DYNAMICS AND SPECIATION OF HEAVY METALS IN THE LOWER REACHES OF CHITRAPUZHA - A TROPICAL TIDAL RIVER

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Certificate

This is to certify that this thesis is an authentic record of the research work carried out by Shri. Joseph P. V. under my supervision and guidance in the Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the degree of ***Philosophiae Doctor*** *of the Cochin University of Science and Technology.*

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Preface

Heavy metal contamination in aquatic system is one of the largest threats to environmental quality and human health. A thorough assessment of the relative concentrations of pollutants in the different environmentally significant compartments of an aquatic system is an essential pre-requisite for any systematic hazard evaluation programme. It is often stated that sediment is the most important reservoir or sink of metals and other pollutants. Toxic metals released into aquatic systems are generally bound to particulate matter, which eventually settles and becomes incorporated into sediments. However, change in environmental conditions might cause some of the sediment-bound metals to be remobilized and to be released back into the waters, thereby exposing the aquatic biota to possible deleterious consequences. Besides the physical, chemical and biological characteristics of the water and the sediment, the chemical partitioning of heavy metals between different sediment forms is very important in determining the bioavailability of heavy metals. Metal fractions have varying mobility, biological availability and chemical behaviour. Thus it is necessary to identify and quantify the metal forms in order to assess the environmental impact of contaminated sediments.

The present study is an attempt to quantify and study the seasonal and spatial variations in the distribution of some selected heavy metals among various geochemical phases in the surficial sediments of Chitrapuzha River. The study also estimates the concentration of heavy metals in dissolved and particulate phases as well as seasonal and spatial distribution. There are long standing local complaints against discharge of effluents from industrial units into the river, which cause fish mortality and serious damage to agricultural crops. Water transportation of imported chemicals from Cochin port to industrial firms located on the banks of Chitrapuzha River may also cause pollution. The river is thus of considerable social and economic importance. Since no systematic study has been done in this tropical tidal river, a detailed and systematic investigation is carried out to assess the dynamics and speciation of heavy metals.

The thesis is presented in 6 chapters.

Chapter 1 is an introduction about estuarine behaviour of heavy me aquatic system with special reference to Cochin backwaters and Chitra River. The importance of chemical partitioning of metals in sediments i: emphasized in this chapter.

Chapter 2 describes the study area and gives details of the material methods employed in this study.

Chapter 3 presents the seasonal and spatial distributional characteris various hydrographical and sediment parameters such as salinity, pH, dis: oxygen, organic carbon, sediment texture etc.

Chapter 4 presents the seasonal and spatial variations of heavy me the dissolved, particulate and sediment compartments. The data is statis analysed to understand the significance of hydrographic parameters in sea and spatial variations. The role of different parameters in the distribution ol metals in the sediments is discussed in the light of Multiple Regression an Enrichment of trace metals in the surficial sediments is estimated by calculati Enrichment Factor.

Chapter 5 describes on chemical partitioning of heavy metals i sediments. The seasonal and spatial variations observed in the distribut various fractions of heavy metals are critically analysed in relation to the v conditions.

Chapter 6 summarizes the salient results of the present investigation.

CONTENTS

Chapter 1

INTRODUCTION

1.1 Estuarine behaviour of heavy metals

1.2 Approaches in heavy metal speciation

1.3 Cochin backwaters

1.4 Scope of the present study

Estuaries encompass river-ocean interface, a region regarded as one of the most important aquatic systems. They are highly dynamic and are subject to changes occurring over a spectrum of durations ranging from very short periods to geologic time spans. Pronounced biogeochemical reactivity, including sorption, flocculation and redox cycling of trace metals, is induced by sharp gradients in the estuarine master variables of salinity, pH, dissolved oxygen, particle character and concentration that result from the mixing of fresh and saline end members. These processes drastically modify the riverine composition and must be fully understood to accurately determine chemical fluxes and to define geochemical mass balances.

Every estuary is unique. There are, however, some general trends, which make it possible to predict the nature of the estuarine environments, the circulation pattern and various processes and interactions taking place in estuaries. From pre-historic times, the banks of rivers and estuaries have been the centres of civilization, because of the favourable features such as the profuse vegetation, fertile soil, access to navigational facilities etc. that have catalysed the flourishing of human habitats in those regions. The growing up of large cities nearby estuaries has in many cases caused environmental disturbances, particularly due to the discharge of domestic and industrial waste. Human activities to improve the standard of living, has led to the introduction of many hazardous, non degradable chemicals into the aquatic ecosystem, the presence of which has attracted serious concern of the environmentalists. Organic effluents such as domestic sewage is a serious problem – the discharge of small quantities of sewage into estuarine systems can actually increase the productivity of ecosystem, but excessive quantities will deplete oxygen causing severe threat to aquatic life. The alarming rate of pollution input far exceeds that of nature's cleansing processes and has consequently resulted in an ecological imbalance.

Once the pollutants enter the environment, they are subjected to a variety of physical, chemical, geological and biological processes that bring about their disintegration or sometimes, their ultimate removal. Persistent chemicals, that do not breakdown, stand to pose serious environmental problems. Heavy metals, because of their relatively long "half life" and biological significance, constitute one such class among non-degradable contaminants causing great concern. The fate and behaviour of heavy metals in estuarine environment are of extreme importance due to their key role in the biogeochemical cycles. Consequently, cycling of heavy metals and their inherent toxicity has formed an integral component of estuarine water quality monitoring programmes.

The various anthropogenic activities by which heavy metals are introduced into the aquatic systems include smelting, mining, shipping, industrial effluent discharge, urbanisation, application of fertilizers, algicides, automobile exhaust etc. The natural processes that contribute metals to the aquatic environment include weathering of rocks, leaching of ore deposits, forest fires, terrestrial and marine volcanism etc. The above sources directly regulate the net flux of heavy metals that interplay with natural/artificial systems and pose relevant questions on their cycling, transport and ultimate removal.

1.1 ESTUARINE BEHAVIOUR OF HEAVY METALS

Estuaries represent geologically ephemeral transition zone, in which many features of geomorphology, water circulation, biogeochemistry and ecology are varied and diverse. An estuary is a mixing zone of riverine and oceanic waters with widely varying compositions where end members interact both physically and chemically. The importance of estuaries lies in the fact that they act as a mediator (filter) in the transfer of elements from continents to oceans. The estuaries thus, can be either a source or sink for different heavy metals. Therefore, it is imperative to study the composition of water, particulate and sediment phases in the estuaries along with temporal fluctuations to identify different biogeochemical processes and pathways in metal cycling.

During estuarine mixing, the trace metals in the dissolved and particulate forms can behave either conservatively or non-conservatively depending on physico-chemical factors such as salinity, pH, Eh and suspended solids. The chemical behaviour of a trace metal during its transport within the estuary is determined to a large extent by the chemical form in which it is transported by the rivers. There are also somewhat conflicting reports on the behaviour of heavy metals during estuarine mixing. Windom et. al. (1988) have reported conservative behaviour of dissolved and particulate metals in Bang Pakong estuary, Thailand. Poucot and Wollast (1997) have reported that the concentration of nickel and chromium in the Scheldt estuary, southwest of the Netherlands decreased with increase in salinity. He also reported that manganese exhibited a non-conservative behaviour. Guieu et. al. (1998) reported that copper and zinc showed conservative behaviour in the Danube river. Much of the disparity between the results of different workers may be attributed to reasons such as decomposition of pre-existing solids (which release the incorporated metals), differences in the rate of mixing, nature of solids supplied by the end members and dependency of solids' association of trace metals on the grain size distribution. Another important factor, which can influence the behaviour of heavy metals in estuaries, is the hydrogenous precipitation of iron and manganese oxides in the low salinity region.

A study of the distribution of heavy metals in the dissolved and particulate phases is very important to understand their role in various biogeochemical processes occurring in estuaries and tidal rivers. In estuarine waters, the different processes controlling metal distribution tend to be superimposed. Inputs can be from rivers, sediments, atmosphere and from degradation of materials formed in situ; removal can be by biological uptake, sorption on to sedimentary particles (both organic or inorganic) and flushing with ocean and coastal waters. Further, a knowledge of the distribution and concentration of heavy metals in estuarine waters would help detect the sources of pollution in the aquatic systems.

Sediments have proved to be excellent indicators of environmental pollution, as they accumulate pollutants to levels that can be measured reliably by a variety of analytical techniques. Heavy metals tend to be adsorbed on to suspended particles and are scavenged from the water column into proximal sediments (Karickhoff, 1984; Daskalakis and O'Connor, 1995; Lee et. al., 1998). To assess the impact of contaminated sediments on the environment, information on total concentrations of metals alone is not sufficient because heavy metals are present in different chemical forms in sediments. Only a part of the metals present may take part in short-term geochemical processes or may be bio-available. For this reason, a series of different extraction procedures have been devised to gain a more detailed insight into the distribution of metals within the various chemical compounds and minerals. In this study, an attempt is made to differentiate the metals in the surficial sediments into exchangeable, carbonate bound, easily reducible, oxidisable and residual fractions.

1.2 APPROACHES IN HEAVY METAL SPECIATION

The rapid increase in the levels of environmental pollution over recent decades has resulted in increasing concern for people's well being, and for global ecosystems. The need to determine different species of trace metals in environmental and biological materials is of paramount importance since the toxicity of an element and its behaviour depend to a great extent on its chemical form and concentration. The growing awareness of this dependence has led to an increasing interest in the qualitative and quantitative determination of specific metal species. Changes in environmental conditions, whether natural or anthropogenic, can strongly influence the behaviour of both essential and toxic elements by altering the forms in which they occur. Some of the more important controlling factors include pH, redox potential and availability of reactive species such as complexing ligands.

Originally, most analytical measurements dealt with the total content of a specific element in an analysed sample (such as lead, mercury or cadmium as examples of toxic elements, or cobalt, selenium or magnesium as examples of essential elements). Biochemical and toxicological investigations have shown that, for living organisms, the chemical form of a specific element, or the oxidation state in which that element is introduced into the environment is crucial. Therefore to get information on the activity of specific elements in the environment, more particularly for those in contact with living organisms, it is necessary to determine not only the total content of the element but also its individual chemical and physical form. Generally, the appearance of multiform is described by speciation, but the process leading to quantitative estimation of the content of the different species is called "Speciation Analysis".

According to the official definition speciation analysis is the process leading to the identification and determination of the different chemical and physical forms of an element existing in a sample (Kot and Namiesnik, 2000). Although this definition tends to restrict the term speciation to the state of distribution of an element among different chemical species in a sample, in practice the use of this term is much wider, specifying either the transformation and/or the distribution of species, or the analytical activity, to identify chemical species and measure their distribution. For the description of these processes the terms "Species Transformation" and "Species Distribution", respectively, are suggested. The analytical activity involved in identifying and measuring species is hence defined as "Speciation Analysis".

The use of chemical extractants to quantify the element in a particular solid phase was originally attempted in soil studies (Jackson, 1958; Jenne et. al., 1986; Bermond and Sommer, 1989) for selective sampling and determination of nutrients of different solubilities. Because of the similarities between soil and aquatic sediments, extraction procedures used in soil have often been adapted for sediment analyses (Tessier et. al., 1979). A number of extraction procedures, varying in manipulative complexity, have been proposed for the partitioning of metal phase. Several methods for determination of different forms of metals in sediments are described in scientific literature (Kersten and Forstner, 1991). Some of these techniques (Agemian and Chau, 1976; Loring, 1976; Malo, 1977) employ a single extractant and are designed to effect separation between residual and non-residual metals. The most widely used methods are based on sequential extraction procedures, whereby several reagents with increasing power, under specified conditions are used consecutively to extract operationally defined phases from the sediment in a set sequence (Gupta and Chen, 1975; Luoma and Jenne, 1976; Engler et. al., 1977; Kerster and Forstner, 1986; Tessier et. al., 1979; Harrisson et. al., 1981; Lopez-Sanchez et. al., 1993; Izquierdo et. al., 1997). The scheme of sequential extractions, although more time-consuming, provides detailed information on the origin, mode of occurrence, biological and physico-chemical availability, mobilization and transport of heavy metals (Tessier et. al., 1979; Campbell and Tessier, 1989; Gunn et. al., 1989; Teraoka and Nakashima, 1990; Ure et. al., 1993; Howard and Vandenbrink, 1999; Xiangdong Li et. al., 2001).

Sequential extraction procedures have yielded valuable insight into the geochemical processes occurring in the sediments (Chester et. al., 1988; Forstner et. al., 1990; Izquierdo et. al., 1997) as well as into the complexities of geochemical association of trace elements (Tessier et. al., 1980; Lion et. al., 1982; Allen et. al., 1990; Bradley and Coax, 1990). These methods have been used widely in environmental studies to quantify those phases of the sediments that determine potential bioavailability and remobilization of heavy metals. Speciation studies of heavy metals is particularly important in estuaries since speciation is likely to be influenced by the constantly changing environmental conditions including salinity, pH and redox potential (Kerston and Forstner, 1986; Calmano et. al., 1993; Lam et. al., 1997).

1.3 COCHIN BACKWATERS

On the south west coast of India, there is an extensive system of backwaters, of which Vembanad Lake is the largest. The backwaters of Kerala support as much biological productivity and diversity as tropical rain forests. The Cochin backwaters situated at the tip of the northern Vembanad lake is a tropical positive estuarine system extending between 9° 40′ and 10° 12′ N and 76° 10′ and 76° 30′ E with its northern boundary at Azheekode, and southern boundary at Thanneermukkam bund. The lake has a length of 80 km and the width varies between 500 and 4000m. A channel, about 450 m wide at Cochin gut and another at Azheekode, make permanent connection with the Arabian Sea. The depth of the backwaters varies considerably. While the shipping channels are maintained at a depth of 10-13 m, the major portion of it has a depth range of ~ 2-7 m. Water from two major rivers viz. Periyar and Muvattupuzha and a comparatively minor river Chitrapuzha drain into the backwaters. The major hydrographical variable in this backwater system is salinity.

The intensity of research effort expended in elucidating the physical, biological and chemical characteristics of the Cochin backwater system during the last three decades is indicative of the economic and social importance enjoyed by it. Extensive studies have been carried out in Cochin backwaters especially on the physical, chemical and biological aspects and impacts due to dredging were discussed by Gopinathan and Qasim (1971), Anto et. al. (1977), Sundaresan (1989), Rasheed and Balchand (1995) and Rasheed (1997). Cochin backwater system faces serious environmental threats by inter-tidal land reclamation, pollution discharges, expansion for harbour development, dredging activities and urbanization (Gopalan et. al., 1983; Balchand, 1984; Balchand and Nambisan, 1986; Lakshmanan et. al., 1987; Joy et. al., 1990). The construction of Thanneermukkam bund near Vaikom also created severe environmental consequences within and out of adjacent Kuttanad agricultural fields.

