28	21.71	4.8	8.29
10 - 15	43.13	25.97	16.54	28.61	15.65	12.07
15 - 20	27.5	11.95	16.52	18.08	15.36	11.3
20- 25	19.57	17.08	14.27	12.07	11.48	6.71
25 - 30	18.61	16.01	12.47	19.68	10.37	5.16

Depth	Manganese			Zinc		
	Mon	Post mon	Pre mon	Mon	Post mon	Pre mon
0 - 5	152.5	72.1	71.39	233.75	110.38	105.27
5 - 10	102.27	55.43	55.43	171.72	77.21	56
10 - 15	142.31	95.01	95.01	155.96	120.76	48.99
15 - 20	92.99	38.53	38.53	129.05	4.13	49.99
20- 25	72.23	56.64	56.64	65.36	64.77	46.41
25 - 30	66.06	56.77	56.77	62.36	48.22	26.6

List of Abbreviations

Pre Mon - Pre Monsoon

Mon - Monsoon

Post Mon - Post manosson

OC / C–org - Organic Carbon

BDL - Below Detectable Limit

ND - Not Detected

Ac - *Acanthus ilicifolious*

Av - *Avicennia officinalis*

R m - *Rhizophora mucronata*

B c - *Bruiguiera cylindrica*

E a - *Exocoearia agallocha*

B g - *Bruiguiera gymnrorphiza*

C i - *Clerodendrum inermi*

A co - *Aegiceras corniculatum*