Many hazardous substances including heavy metals, discharged into the aquatic environment are known to accumulate in the estuarine sediments. Venugopal et. al. (1982) studied the levels of copper, manganese, cobalt, nickel and zinc in the sediments of the northern limb of Cochin backwaters, which runs through the industrial belt. All the metals showed some degree of variations over the area studied. Nair et. al. (1991) found that the metal concentration in recently deposited sediments show varying and different behaviour being influenced by natural as well as anthropogenic factors.

For Cochin backwaters, seasonal hydrographic changes play a predominant role in regulating metals in sediments. Generally, post monsoon is associated with build up of metals, which become enriched in the accumulative phases of the sedimentary material. Terrestrial transport appears to occur mostly during monsoon, which is associated with higher river discharge and bed-load movements. The distribution pattern of chromium and strontium were positively correlated to hydrographic features and sediment grain size (Jayasree and Nair, 1995).

Radionuclides like Ra^{228} and Ra^{226} were found in high concentrations in the vicinity of the industrial zone. The Ra^{226} inventory went up by nearly 100% (Paul and Pillai, 1981). This daughter product of uranium is found in phosphate ore, which is extensively used by fertilizer industry. The levels are modified at the backwater due to dissolution during monsoon and precipitation during non-monsoon.

Chemical speciation of metals, together with reactions involved in the transformation of species, is often the factor determining bioavailability of the pollutant in the aquatic environment. Shibu et. al. (1990) reported that speciation of metals in the Cochin estuary is influenced by environmental factors such as influx of riverine input, introduction of industrial effluents and sewage, modification arising out of anthropogenic activities and hydrographic changes related to complexity of water use. Levels of iron, manganese, zinc copper cadmium, lead, chromium, cobalt and nickel in surficial sediments of estuary were studied by Nair et. al. (1990). These studies revealed that the metal behaviour in the surficial sediments is influenced by natural as well as anthropogenic factors. Most of the metals considered were found to be significantly enhanced in the lower reaches of the northern parts of the estuary. The speciation of chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium and lead in the sediments of lower reaches of rivers Periyar and Muvattupuzha and at locations within the estuary was studied by Nair et. al., (1991) and Nair and Balchand (1993). An attempt was made by them to identify anthropogenic sources and enrichment factors, in addition to understanding the importance of selective accumulative phases for this region. The studies have also indicated the predominant role of seasonal hydrographical changes in regulating metal levels in the sediments.

1.4 SCOPE OF THE PRESENT STUDY

Heavy metal distribution in Chitrapuzha River is considerably influenced by the tropical features of the location and by human activities. The industrial units located along the banks of the river discharge treated and untreated effluents into the river. The quantity of effluents discharged from these industries into Chitrapuzha River is estimated to be around 80 million litres per day. There are long standing local complaints about water pollution causing fish mortality and serious damage to agricultural crops resulting in extensive unemployment in the area. Prawn farming is yet another area that is adversely affected by industrial discharge. The lower reach of this river became part of National waterways and is mainly used for transporting imported chemicals from Cochin port to industrial firms located on the banks of the river. River Chitrapuzha is thus of considerable social, economic and commercial importance. Though several references are available on the distribution of heavy metals in Cochin backwaters, information regarding the same in the Chitrapuzha tidal river is woefully lacking.

The objectives of the present study were five fold:

1) to establish the background levels of heavy metals chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium and lead in the dissolved, particulate and sediment compartments.
2) to study the role of hydrographic parameters in the seasonal and spatial variations of dissolved and particulate metals.
3) to quantify the enrichment of trace metals in the surficial sediments during various seasons.
4) to assess the contribution of different parameters that influence the seasonal distribution of trace metals in sediments using Multiple Regression Analysis.
5) to quantify and study the seasonal and spatial distribution of heavy metals among the various geochemical phases of sediments.

A scheme of study encompassing all these objectives provides the framework for the present investigation. Water and sediment samples were collected from the lower reaches of Chitrapuzha River and subjected to heavy metal analysis along with hydrographic and sediment parameters. Since the characteristics of this tidal river system are greatly influenced by the monsoonal cycle, a seasonal study is expected to throw light on the behaviour of metals within the study area. Sediment samples were sequentially extracted to separately analyse the different chemically extractable geochemical species present in them.

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Chapter 2

MATERIALS AND METHODS

2.1 Description of the study area

2.2 Sampling and storage

2.3 Laboratory procedure

2.4 Statistical analysis

2.1 DESCRIPTION OF THE STUDY AREA

The area of study, the Chitrapuzha tidal river system forms part of the Cochin backwaters as well as the National Inland waterway No.III (9°52′ - 10°00′N; 76°15′ - 76°25′E), is shown in the Fig. 2.1. The Cochin backwaters are the largest of the backwaters on the Kerala coast. The hydrography of these backwaters is controlled mainly by discharges from Periyar, Muvattupuzha and Chitrapuzha rivers and also by tidal action through the Cochin barmouth. Saline water intrusion to the southern parts of the estuary is regulated by the Thanneermukkam bund, a salt-water barrier commissioned in 1975. A large number of heavy industrial units are situated on either banks of River Periyar and hence northern parts of the backwaters receive large quantities of treated and untreated industrial effluents. Chitrapuzha River hosts diverse aquatic organisms and many areas have been transformed into breeding pools so as to increase fish production for commercial exploitation. The river originates as a small stream from the upper reaches of high ranges in the eastern boundary of Kerala and passes through the valley and finally joins the southern arm of Cochin backwaters. The depth of the study area varies considerably. While the shipping channels of Cochin port are maintained at a depth of 10 – 13m, the major portion of the study area has a depth range of 3-5m. Numerous industrial units including a diesel power project, fertilizer manufacturing unit and a petrochemical unit, are located along the banks of the Chitrapuzha River. Effluents from these industrial units along with agricultural and other anthropogenic effluents find their way into Chitrapuzha River ultimately into Cochin backwaters. There are long standing local complaints about water pollution causing fish mortality and serious damage to agricultural crops resulting in extensive unemployment in the area. The lower reaches of this river became part of National Waterways in 1993 and is now mainly used for transporting chemicals from Cochin Port to the industrial units located on the banks of the river. The river Chitrapuzha is thus of considerable social and economic importance. Though numerous studies were carried out to elucidate the metal distribution in the aquatic system of Cochin estuary, very little is known about the same in the Chitrapuzha aquatic system.

Based on specific geographical features, water flow regimes and anthropogenic activities, 9 sampling locations were selected (Fig. 2.1). Samples were collected at monthly intervals between January and December 1999. Stations 1 - 3, (Zone 1) are saline, Stations 4 - 6 (Zone 2) are of intermediate salinities and Stations, 7 - 9, (Zone 3) are fresh water Zones. In addition to these nine Stations samples were collected from a far upstream station (Station R), which is free from industrial pollution and is therefore regarded as a reference site.

Station 1 is at the Cochin bar-mouth. Station 2 is near the oil tanker berth. Station 3 is near Thoppumpady fishing harbour. All the three Stations in the Zone 1 are saline through out the year. Station 4 is Thevara Ferry point, Station 5 is near Thykoodam N H Bridge and Station 6 is near Kaniyampuzha Railway Bridge. These Stations in the Zone 2 are of intermediate salinities; salinity at Station 6 was practically nil during the monsoon season. Station 7 is near Eroor Bridge Station 8 is near the discharge outlet of FACT - Cochin Division and Station 9 is near FACT Barge jetty. These three Stations constitute Zone 3, which is the recipient of industrial effluents. The reference Station R is near Mamala.

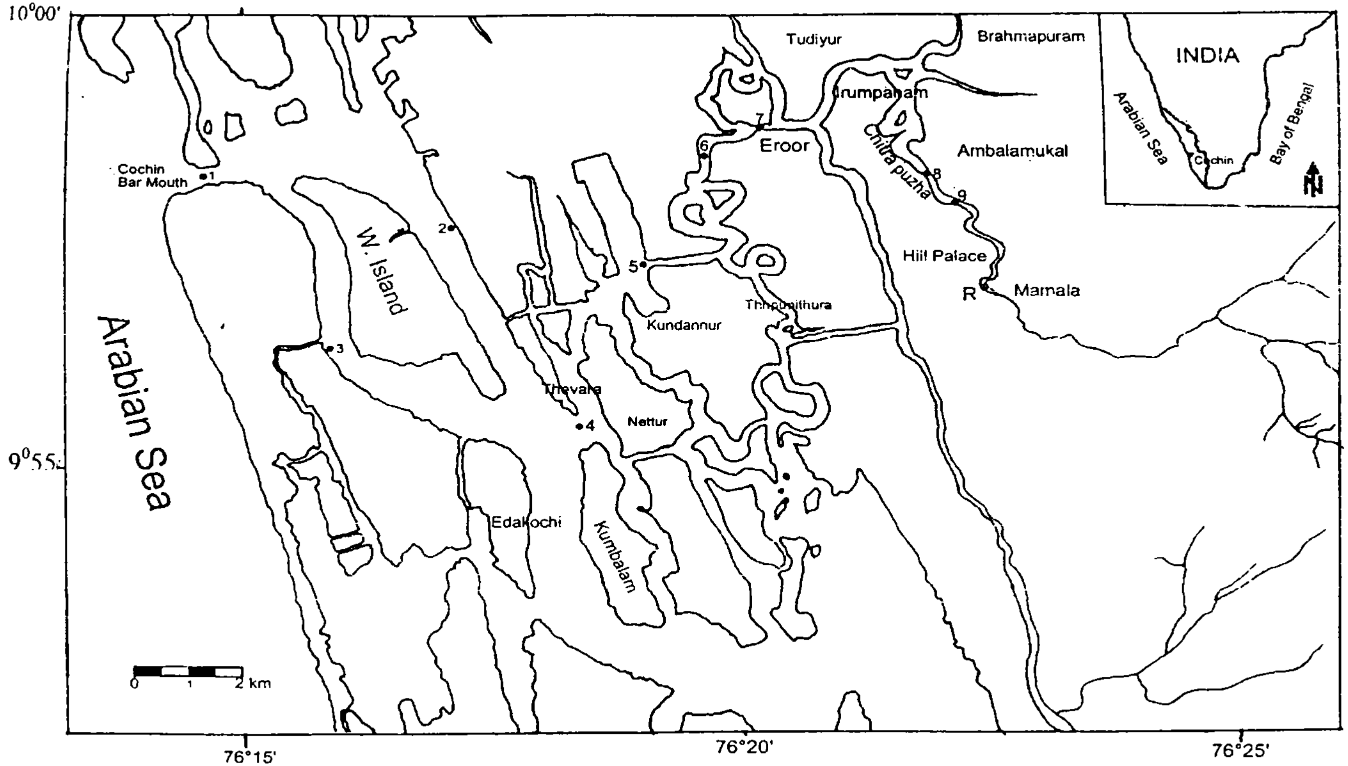

Fig. 2.1 Map of Chitrapuzha River showing location of sampling stations (R - Reference Station)

2.2 SAMPLING AND STORAGE

The sampling surveys were conducted using a fibreglass research vessel "King Fisher" thus eliminating all possible metal contamination from the collecting vessel. A stainless steel plastic-lined Van Veen grab was used to collect sediment samples. At each Station five grab-full of sediments were sampled and the top 5 cm layer was carefully skimmed from all the grabs using a polyethylene scoop, homogenized and stored at –5°C, in double polyethylene containers. Surface water samples were collected in a 2-litre conventional polyethylene container. A pre-cleaned Teflon High-tech water sampler was used to collect bottom water samples. Water samples meant for metal analysis were filtered immediately after collection, through thoroughly acid washed; pre weighed 0.45 µm Whatman membrane filters. The filtrate was used for the analysis of dissolved metals while the residue retained on the membrane filters was dried to constant weight.

2.3 LABORATORY PROCEDURE

All glassware and plasticware used in the experiments were previously washed, soaked in dilute nitric acid and then rinsed with Milli-Q water. All reagents used were of analytical grade and were checked and excluded for possible trace metal contamination. Reagents and standard solutions were prepared with Milli-Q water and the whole laboratory procedure for metal analysis was carried out under laminar flow hood with caution to avoid contamination.

Dissolved metals

Dissolved chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium and lead were pre-concentrated using solvent extraction of the chelates formed with a mixture of complexones (ammonium pyrrolidine dithiocarbamate and diethylammonium diethyl dithiocarbamate (APDC-DDDC) into chloroform, followed by back-extraction into nitric acid (Danielsson et al., 1978,1982). Determinations were carried out on the concentrates by graphite-furnace atomic absorption spectrometry (Perkin Elmer model 3110, with HGA 600), calibrated using standard solutions prepared by dilution of 1000 mg/l standard solutions (Merck). Analytical blanks were prepared using the same procedures and reagents.

Particulate metals

The particulate matter separated as above was digested according to the APHA (1995) procedure. The dry residue in the membrane filter was leached with 10 ml of concentrated acid solution ($HClO_4$, HNO_3 and HCl in the ratio 1:1:3) at 90°C for 6 hours. The resultant solution was centrifuged and then made up to 25 ml with 0.1 M HCl for analysis on the (Perkin Elmer- Model 3110) AAS.

Total metals in the sediment

The oven dry sediment samples were ground to a fine powder in an agate mortar and 0.5g aliquots were weighed into beakers for estimation of total metal. 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 evaporated to incipient dryness. After cooling, the sides of the beaker were rinsed with Milli-Q water, centrifuged and the centrifugate made up to 50 ml. The metal concentrations in the solution were determined by atomic absorption spectrophotometry (Perkin-Elmer 3110 AAS), calibrated using standard solutions prepared by dilution of 1000mg/l standard solutions (Merck). Analytical blanks were prepared using the same procedures and reagents.

Moisture percentage

Known amounts of wet sediment samples were dried at 105°C in an electric oven to constant weight (Hakanson and Jansson, 1983). The moisture content was expressed as the percentage weight of the sample. From the percentage moisture values, the sediment metal values were recalculated and the same was expressed in terms of oven dry weight basis.

Sediment organic carbon

The organic carbon content in the sediment was estimated by the dichromate method (Walkley and Black, 1934) as modified by El Wakeel and Riley 1957).

Total phosphorus

The total phosphorus was determined in the nitric acid - perchloric acid extract using phosphomolybdic acid method (Strikland and Parsons, 1977)

Grain size analysis

Textural analysis was carried out to study the variations in grain sizes of sediments. A known amount of wet sediment was dispersed overnight in sodium hexametaphosphate. The sand was separated from the dispersed sediments by wet sieving using a 230 mesh (63 µm) sieve (Carver, 1971). The filtrate containing the silt and clay fractions was subjected to pipette analysis (Krumbein and Pettijohn, 1938).

Complimentary analysis

Concurrent recording of water quality parameters such as salinity, dissolved oxygen pH and suspended solids were performed by standard procedures as detailed below:

pH	Portable pH Meter (Merck)
Salinity	Argentometry (Strickland and Parsons, 1977)
Dissolved oxygen	Iodometry (Strickland and Parsons 1977)
Suspended solids	Gravimetry (Butler and McManus, 1979)

Chemical partitioning

Trace metals in the sediments were extracted according to the scheme depicted in the Fig. 2.2. The extractants, the sequence and the procedure followed were adapted from the method employed by Tessier et al. (1979). The different metal species studied were:

Fraction 1	Exchangeable
Fraction 2	Bound to Carbonates
Fraction 3	Easily reducible fraction (metals bound to Fe-Mn oxides)
Fraction 4	Bound to organic matter (oxidizable)
Fraction 5	Residual.

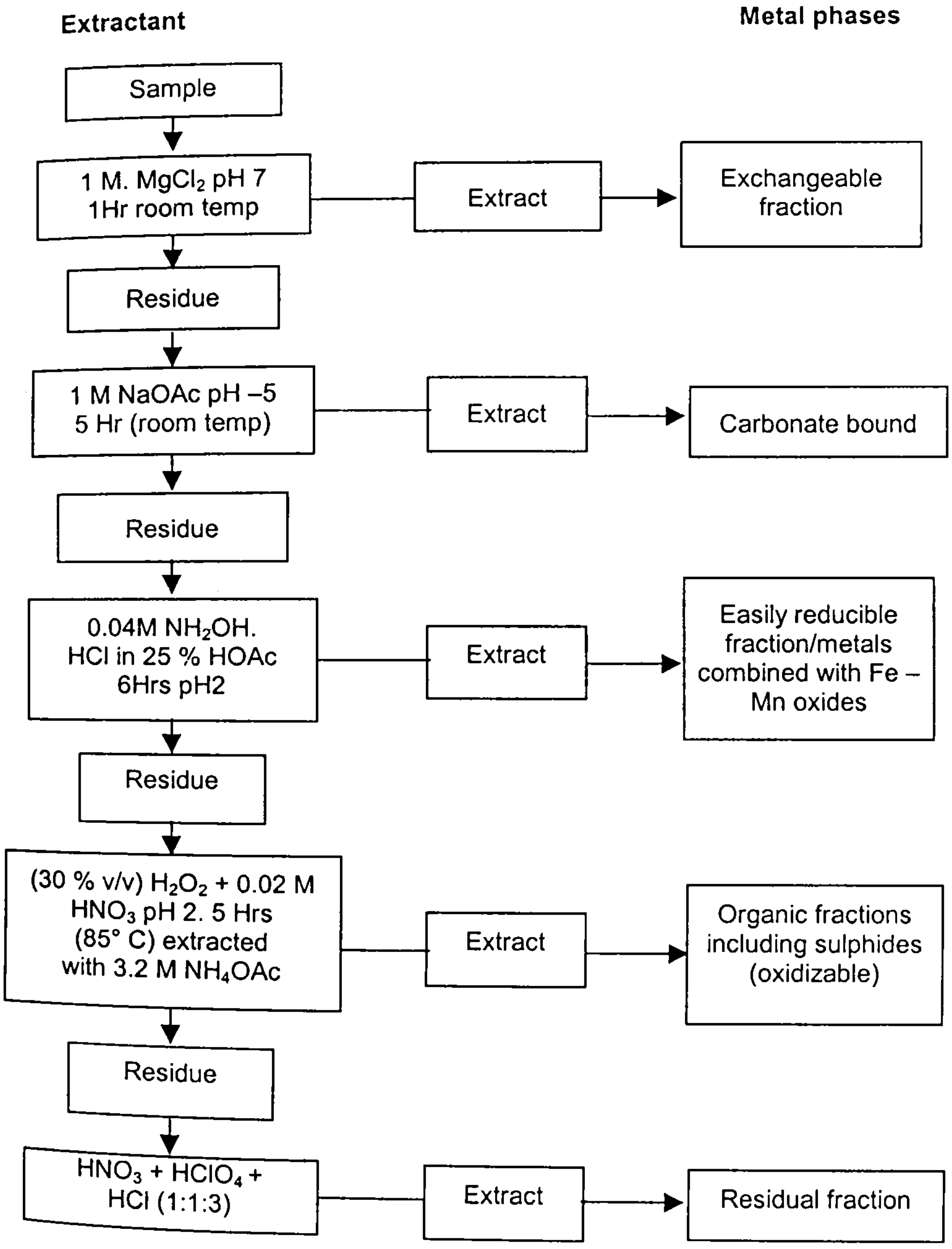

Fig. 2.2 Sequential extraction scheme

Four to five gram aliquots of the wet sediment samples were used for the sequential chemical extraction. Wet sediments were analyzed, as the drying process is known to significantly alter metal speciation (Kerster and Forstner, 1986; Jones and Turki, 1997). The extractions were done in 250 ml Erlen meyer flasks with continuous agitation. The phases were separated by centrifugation at 6000 rpm for 10 minutes. The centrifugate was analysed for metal concentration by atomic absorption spectrophotometry (Perkin-Elmer 3110 AAS), calibrated using standard solutions prepared by dilution of 1000 mg/l standard solution (Merck), whereas the residue was carefully transferred to the container with the next extractant to be used. Washings in between the extractions were dispensed with to avoid excessive solubilisation of solid phases. The moisture content in the sediment was determined separately and simultaneously and the concentrations were expressed in mg/kg dry weight. The samples were analysed in duplicate and the mean of the two determinations has been reported.

2.4 STATISTICAL ANALYSIS

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. Both spatial and temporal variations were significant. The spatial variations are discussed mainly on the basis of annual mean concentrations recorded at each Station as well as in each Zone. Correlation study was carried out to find out the influence of various hydrographic parameters on the distribution of dissolved and particulate metals. Three seasons viz. Pre-monsoon (February - May), Monsoon (June - September) and Post - monsoon (October - January) have been recognized. The seasonal and annual mean values are represented graphically, Station-wise and Zone-wise to bring out seasonal and spatial variations. Multiple regression analysis was performed on the total metal concentrations to assess the role of different parameters in determining distribution pattern of heavy metals. An attempt was also made to quantify the natural and anthropogenic contribution of heavy metals to the sediment.

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Chapter 3

HYDROGRAPHIC AND SEDIMENT CHARACTERISTICS

3.1 Introduction

3.2 Results and discussion

3.2.1 Hydrographical features

3.2.2 Sediment characteristics

3.1 INTRODUCTION

Hazardous substances discharged into the aquatic environment are known to adsorb onto suspended particles and to be scavenged from the water column into proximal sediments (Karickhoff, 1984; Daskalakis and O'Conor, 1995; Lee et. al., 1998). Several studies, which recognized the adverse effects of heavy metals on health, have suggested that water quality standards should account for the accumulation and release of toxic metal compounds. Monitoring of trace metal concentration in different compartments of aquatic system is thus an integral part of any environmental management programme such as pollution assessment (Forstner and Wittmann, 1979; Sinex and Wrigt, 1988; Hoshika et. al., 1991). Heavy metals are transported to the ocean in dissolved and particulate forms by rivers. In estuaries, where river water and coastal waters of widely different compositions are mixed, strong gradients in chemical properties occur (Burton and Liss, 1976). The variations in the hydrographic parameters in estuaries, when river water mixes with seawater, affect the transport mechanisms of dissolved and particulate components of heavy metals. Metal concentrations in sediments vary largely with sediment parameters such as grain-size, organic carbon content, sediment moisture content, total phosphorus and sources of anthropogenic inputs. Assessment of hydrographical and sediment characteristics thus constitute an inevitable part of the study of heavy metals. The large variations in metal concentrations in dissolved and particulate phases cannot be explained without the knowledge of hydrographic parameters such as salinity and pH. So also any satisfactory, scientific explanation for the seasonal and spatial distribution of heavy metals in the sediments would inevitably require inputs on sediment characteristics. Several investigators like Cherian (1967), Qasim and Gopinathan (1969), Josanto (1971), Murty and Veerayya (1972), Balakrishnan and Shynamma (1976), Sarala Devi et. al. (1979), Lekshmanan et. al. (1982), Balchand and Nambisan (1986), Anirudhan and Nambisan (1990), Nair (1992), Harikrishnan (1997) and Sureshkumar (1998) have carried out comprehensive studies in Cochin estuary. Babu Jose (1999) investigated the variations in hydrographical parameters and nutrients in Chitrapuzha River. They have taken cognizance of the influence of varying hydrological and sedimentological parameters.

This chapter is devoted to discussion on the spatial and the seasonal distribution of hydrographical (salinity, pH, dissolved oxygen and suspended solids) and sediment parameters (moisture content, grain size distribution, sediment organic carbon and total phosphorus).

3.2 RESULTS AND DISCUSSION

3.2.1 Hydrographical Features

A number of laboratory studies have addressed the influence of hydrographic parameters pH, turbidity, salinity and dissolved oxygen on the chemistry of heavy metals under estuarine conditions (Sholkovitz, 1976, 1978; Duinker and Nolting, 1978; Salamons, 1980; Millward and Moore, 1982; Santschi et. al., 1982; Bourg, 1983; Windom et. al., 1983). The general hydrographical features of Cochin backwaters have been attempted by several workers. Most of these studies conducted focused on the region around Cochin harbour. Since a systematic study on the role of hydrographical parameters in determining the distribution of heavy metals in Chitrapuzha tropical tidal river is lacking, such an investigation was carried out. Hydrographic conditions in a tidal river mainly depend on the intrusion of seawater associated with tides, influx of fresh water from rivers, precipitation/ evaporation processes and also on weather. Sediment characteristics are in turn mainly governed by the hydrography of the overlying waters.

The overall summary statistics on the distribution of hydrographical and sediment parameters are given in Table 3.1. The Station-wise summary statistics on salinity, dissolved oxygen, pH and suspended solids recorded at the surface and bottom waters are presented in Tables 3.2 to 3.5. Seasonal and spatial variations are depicted in Figures 3.1 to 3.4.

Table 3.1 Overall summary statistics on distribution of hydrographical and sediment parameters

Parameter	Min		Max		Mean		SD		%CV	
	S	B	S	B	S	B	S	B	S	B
Salinity (10^{-3})	0.03	0.03	32.30	32.60	8.19	10.59	9.49	11.38	115.80	107.39
DO (ml/l)	2.16	2.25	10.30	7.96	4.04	3.99	1.15	0.91	28.46	22.88
pH	6.10	6.20	8.10	10.60	7.06	7.19	0.58	0.70	8.27	9.72
SS (mg/l)	0.80	1.33	28.27	98.90	7.04	17.64	4.93	17.78	70.07	100.82
SMC (%)	21.71		77.58		52.37		14.37		27.43	
SOC (mg/g)	1.34		90.24		23.37		16.22		69.43	
TP (mg/g)	0.29		101.44		16.10		25.34		157.40	

DO - Dissolved oxygen; SS - Suspended solids; SMC - Sediment moisture content; SOC - Sediment organic carbon; TP - Total phosphorus; S- Surface, B-Bottom Min-Minimum; Max-Maximum; SD-Standard Deviation, CV-Coefficient Variation.

Salinity

Salinity plays a dominant role in influencing metal concentrations in water and sediments and its distribution strongly depends on seawater intrusion through the bar-mouth and on the influx of river water. Salinity of estuarine waters has been considered as an index of the estuarine mixing processes and tidal effects.

Salinity values ranged from 0.03 x 10^{-3} to 32.30 x 10^{-3} in surface waters a 0.03 x 10^{-3} to 32.60 x 10^{-3} in bottom waters (Table 3.1) during the study period. T overall mean salinity values of surface and bottom waters were 8.19 x10^{-3} a 10.59 x 10^{-3} respectively. Salinity values of both surface and bottom wat exhibited significant spatial and seasonal variations in the lower reaches Chitrapuzha River (Fig. 3.1). Surface and bottom salinities showed an increasi trend from riverine to estuarine region during the study period. Stations 1, 2 and of Zone 1 had the highest salinity through out the year whereas salinity intrusi was very low in the upstream Stations 7, 8 and 9 of Zone 3 (Table 3.2).

Table 3.2 Station - wise summary statistics on salinity (x 10^{-3})

	Surface					Bottom				
Station	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
1	0.90	32.30	15.48	10.42	67.36	1.28	32.60	22.28	9.22	41.39
2	1.61	27.63	16.09	9.26	57.58	2.17	28.24	20.51	9.73	47.46
3	0.90	30.80	16.75	10.43	62.29	2.89	32.00	24.65	8.54	34.65
4	0.30	27.66	12.08	9.22	76.31	0.30	28.30	13.45	10.01	74.45
5	0.06	15.28	7.77	6.47	83.33	0.08	15.25	8.02	6.24	77.84
6	0.04	8.60	4.04	3.50	86.76	0.06	9.26	4.36	3.70	84.93
7	0.03	3.20	0.81	1.08	133.17	0.03	5.43	1.37	1.76	128.24
8	0.03	1.89	0.36	0.56	153.68	0.05	1.03	0.28	0.32	117.12
9	0.03	2.40	0.37	0.72	191.78	0.04	2.10	0.43	0.65	153.06

The highest salinity (32.6 x 10^{-3}) was recorded at bar-mouth during pre monsoon season. Both surface and bottom salinities decreased with the onset o the monsoon and it was practically nil in the Zone 3 during this period. The averag surface to bottom gradient in the estuarine region (Stations 1 to 6) was high durin monsoon and low during the pre-monsoon season. It showed an increasing tren from surface to bottom at all Stations during all seasons. This can be attributed t fairly high river discharge in monsoon resulting in a partially mixed type of estuarin system (Padmavathi and Satyanarayana, 1999; Vazquez et. al., 1999) Thus th available data on the salinity unambiguously established the influence of the influ of fresh water from rivers and intrusion of seawater into the estuary an Chitrapuzha River via Cochin bar-mouth, on salinity distribution. The stratificatio recorded might play an important role in the settling of detritus and hence in th metal fluxes.

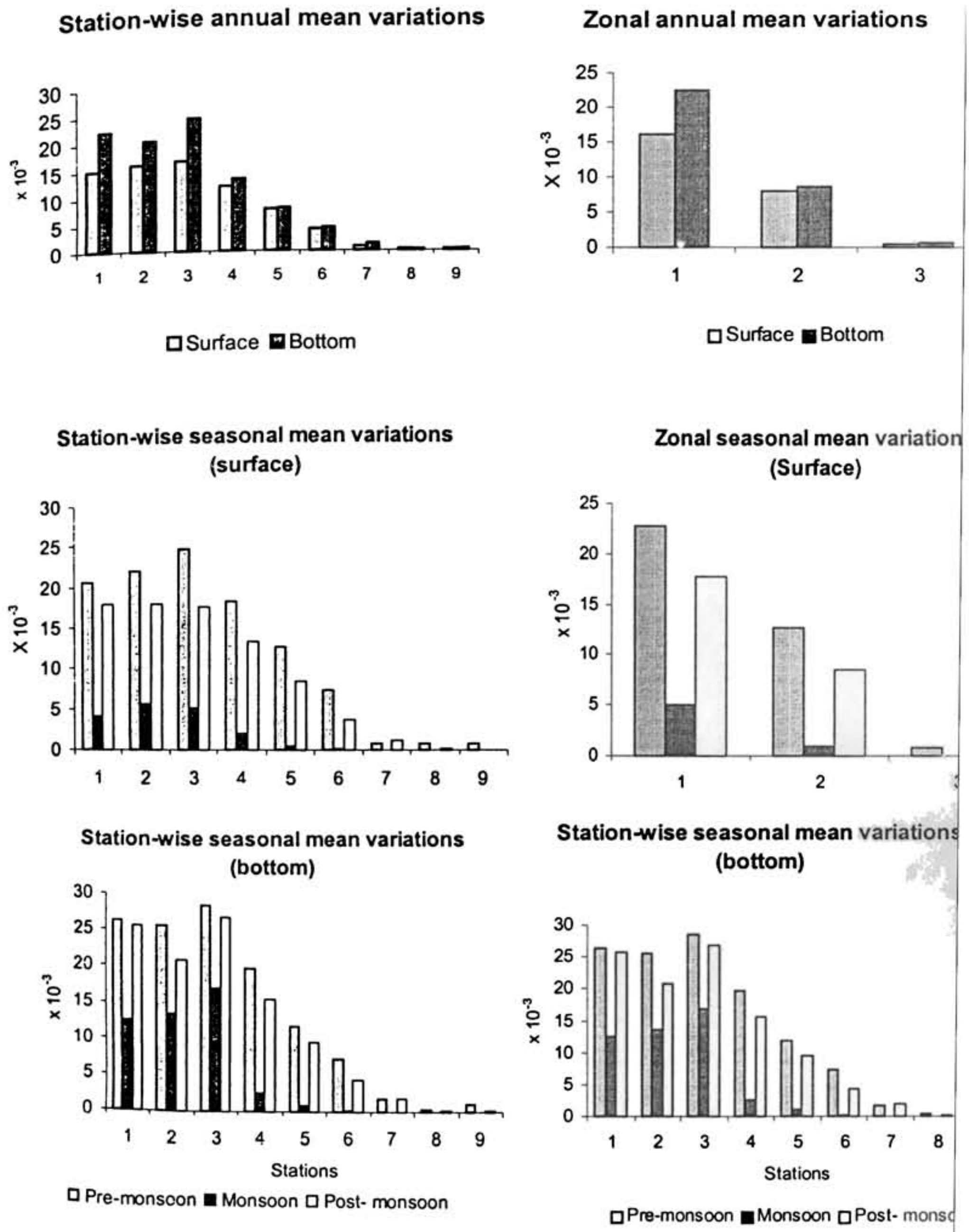


Fig. 3.1 Seasonal and spatial variations of salinity in surface and bottom waters

Dissolved oxygen

The amount of dissolved oxygen in natural waters depends upon temperature, salinity, turbulence of water and atmospheric pressure. The depletion of oxygen content in water leads to undesirable obnoxious odour under anaerobic conditions and damage to aquatic life. Study on the dissolved oxygen concentration may also help to explain the various physical, chemical and biological processes taking place in natural waters (De Sousa and Sen Gupta, 1986). The dissolved oxygen requirement depends on temperature and varies from organism to organism. The decomposition of organic waste and oxidation of inorganic waste may reduce the dissolved oxygen to extremely low levels, which may prove harmful to organisms in the aquatic environment.

No deoxygenated conditions were observed at any Station in the lower reaches of Chitrapuzha. Variations in dissolved oxygen ranged between 2.16 to 10.30 ml/l in surface waters and between 2.25 to 7.96 ml/l in bottom waters (Table 3.1). The overall mean value of dissolved oxygen surface and bottom waters were 4.04 and 3.99 ml/l respectively. In the Zones 1 and 3, the surface values were higher than bottom values (Fig.3.2). This may be attributed to the direct dissolution of atmospheric oxygen or photosynthesis by phytoplankton, which exceeds respiration. Station 6 showed generally lower values during all seasons (Table 3.3). The depletion of dissolved oxygen due to the rapid decay and decomposition of water hyacinth and Molesta salvinia in this area may be the main reason for the low values of dissolved oxygen. The generally higher values during monsoon could be ascribed to the high turbulence in river flow during the rainy season (Nair, 1992).

Table 3.3 Station-wise summary statistics on dissolved oxygen (ml/l)

	Surface					Bottom				
Station	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
1	2.83	4.81	3.98	0.60	15.03	2.47	5.33	4.13	0.92	22.35
2	2.99	5.03	4.14	0.57	13.72	3.29	5.33	4.19	0.67	16.08
3	2.61	5.25	4.12	0.81	19.66	2.25	5.11	3.81	0.81	21.21
4	3.27	5.68	4.42	0.85	19.16	3.57	5.55	4.54	0.71	15.72
5	2.90	5.03	3.91	0.79	20.12	2.87	5.33	4.09	0.69	16.79
6	2.16	4.15	2.95	0.65	21.91	2.94	4.45	3.48	0.50	14.43
7	2.16	6.35	4.24	1.33	31.36	2.45	5.55	3.90	1.04	26.72
8	2.39	5.69	4.15	1.10	26.50	2.65	4.87	3.80	0.71	18.60
9	2.55	10.30	4.47	2.26	50.62	2.47	7.96	3.97	1.62	40.75

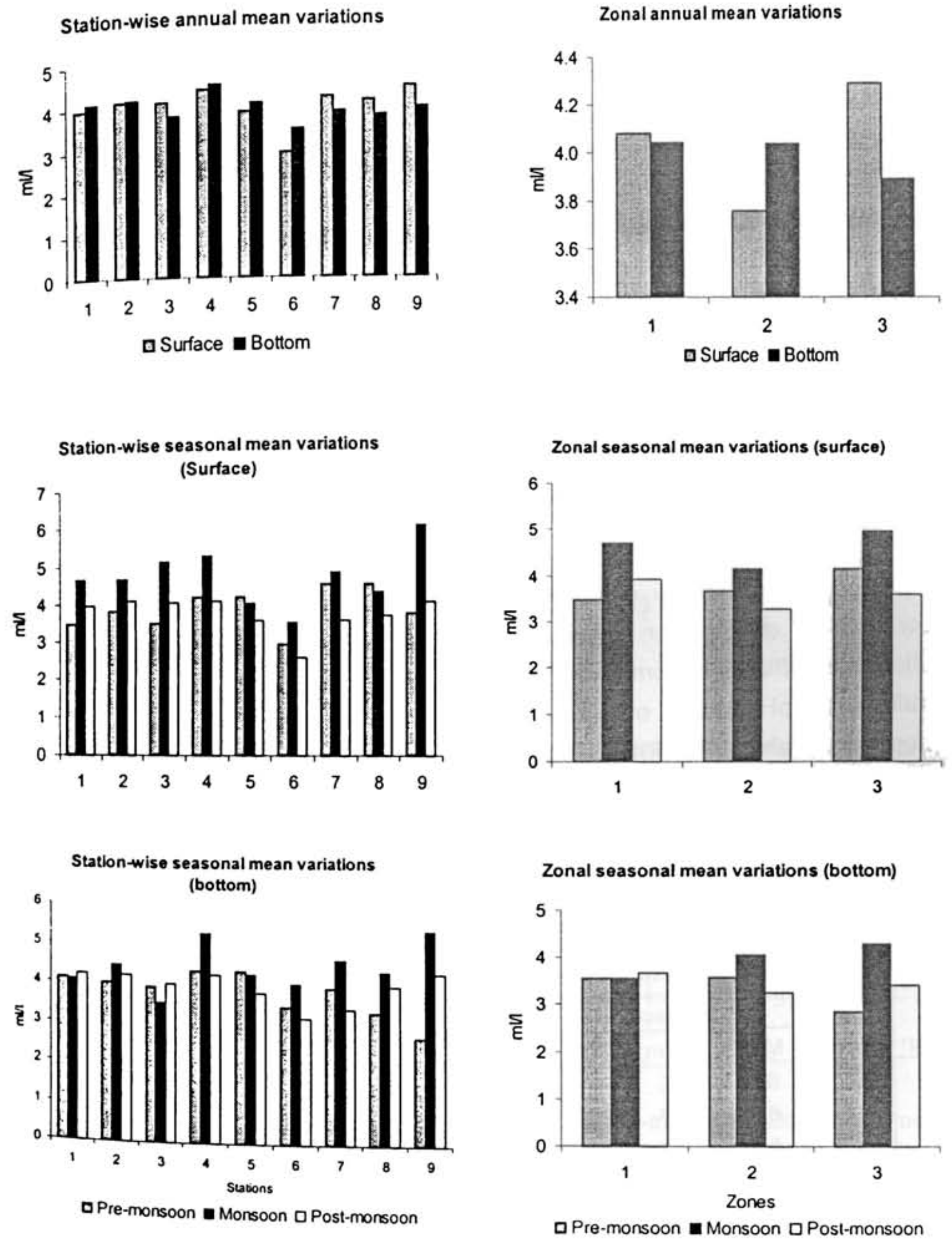


Fig. 3.2 Seasonal and spatial variations of dissolved oxygen in surface and bottom waters

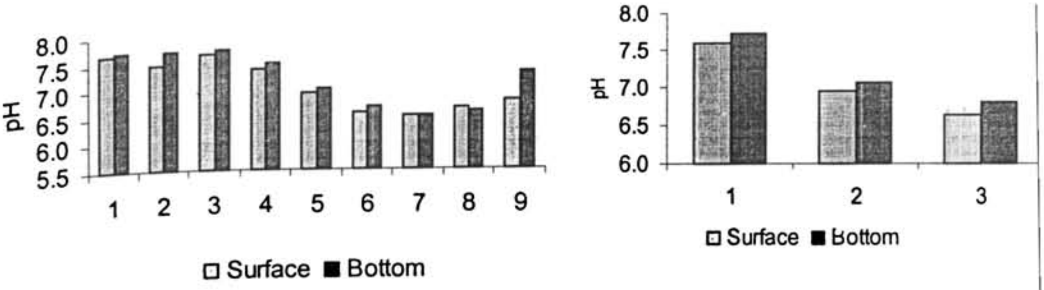
pH

Many of the life processes are sensitive to the hydrogen ion concentration (pH) of the surrounding medium. It is an important hydrographical parameter indicating the level of dissolved carbon dioxide in the water, which may in turn reflect the activity of phytoplankton and the level of dissolved oxygen (Skirrow, 1975). Variation in pH due to chemical and other industrial discharges renders a stream unsuitable not only for recreational purposes but also for the rearing of fish and other aquatic life (Webb, 1982). The pH of natural water ranges from 6.0 to 8.5. The pH influences to a large extent the speciation of metals in aquatic environments as well as decides their inter-phasial partitioning between dissolved and particulate. Photosynthesis, salinity, mineralization processes rainfall, nature of dissolved materials and the discharge of industrial effluents are the major factors that influence the pH. Natural turbulence with concomitant aeration can also influence the pH (Zingde and Desai, 1987).

The important factors, which influence the pH in Chitrapuzha aquatic system are photosynthetic activity of phytoplankton, discharge of fresh water from the upper reaches of the river, salinity changes during salt water intrusion and the discharge of effluence from industries situated on the banks of the river. The overall mean pH values of surface and bottom waters were 7.06 and 7.19 respectively (Table 3.1). The highest (10.6) and lowest (6.1) pH values were recorded at Station 9 (Table 3.4) during the month of May and June respectively, and indicated the discharge of strongly alkaline effluents during May and highly acidic effluents during June. The seasonal and spatial variations of pH in surface and bottom waters are depicted in the Figure 3.3.

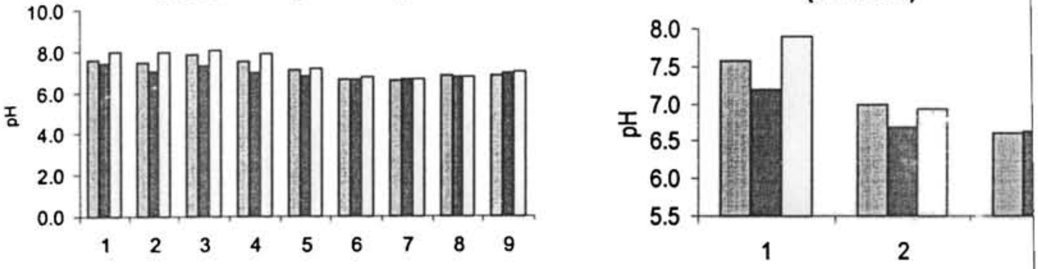
Table 3.4 Station-wise summary statistics on pH

Station	Surface					Bottom				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
1	6.7	8.1	7.5	0.5	6.7	7	8.2	7.7	0.4	5.1
2	7	8.1	7.7	0.4	5.4	7	8.2	7.7	0.4	5.0
3	6.9	8.1	7.7	0.4	5.1	6.9	8.1	7.7	0.4	5.1
4	6.5	8.1	7.4	0.5	6.5	6.7	8.1	7.5	0.5	6.1
5	6.6	7.4	6.9	0.3	4.0	6.6	7.5	7.0	0.3	4.0
6	6.2	6.8	6.5	0.2	2.8	6.5	6.9	6.7	0.1	2.1
7	6.2	6.8	6.5	0.2	3.5	6.2	6.8	6.5	0.2	3.0
8	6.3	7.2	6.6	0.4	5.4	6.2	7.1	6.6	0.3	4.4
9	6.1	7.7	6.8	0.5	6.9	6.3	10.6	7.3	1.2	16.8



Station-wise seasonal mean variations (surface)

Zonal seasonal mean variatio (surface)



Station-wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

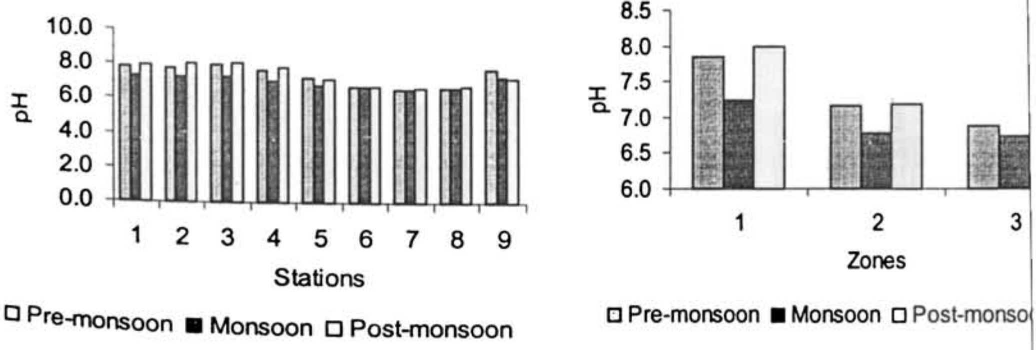


Fig. 3.3 Seasonal and spatial variations of pH in surface and bottom waters

The pH variations were in the range of 6.10 to 8.10 (in surface water) and 6.2 to 10.60 (in bottom water). The pH values of both surface and bottom waters exhibite significant spatial and seasonal variations. Bottom values were slightly higher tha those of surface, which may be attributed to the mixing of fresh water with saline wate of high pH (Fig. 3.3). The average seasonal values showed only slight variations Stations in the Zones 1 and 2 recorded higher values during pre-monsoon and post-monsoon seasons. This may be due to saline intrusion during these seasons.

Suspended solids

In aquatic systems, most contaminants and especially trace metals show a high affinity for suspended particulate matter. The importance of suspended solids in the estuarine geochemistry of trace metals is related to many factors such as a) large surface area and a consequent large capacity for trace element adsorption desorption reactions (Boyden et. al., 1979; Rae and Aston, 1982) b) indiscriminate consumption of suspended matter by filter feeders (Bligh, 1972; Rae and Aston, 1982) and c) the estuarine transport of trace metals (Cline et. al., 1973; Rae and Aston, 1982). The partitioning of metals between dissolved and particulate phases is important in explaining the geochemical properties of elements in these systems. The estimation of suspended matter is thus an obligatory parameter in the study of trace metal dynamics (Martin and Whitefield, 1983). The station-wise summary statistics on suspended solids are furnished in the table 3.5.

Table 3.5 Station-wise summary statistics on suspended solids (mg/l)

	Surface					Bottom				
Station	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
1	3.3	28.3	10.7	7.2	67.1	8.5	63.7	25.3	18.2	72.0
2	3.1	17.5	9.0	4.6	50.8	7.6	57.0	26.4	17.0	64.6
3	3.3	19.5	8.1	4.4	54.5	8.6	98.9	26.6	26.3	99.0
4	5.7	17.4	9.3	3.8	41.2	5.9	78.9	20.4	21.3	104.4
5	1.8	10.4	5.9	2.8	48.3	1.3	20.6	8.6	6.2	73.0
6	1.5	15.5	4.2	4.1	97.2	1.6	22.7	6.3	6.1	96.1
7	0.8	10.0	5.1	3.1	60.2	4.0	23.0	10.6	6.0	56.8
8	0.8	16.9	6.1	5.8	94.9	4.6	26.2	10.8	6.6	61.1
9	1.2	9.7	5.0	2.9	59.0	4.5	78.9	23.7	22.0	92.7

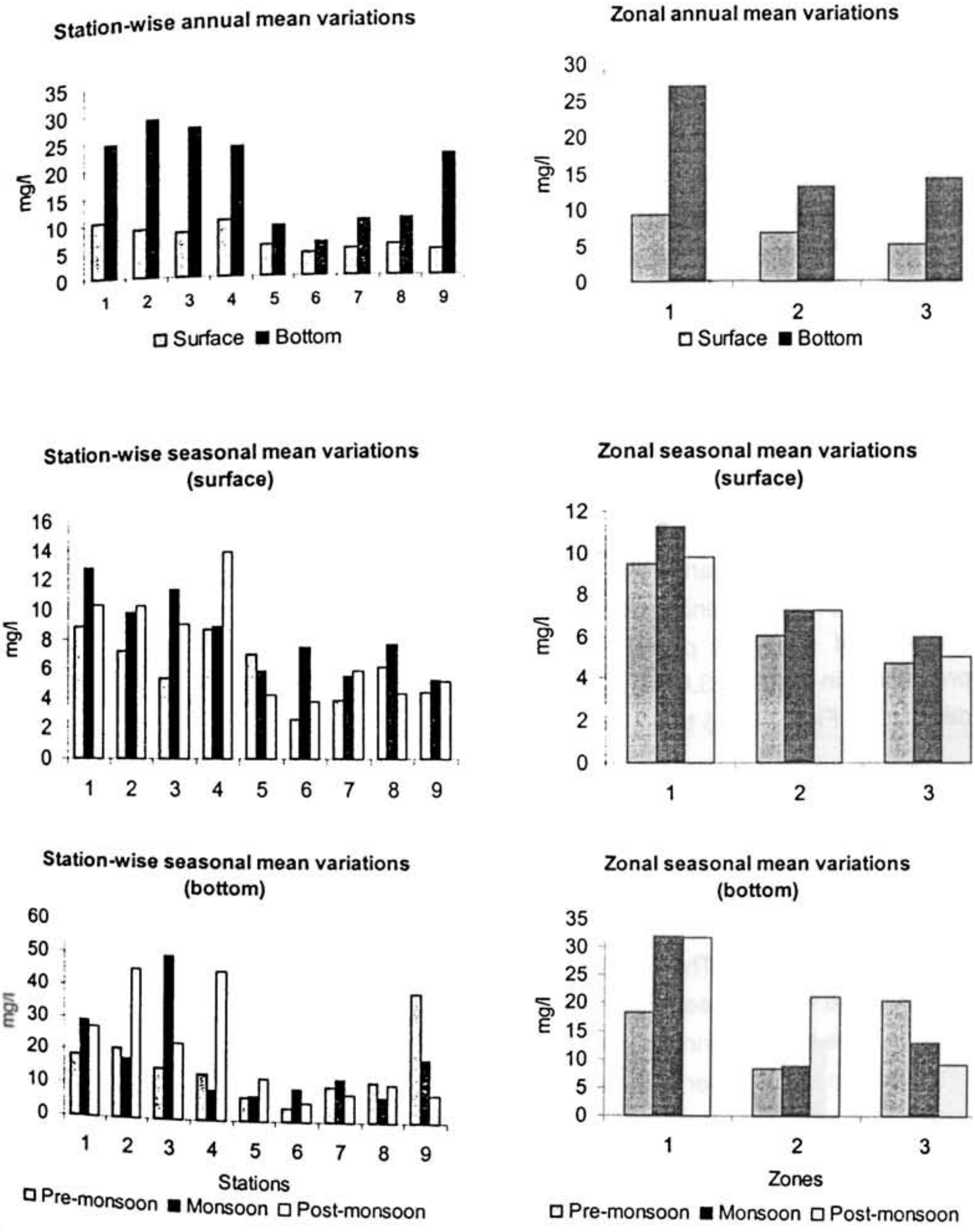


Fig. 3.4 Seasonal and spatial variations of suspended solids in surface and bottom waters

The values of suspended solids ranged between 0.80 mg/l to 28.27 mg/l in surface waters and 1.33 mg/l to 98.90 mg/l in bottom waters (Table 3.1). The mean value of suspended solids recorded in the surface and bottom waters was 7.04 mg/l and 17.64 mg/l respectively. Bottom values were higher than the surface water values. Generally monsoon season recorded higher values for suspended solids in the surface waters (Fig. 3.4). This may be due to high river run off during monsoon months. Station 3 recorded the highest value of suspended solids (98.90 mg/l) during the period of study (Table 3.5). The concentration of suspended solids varied widely, bottom waters showing more fluctuations (%CV 100.8) than surface waters (%CV 70) (Table 3.1). The Station-wise annual mean values indicate that the bottom waters of Stations 1 to 4 contain higher amounts of suspended solids than the other Stations (Fig. 3.4).

3.2.2 Sediment Characteristics

The sediment parameters investigated were grain size distribution, moisture content, sediment organic carbon and total phosphorus. The Station-wise summary statistics of sediment parameters and the size composition of sediments are presented in Tables 3.6 to 3.10. The seasonal and annual mean values are depicted in Figures. 3.5 to 3.8.

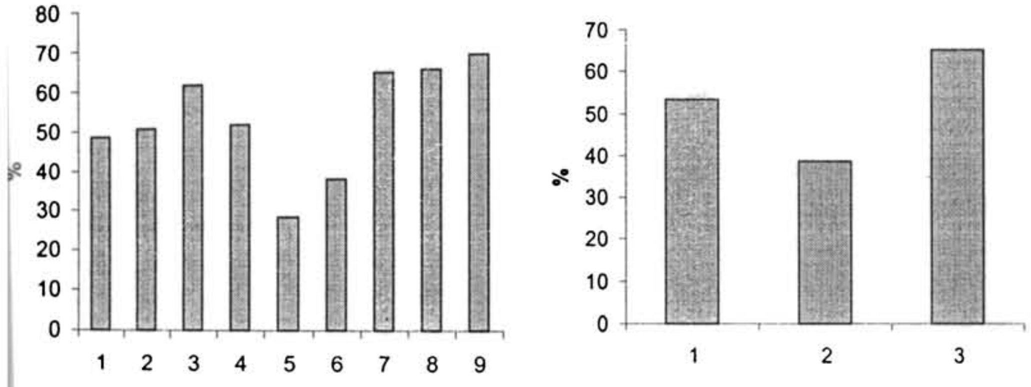
Moisture

Moisture content in sediments of the study area varied between 21.71% and 77.58% (Table 3.1). The moisture content was found to be lower for sediments of Stations 5 and 6 whereas higher values were recorded for the sediments of other Stations (Table. 3.6). The comparatively lower percentage of moisture content at Station 5 and 6 was associated with the sandy nature of sediments found at these Stations. The highest annual mean of moisture content was observed at Station 9 (67.9%). Generally higher values were recorded during monsoon season (Fig. 3.5). Zonally the variation in moisture content could be attributed to the variation in organic matter and grain size of the sediment.

Table 3.6 Station - wise summary statistics on Moisture %

Station	Min	Max	Mean	SD	%CV
1	28.1	59.1	48.5	8.7	17.3
2	30.8	61.1	50.1	9.4	19.3
3	51.8	67.7	61.0	4.6	7.6
4	39.1	58.5	50.9	7.1	14.0
5	21.7	34.8	28.0	5.2	18.7
6	22.8	54.4	37.2	8.2	22.1
7	52.4	71.8	63.4	5.6	8.9
8	47.6	72.3	64.2	7.9	12.3
9	54.9	77.6	67.9	5.7	8.4

Station-wise annual mean variations **Zonal annual mean variations**



Stationwise-seasonal mean variations **Zonal seasonal mean variations**

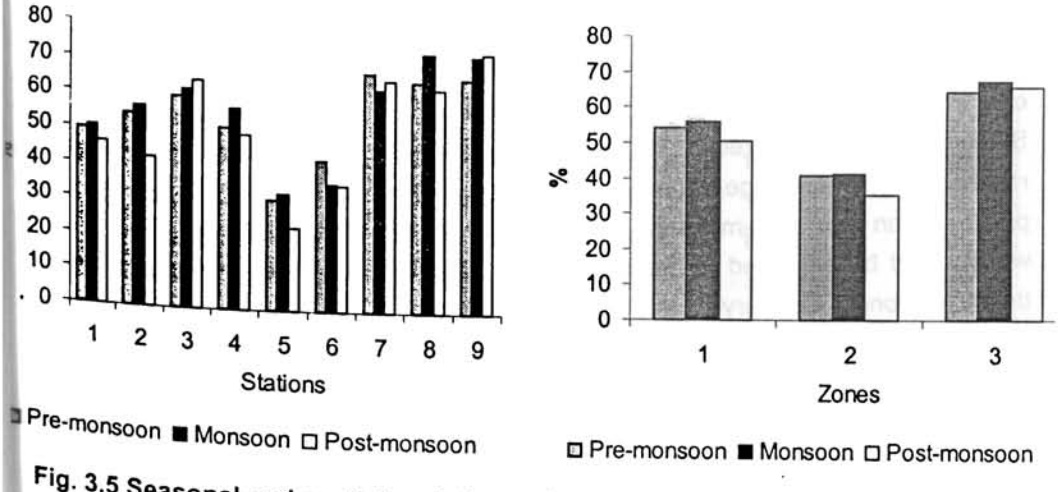


Fig. 3.5 Seasonal and spatial variations of moisture percentage in sediments

Grain size distribution

Grain size analysis is a fundamental procedure in sedimentology and limnology and it gives basic information on the sediment composition and depositional environment. Natural sediments consist of particles of different sizes, and for deciding the size groups, several class intervals based on average diameter have been suggested. One such system includes the grading of particles into sand (> 63 µm), silt (4 – 63 µm) and clay (< 4 µm) sizes (Krumbein and Pettijohn, 1938). The annual mean values of various grain fractions are presented in the Table 3.7 along with summary statistics. The composition of sediments during different seasons in the study area is shown in the Table 3.8. The seasonal and spatial variations of sand, silt and clay are depicted in the Figure 3.6. The sediments of Stations in Zone 2 were mainly composed of sand particles (Table 3.7). Stations 1, 2 and 3 have almost equal percentage for sand and clay irrespective of seasons.

The sediment distribution pattern depends on several factors such as sediment sources, the texture of the sedimentary materials supplied, the bottom topography of the basin and general hydrographic features (Veerayya and Murty, 1974; Seralathan, 1986; Nair, 1992). At Stations 1, 2 and 3, the bulk of the sedimentary materials is supplied by the Muvattupuzha River, whereas at the other six Stations, the sedimentary material is supplied from upstream of the river Chitrapuzha. Clay acts as nucleation centres for Fe/Mn oxides in the fresh water region (Forstner, 1977) and during estuarine mixing. It also acts as centres for flocculation and precipitation of dissolved and colloidal organic matter during estuarine mixing (Aston and Chester, 1973; Sholkovitz, 1976). The percentage of clay in the present study, varied from 4.49 to 57.85 (Table 3.7). Generally the Stations in the Zone 3 recorded high clay content while the Stations in the Zone 2 recorded high percentage of sand. Percentage of clay was generally higher during pre-monsoon and post-monsoon seasons at the estuarine Stations 1, 2 and 3, which could be attributed to the settling of finer fractions of the sediments during these seasons. Contrary to this finding, the Stations 7, 8 and 9 showed higher values for silt during monsoon. This may be due to flushing of phosphogypsum, a waste product dumped in the premises of fertilizer manufacturing unit, into the river during the monsoon season.

Table 3.7 Station wise summary statistics on grain size

Sand %

Station	Min	Max	Mean	SD	%CV
1	7.54	41.24	32.14	12.37	42.56
2	10.73	59.55	40.84	18.21	50.89
3	1.79	28.78	21.72	11.91	67.91
4	20.12	82.53	52.71	22.46	46.83
5	9.89	93.22	83.70	31.25	43.19
6	13.55	84.28	74.68	26.56	40.67
7	13.67	48.62	30.93	11.86	38.73
8	11.21	33.34	17.81	7.78	36.09
9	13.92	44.62	20.42	12.05	47.70

Silt %

Station	Min	Max	Mean	SD	%CV
1	22.12	50.10	32.45	10.63	32.78
2	19.89	43.52	30.58	10.02	32.76
3	21.22	58.89	41.56	15.47	37.23
4	7.56	46.27	23.95	13.75	57.43
5	1.77	9.99	5.96	3.57	59.86
6	4.49	16.09	9.32	4.73	50.82
7	23.61	33.90	28.18	3.71	13.17
8	22.89	47.90	37.00	9.03	24.41
9	31.73	55.21	40.52	8.47	20.90

Clay %

Station	Min	Max	Mean	SD	%CV
1	12.45	56.09	35.41	14.37	40.60
2	18.88	45.75	28.58	9.56	33.45
3	25.58	52.71	36.56	10.53	28.82
4	4.49	31.24	23.35	9.73	41.70
5	5.02	14.56	10.34	3.64	35.22
6	9.89	32.82	16.00	8.54	53.34
7	27.76	57.85	40.89	11.46	28.03
8	34.93	55.78	45.18	7.78	17.22
9	23.65	57.78	39.06	13.64	34.92

Table 3.8 Size composition of sediments

Station	Season	Sand%	Silt%	Clay%
1	Pre-monsoon	30.47	31.71	37.82
	Monsoon	52.62	27.71	19.67
	Post-monsoon	39.42	32.32	28.26
2	Pre-monsoon	24.21	29.4	46.39
	Monsoon	32.88	28.93	38.18
	Post-monsoon	39.34	39	21.66
3	Pre monsoon	34.2	22.75	42.58
	Monsoon	28.29	45.53	26.18
	Post-monsoon	2.68	56.4	40.92
4	Pre-monsoon	39.13	33.2	27.68
	Monsoon	46.5	28.38	25.12
	Post-monsoon	72.49	10.27	17.24
5	Pre-monsoon	81.41	6.71	11.87
	Monsoon	78.14	8.61	13.26
	Post-monsoon	91.55	2.55	5.9
6	Pre-monsoon	66.24	9.02	24.75
	Monsoon	80.05	7.97	11.98
	Post-monsoon	77.76	10.96	11.29
7	Pre-monsoon	22.07	28.57	49.32
	Monsoon	34.12	31.84	34.04
	Post-monsoon	36.59	24.14	39.27
8	Pre-monsoon	17.7	33.68	48.62
	Monsoon	13.38	43.38	43.24
	Post-monsoon	22.36	33.96	43.69
9	Pre-monsoon	25.59	33.7	40.71
	Monsoon	19.32	46.23	34.45
	Post-monsoon	16.35	41.64	42.01

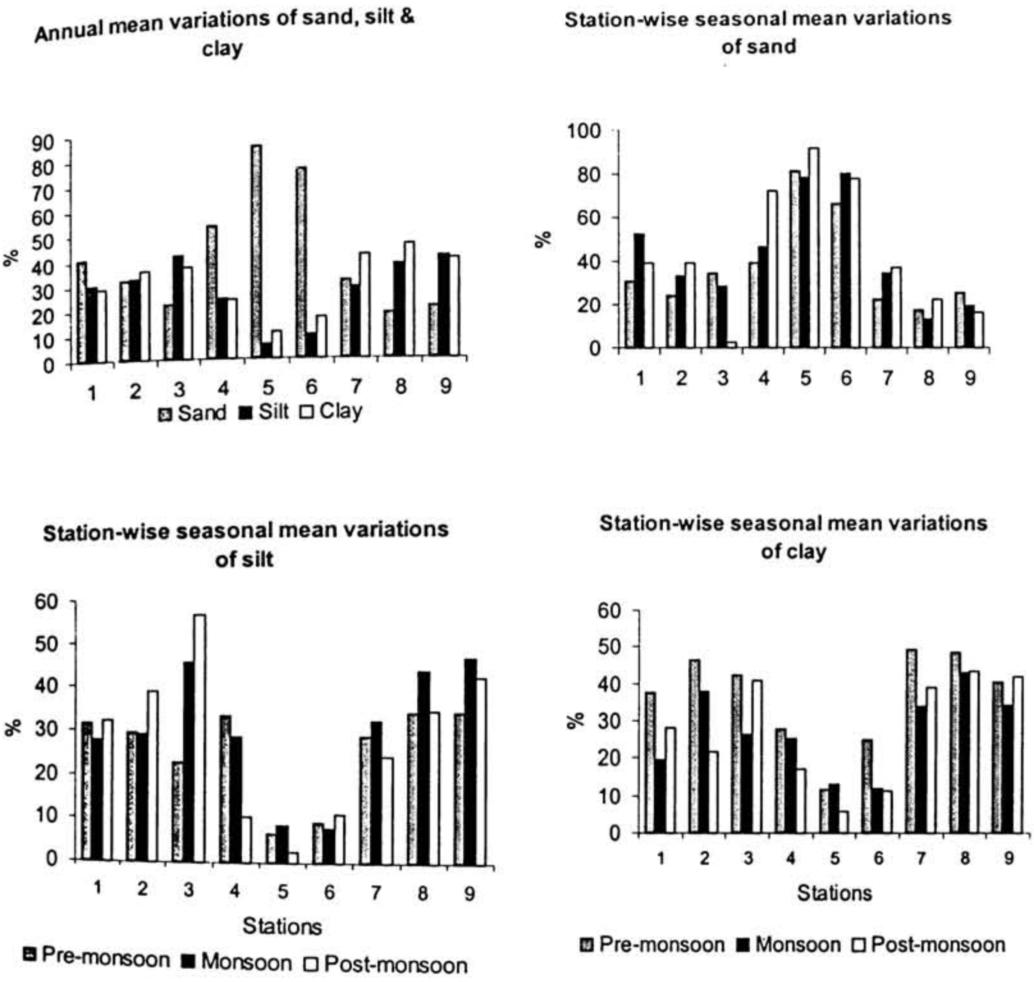


Fig. 3.6 Seasonal and spatial variations of sand, silt and clay

Sediment organic carbon

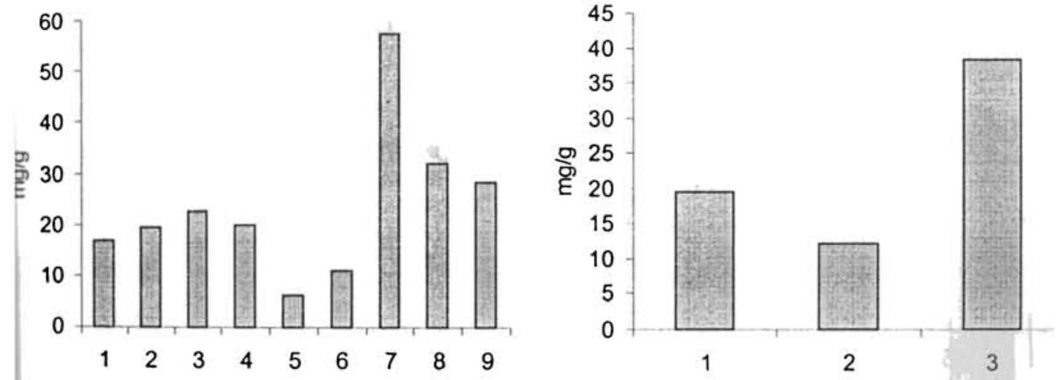
The organic carbon content of the sediment has a major role in maintaining the fertility of the sediment and thereby flourishing the biological productivity. It is a prerequisite for explaining metal distribution in the sediment. The origin of sedimentary organic matter is primarily from the residues of organic life in the aquatic system. Organic material transported by rivers from anthropogenic and biological sources on land also contributes to this. The autochthonous materials, which resemble more closely the primary biological products, are more susceptible to biodegradation, and therefore, ecologically less persistent. The allochthonous fraction is mainly composed of diagenetically formed secondary reaction products which are less susceptible to biodegradation, and therefore, ecologically more persistent. Knowledge of the nature, origin and transformations of organic matter in sediments provides valuable information on the cycling of trace metals in the aquatic environment. The distribution of sediment organic carbon in Cochin estuary was studied by Murty and Veerayya (1972), Sankaranarayanan and Panampunnayil (1979) and Sunil Kumar (1996). However, these studies do not relate to Chitrapuzha River.

The distribution of organic carbon content in the study area exhibited distinct spatial and seasonal variations and was found to be within the range 1.34 mg/g to 90.24 mg/g with a mean value of 23.37 mg/g (Table 3.1). These values are generally less than the limit for a polluted estuary. The variations of Station-wise annual mean values are depicted in Figure 3.7. Zone 1 and 3 recorded higher values during all seasons whereas Zone 2 (especially Stations 5 and 6) recorded minimum values. Lower organic content at Stations 5 and 6 was associated with the prominent coarse sandy sediment fractions. In Zone 1 and 2, the pre-monsoon values were higher than monsoon values but there was no significant trend in the Zone 3. In Zone 1, sediment organic carbon exhibited a decreasing trend towards the bar-mouth. This may be due to flushing of organic matter and finer fractions of the sediments by tidal action. The minimum and maximum values were recorded at Stations 5 and Station 7 respectively (Table 3.9). One of the features of organic carbon in sediments is that its concentration increases as the particle size of the sediment decreases. Association of higher content of organic matter with the finer fractions of sediments in the Cochin backwater system was reported by Murty and Veerayya (1972). Brook and Moore (1988) also showed the significance of small particles in concentrating organic carbon. There is a significant relationship between concentration of metals in the sediment and total phosphorus, which will be discussed in detail while discussing multiple regression analysis.

Table 3.9 Station-wise summary statistics on sediment organic carbon (mg/g)

Station	Min	Max	Mean	SD	%CV
1	9.66	24.75	19.30	5.32	27.55
2	10.05	22.41	16.98	4.12	24.25
3	17.13	28.06	22.40	2.90	12.97
4	14.01	26.40	19.70	4.22	21.41
5	1.34	11.79	6.00	3.64	60.68
6	5.77	18.27	10.84	3.31	30.49
7	22.42	90.24	56.15	16.19	28.84
8	3.39	55.20	31.18	15.66	50.22
9	7.04	45.53	27.77	11.08	39.89

Station-wise annual mean variations **Zonal annual mean variations**



Station-wise seasonal mean variations **Zonal seasonal mean variations**

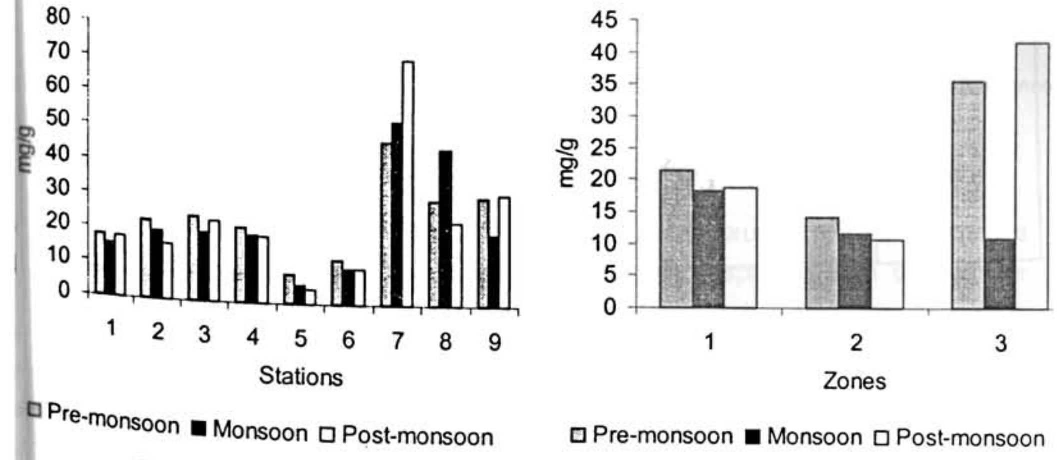


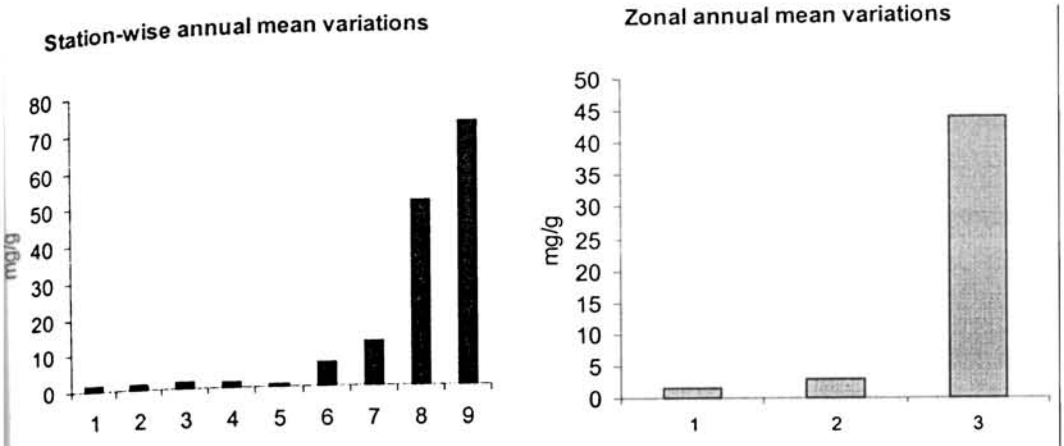
Fig. 3.7 Seasonal and spatial variations of organic carbon in sediments

Total phosphorus

The overall and Station-wise summary statistics on distribution of total phosphorus are furnished in Tables 3.1 and 3.10 respectively. The concentration of total phosphorus varied from 0.29 mg/g to 101.44 mg/g (Table 3.1). The average concentration during the period of study was 16.10 mg/g. The total phosphorus in the surficial sediments exhibited an increasing trend from Station 1 to 9 except Station 5 where the sediments were sandy (Fig. 3.8). The very high concentration of phosphorus at Stations 7 to 9 may be attributed to the discharge of effluents containing phosphorus fertilizers and from the fertilizer manufacturing company situated near Station 9. This may also be due to the spilling of phosphoric acid while pumping acid from the cargo barge to the fertilizer factory near Station 9. The highest value (101.44 mg/g) was recorded at Station 9 (Table 3.10).

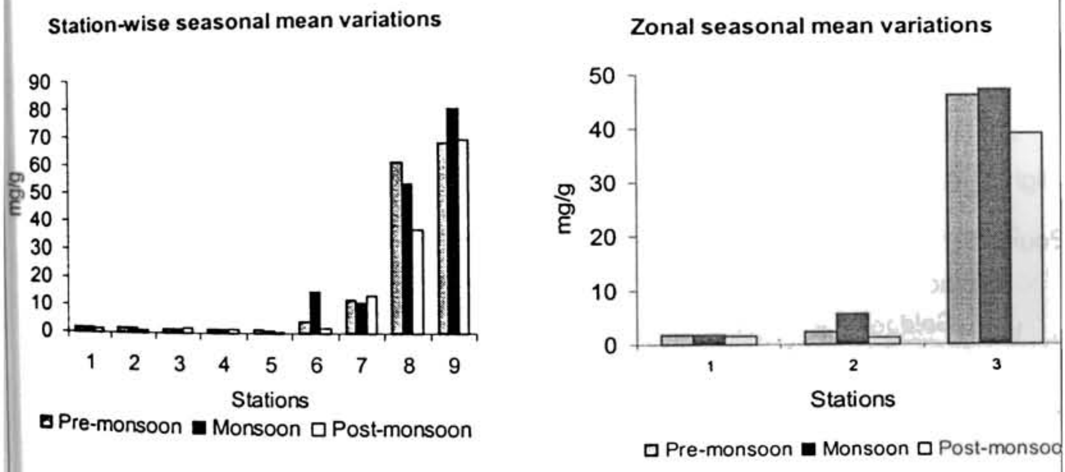
Table 3.10 Station-wise summary statistics on total phosphorus (mg/g)

Station	Min	Max	Mean	SD	%CV
1	0.46	2.75	1.57	0.59	37.70
2	0.90	2.18	1.62	0.37	22.76
3	1.42	2.06	1.74	0.23	12.97
4	0.72	1.92	1.43	0.41	28.68
5	0.29	2.85	0.88	0.75	84.72
6	1.44	28.28	6.23	8.21	131.87
7	7.12	17.86	12.01	3.19	26.58
8	8.68	68.67	49.16	17.51	35.61
9	53.43	101.44	70.28	13.08	18.61



Station-wise annual mean variations

Zonal annual mean variations



Station-wise seasonal mean variations

Zonal seasonal mean variations

Fig. 3.8. Seasonal and spatial variations of total phosphorus in sediments

Comparatively higher concentration of total phosphorus in the lower reaches during monsoon season may be due to leaching of phosphorus from the fertilizer factory (Fig 3.8). The concentration of total phosphorus in the estuarine Zone is in agreement with earlier observations made by Murthy and Veerayya (1972) and Nair (1992). There is a significant relationship between metal concentration in the sediment and total phosphorus, which will be discussed in detail while discussing multiple regression analysis.

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Chapter 4

DISTRIBUTION OF HEAVY METALS IN THE DISSOLVED, PARTICULATE AND SEDIMENT COMPARTMENTS

4.1. DISTRIBUTION OF HEAVY METALS IN THE DISSOLVED PHASE

4.1.1 Introduction

Rivers are one of the most important pathways for the transport of continental material to the oceans. Estuaries encompass the river-ocean interface, a region, which is both physically and chemically dynamic. Because estuaries are characterized by strong hydrodynamic and physico-chemical gradients, they are responsible for modifications of the distribution of trace elements between various dissolved and particulate species. The chemical behaviour of heavy metals during estuarine mixing is assumed to play an important role in their geochemical cycles. It is well established that, during mixing of fresh and saline waters, the partitioning of metallic species between solution and suspended particles is controlled by two counteractive biological processes. One is the removal of metals by flocculation of humic and fulvic acids-metal complexes and precipitation of iron and manganese oxides. The other process is the gain by desorption of dissolved metals from particles (Roux et. al., 1998). Numerous studies on the distribution and behaviour of heavy metals in various estuaries in different parts of the world have revealed that individual metals exhibit contrasting behaviour between estuaries, and sometimes even within the estuary. Factors which are important in controlling heavy metal behaviour include estuarine flushing time (Morris, 1990; Owens and Balls, 1997), complexation with dissolved inorganic and organic spcies (Comans and van Dijk, 1988; Owens and Balls, 1997; Van den Berg et. al., 1987; Owens and Balls, 1997) and interactions with suspended solids (Turner et. al., 1993; Benoit et. al., 1994) and sediments (Evans et. al., 1977; Owens and Balls, 1997). Within a particular estuary, one or more of these factors may be dominant in determining the behaviour of dissolved heavy metals.

An estuary is a mixing Zone of riverine and oceanic waters with widely varying compositions where end members interact both physically and chemically. During estuarine mixing, the trace metals in the dissolved and particulate forms can behave either conservatively or non-conservatively depending on physico-chemical factors such as pH, Eh and suspended solids etc. There are also somewhat conflicting reports on the behaviour of heavy metals during estuarine mixing. Poucot and Wollast (1997) have reported that the concentration of nickel and chromium in the Scheldt estuary decreased with increase in salinity. He also reported that manganese exhibited a non-conservative behaviour in Scheldt estuary. Guieu et. al. (1998) reported that copper and zinc showed conservative behaviour in the Danube river. A study of the distribution of heavy metals in the dissolved, particulate and sediment phases is very important to understand their role in various biogeochemical processes occurring in estuary and tidal rivers. In estuarine waters, the different processes controlling metal distribution tend to be superimposed. Inputs can be from rivers, sediments, atmospheric and degradation of materials formed in situ; removal can be by biological uptake, sorption in or on to the sedimentary particles both organic or inorganic and flushing with ocean and coastal waters. Further, knowledge on the distribution and concentration of heavy metals in estuarine waters would help to detect the sources of pollution in the aquatic systems.

Several investigators like Danielsson (1980), Moore (1981), Duinker and Nolting (1982), Campbel et. al. (1988), Windom et. al. (1988) Harper (1991), Laslett and Balls (1995), Kremling et. al. (1997) and Owens and Balls (1997) have reported on the distribution of trace metals in the water column. Data on distribution of dissolved heavy metals in Indian estuaries and rivers are relatively scanty. Braganca and Sanzgiry (1980) studied the trace metals in the coastal and offshore regions of the Bay of Bengal. Shibu et. al. (1990), Babukutty (1991) and Ouseph (1992) made investigations on the trace metals in Cochin estuary.

This chapter presents the seasonal and spatial variations of heavy metals in dissolved, particulate and sediment compartments of the study area. The data is statistically analysed to bring out the significance of hydrographic parameters in the seasonal and spatial variations. A comparison is made between the annual mean concentration of metals in the dissolved, particulate and sediment compartments of Chitrapuzha River and other major rivers. Multiple regression analysis is being done to distinguish the role of different parameters in the distribution of trace metals in the sediments in addition to quantification of enrichment. The quantification of enrichment of trace metals in the surficial sediments is estimated by calculating the Enrichment Factor.

4.1.2 Results And Discussion

The overall summary statistics on dissolved metals is given in Table 4.1. The Station-wise summary statistics showing the minimum and maximum values, mean, standard deviations and %CV of total dissolved metals are furnished in Tables 4.4 to 4.12.

Table 4.1 Overall summary statistics on dissolved metal distribution (n = 99) Concentration (µg/l)

	Surface					Bottom				
Metal	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Cr	2.55	7.79	4.55	0.99	21.81	2.44	7.76	4.85	1.00	20.56
Mn	9.09	24.68	13.01	3.95	30.34	9.02	25.00	14.30	4.35	30.39
Fe	3.33	404.58	60.89	81.48	133.81	2.46	449.36	63.76	94.98	148.97
Co	0.83	5.23	1.77	0.97	54.95	0.83	5.34	1.91	0.83	43.55
Ni	5.83	30.53	12.85	6.44	50.08	6.12	30.75	13.79	6.86	49.75
Cu	3.56	12.44	5.69	1.51	26.50	4.15	14.67	6.19	2.25	36.41
Zn	10.70	78.56	27.66	16.12	58.26	11.20	88.68	28.17	16.88	59.92
Cd	1.73	4.65	2.49	0.43	17.47	1.96	7.95	2.69	0.76	28.07
Pb	2.25	19.45	8.47	5.37	63.48	2.00	19.78	8.48	5.43	64.08

Min - Minimum; Max - Maximum; SD - Standard deviation; CV - Coefficient of variation

The concentration of these metals varied over a wide interval; iron was the most abundant (surface annual mean 60.89 µg/l; bottom annual mean 63.76 µg/l) and cobalt (surface annual mean 1.77 µg/l and bottom annual mean 1.91 µg/l) was the least abundant in the study area. The observed order of abundance was iron > zinc > manganese > nickel > lead > copper > chromium > cadmium > cobalt in both surface and bottom waters. All the metals recorded higher annual mean concentrations in the industrial Zone (Zone 3) of Chitrapuzha River. The average concentrations of dissolved metals in Chitrapuzha River were found much higher than the world average but they generally conform to metal levels in Indian rivers (Table 4.2).

***Table 4.2* Comparison of average concentration of dissolved metals in the Chitrapuzha River and other rivers (µg/l)**

River	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Reference
Chitrapuzha *	4.70	13.66	62.33	1.84	13.32	5.94	27.92	2.59	8.47	Present study
Periyar and Muvattupuzha, India	-	-	-	-	-	1.40 - 6.40	14.0 - 115	0.40 - 8.00	-	Shibu et al.(1990)
Subarnarekha, India	-	6.438	46.333	0.602	15.751	10.125	28.875	-	31.125	Senapati & Sahu (1996)
Ob-Irtysh, Russia	0.06 - 0.34	-	-	-	-	1.83 - 4.81	-	-	-	Moran and Woods (1997)
Tay, Scotland	-	2.28 - 8.95	-	-	0.22 - 0.66	0.59 - 1.56	0.61 - 3.60	0.003 - 0.02	-	Owens and Balls (1997)
Gota, Sweden	-	-	25.0 - 75.0	-	0.70 - 0.90	1.0 - 1.4	6.0 - 7.0	-	10 - 200	Danielsson et al (1983)
Lena, Russia	-	-	22.898	-	0.299	0.597	0.353	.003-.008	0.017	Martin et al. (1993)
Amazon, S. America	-	-	9.885-70.929	-	0.299	1.512	.019-.242	0.01	-	Martin et al. (1993)
Mississippi, N. America	-	-	1.675	-	1.333	1.443	0.184	0.013	-	Martin et al. (1993)
Danube, Austria	-	1.04	1.12	0.02	0.88	2.29	0.39	0.01	0.02	Guieu et al. (1998)
World average	-	8.241	39.989	0.1	0.499	1.5	0.601	0.01	0.031	Guieu et al. (1998)

* Average of surface and bottom values

Salinity plays an important role in the distribution of metals in the study area. The concentration of metals except cadmium in water was high during low salinity period (monsoon) indicating an inverse relationship (Table 4.3).

Table 4.3 Correlation coefficient (r) between dissolved metal concentration and salinity (n = 36)

Metal	Surface			Bottom		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
Cr	-0.0998	-0.3247*	-0.1957	-0.3020	-0.3464*	-0.2525
Mn	-0.4568***	-0.3756*	-0.3682*	-0.2620	-0.3336*	-0.2394
Fe	-0.2242	-0.4078**	0.3256*	-0.2256	-0.3867*	-0.6022***
Co	0.3248*	-0.1170	-0.3310*	-0.3871**	0.1627	-0.3285*
Ni	-0.3570*	-0.1292	-0.1515	-0.3503*	-0.0750	-0.3628
Cu	-0.4132**	-0.2930	-0.3254*	-0.3255*	-0.2815	-0.3508*
Zn	-0.3265*	-0.2446	-0.3248*	-0.3730*	-0.3597*	-0.3038*
Cd	-0.3513*	-0.2149	-0.1858	-0.3755*	-0.2472	-0.4714***
Pb	-0.4491***	-0.1449	-0.4324***	-0.3580*	-0.2039	-0.3558*

$p < 0.01$ *** $p < 0.02$ ** $P<0.05$ *

A decrease in metal concentration with increase in salinity has been reported by several workers (Roux et. al., 1998;). Zeri et. al. (2000) has reported that concentration of copper and nickel decreased with increasing salinity. Studies carried out by Roux et. al. (1998) in the waters of macro tidal estuary of Aber-Wrac'h, (France) revealed that the concentration of iron, copper, manganese and cadmium decreased with increase in salinity. The inverse relationship between metal levels in water and salinity was partially attributed to the dilution of metal rich fresh water by metal impoverished seawater and the high sedimentation processes in the estuary (Paucot and Wollast, 1997). The sharp change in salinity as the fresh water mixes with seawater would result in the precipitation and coagulation of colloidal clay particles and co precipitation of metal with/or adsorption on to the particles resulting in the removal of considerable amount of metals from the solution phase (Bryan and Langston, 1992; Senthilnathan and Balasubramanian, 1999). No significant correlation was struck between the dissolved metals and the hydrographic parameters pH, dissolved oxygen and suspended solids.

Dissolved chromium

Chromium is one of the least toxic of the trace elements on the basis of its over supply and essentiality (Forstner and Wittmann, 1979). Generally mammalian body can tolerate 100 – 200 times its total body content of chromium without harmful effects. Chromium (VI) compounds are approximately 100 times more toxic than Cr (III) salts. In the natural environment, Cr (VI) is likely to be reduced to Cr (III), thereby reducing the toxic impact of chromium discharges. The anthropogenic sources of chromium include metal plating, organic and petro-chemicals, fertilizers, petroleum refining and industrial dyes. Of these sources, electroplating industry is the major contributor of chromium. Cr (III) is the most stable and important oxidation state. It forms a large number of relatively kinetically inert complexes. Being a hard acid, Cr (III) forms relatively strong complexes with oxygen donor ligands.

Published literatures on the behaviour of dissolved chromium are not many. Campbell and Yeats (1984) have reported that dissolved chromium is removed at low salinity in St. Lawrence estuary. Paucot and Wollast (1997) have studied the transport and transformation of dissolved chromium in the Scheldt estuary. They proved that dissolved chromium behaved conservatively during estuarine mixing.

Concentration of dissolved chromium varied from a minimum of 2.55 to a maximum of 7.79 µg/l in the surface waters and 2.44 to 7.76 µg/l in bottom waters (Table 4.1). There was not much variation in the annual mean concentration of chromium between surface and bottom waters (Fig. 4.1). The annual mean concentration was 4.55 µg/l in surface and 4.85 µg/l in bottom waters. Station-wise annual mean concentrations were in the range 4.13 to 5.30 µg/l for surface waters and 4.54 to 5.54 µg/l in bottom waters (Table 4.4).

Table 4.4 Station- wise summary statistics on dissolved chromium distribution (µg/l

	Surface					Bottom				
Station	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	2.55	6.57	4.46	1.06	23.70	4.05	6.07	4.55	0.57	12.45
2	4.18	6.89	5.30	1.13	21.26	2.44	6.78	5.02	1.35	26.93
3	3.65	7.78	4.65	1.16	24.98	4.13	6.88	4.76	0.89	18.75
4	3.68	6.78	4.45	0.90	20.35	2.89	7.68	4.78	1.33	27.77
5	3.62	4.90	4.18	0.50	11.91	4.075	5.54	4.58	0.50	10.87
6	3.65	5.90	4.18	0.66	15.88	4.05	6.42	4.76	0.73	15.31
7	3.66	5.03	4.13	0.46	11.15	4.05	6.35	4.54	0.69	15.29
8	3.70	5.56	4.47	0.71	15.90	4.1	7.23	5.10	1.07	20.99
9	3.73	7.79	5.12	1.48	28.87	4.08	7.76	5.54	1.29	23.38

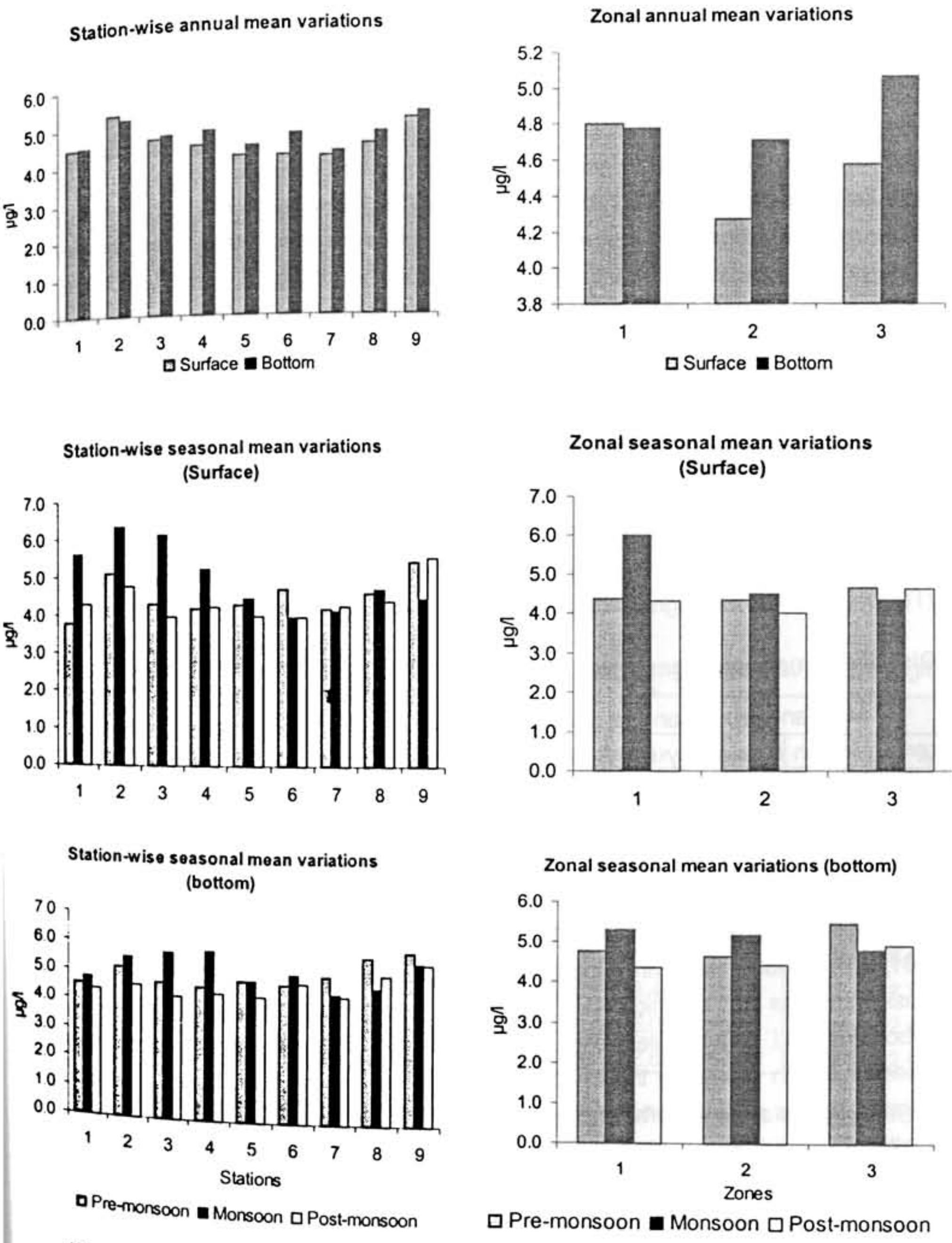


Fig. 4.1 Seasonal and spatial variations of dissolved chromium in surface and bottom waters

The lowest and highest annual mean concentrations were observed Stations 7 and 2 respectively for surface waters and at Stations 7 and respectively for bottom waters. All the Stations except Station 2 recorded slight higher annual mean concentrations in bottom waters (Fig. 4.1). The high botto values may be the result of geochemical processes involving remobilization fro sediments and subsequent diffusion into the overlying waters (Prabhakara Murt and Satyanarayana, 1999). This may also be due to biological uptake and botto water remobilization (Paulson et. al., 1993).

Dissolved chromium exhibited pronounced seasonal variations with genera higher values during monsoon in Zone 1 and 2 both in surface and bottom wate (Fig. 4.1). The higher concentration during monsoon could be mainly due to lar runoff and influx of metal rich fresh water. The increased particulate matter along w suspended sediment load brought in by the river would also be a possible reason f the high values during monsoon. But in the Zone 3, this seasonal trend is ofte disturbed by discharge of effluents from the industries. Statistical studies showe that there was a negative correlation between dissolved chromium and salin (Table 4.3), but it was significant only during monsoon ($p < 0.05$).

Dissolved manganese

Manganese is an essential element in biological systems. Mangane contamination is relatively insignificant except for the common biological toxicity effec found in plants exposed to excess of natural manganese in the soil under some pecul conditions, particularly flooding. In toxic environments, it is present mainly a manganese (IV) oxides and oxyhydroxides. It is a redox-sensitive element and relatively mobile in the marine environment. The thermodynamically stable state manganese in oxygenated water is the insoluble Mn (IV) ion form (Stumm and Morga 1981). The soluble form Mn (II) is found under reducing conditions and the process considered to be both chemical and biochemical. Manganese (II) was found to react w carbonates and bicarbonates and the chemistry of manganese carbonate has important role in controlling the dissolved manganese concentration in soil solution a interstitial waters of sediments. The hydroxides of manganese act as efficient scaveng of other metals (Glasby, 1984). When manganese remobilisation occurs in sub-ox sediments, metals associated with the manganese oxyhydroxide coatings may also b released. This can result in increased interstitial water concentrations of these meta and diffusion into the overlying water column (Duinker et. al., 1982 a). Addition of meta to estuarine waters may also occur when the bottom sediments are disturbed and interstitial waters are injected to the water column (Duinker et. al., 1982 a and b).

Estuarine behaviour of dissolved manganese has been widely studied; Poucot and Wollast (1997) have reported that in Scheldt estuary, manganese is removed from the dissolved phase during estuarine mixing. Guieu et. al. (1998) measured the dissolved manganese concentration in the Danube River and observed that the low concentration was due to the precipitation of hydrated oxide as a consequence of high pH. Vazquez et. al. (1999) measured the dissolved manganese in Terminos lagoon and observed that salinity had no role in the distribution of manganese. Dissolved manganese in the Seine estuary was investigated by Ouddane et. al. (1997) and found to be non-conservative.

The concentration of dissolved manganese ranged from 9.09 to 24.68 µg/l in the surface waters and from 9.02 to 25.00 µg/l in the bottom waters (Table 4.1). The annual mean concentrations during the study period were 13.01µg/l and 14.30 µg/l in surface and bottom waters respectively. Station-wise annual mean concentrations in surface waters varied from 10.43 to 16.22 µg/l and in bottom waters it ranged from 11.16 to 17.43 µg/l (Table 4.5).

Table 4.5 Station- wise summary statistics on dissolved manganese distribution (µg/l)

	Surface					Bottom				
Station	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	9.09	14.44	10.43	1.64	15.72	10.26	18.55	13.60	3.60	26.48
2	9.25	16.58	11.74	2.96	25.24	9.02	16.68	12.02	2.63	21.90
3	9.10	16.45	11.75	2.99	25.44	9.48	19.98	14.18	4.06	28.64
4	9.15	15.76	11.51	2.80	24.33	9.03	22.44	14.45	4.96	34.35
5	9.33	18.77	12.73	3.92	30.76	9.25	18.34	11.16	2.61	23.37
6	9.35	21.45	13.87	4.25	30.68	9.13	20.78	13.41	3.83	28.59
7	9.25	20.55	12.86	3.91	30.38	10.30	23.45	15.55	4.32	27.76
8	9.40	24.68	16.02	4.81	30.03	11.40	25.00	16.95	5.49	32.40
9	10.08	22.56	16.22	4.14	25.55	10.90	22.68	17.43	3.95	22.67

The lowest annual mean values in surface and bottom waters were recorded at Station 1 and 5 respectively whereas Station 9 recorded highest annual mean concentration in both layers. The comparatively higher concentration of manganese at Station 9 may be due to the discharge of effluents containing manganese from nearby industrial area. Bottom annual mean concentrations were higher than surface annual mean values except at Station 5 and 6 (Fig.4.2).

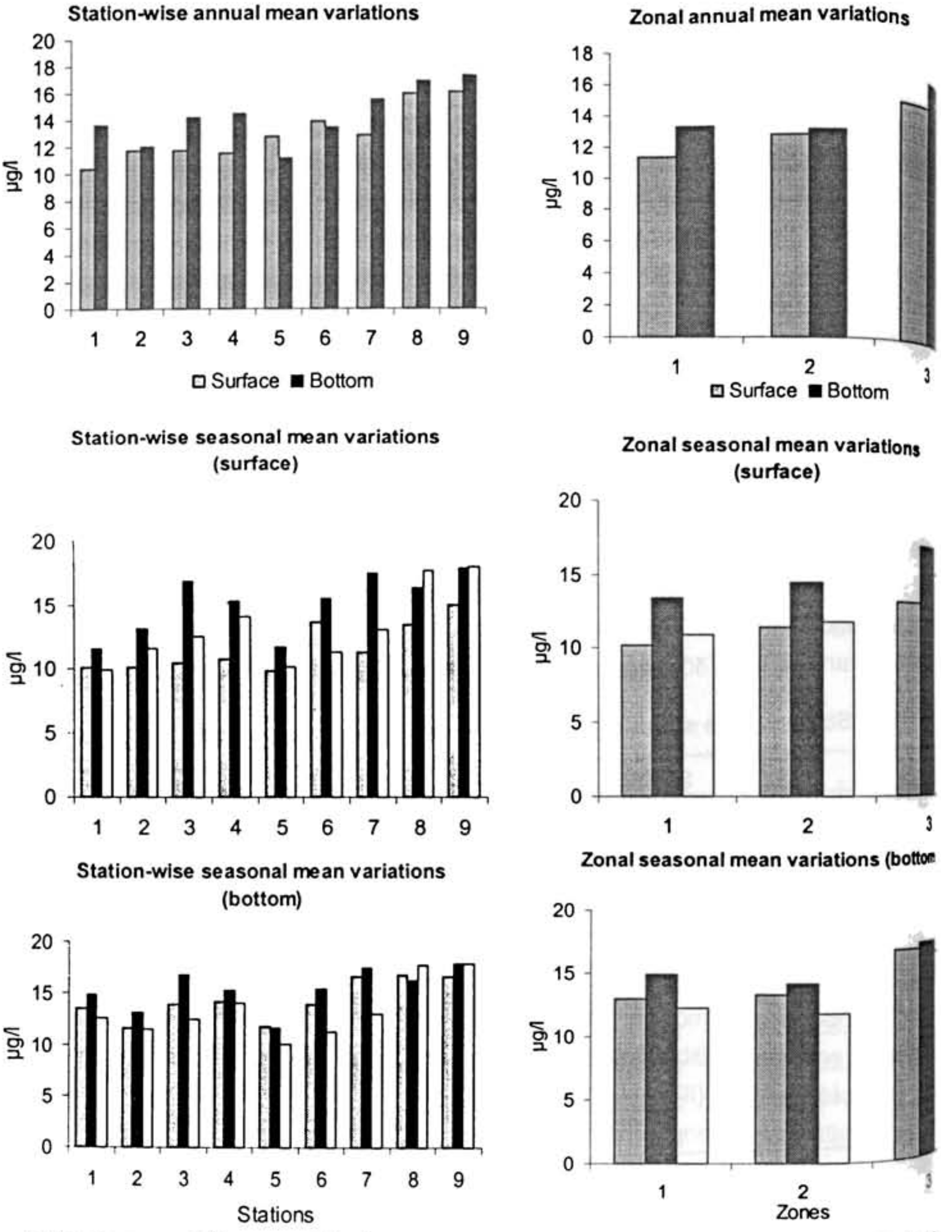


Fig. 4.2 Seasonal and spatial variations of dissolved manganese in surface and bottom waters

Manganese exhibited significant seasonal variations with high values during monsoon (Fig. 4.2). High monsoon values may be attributed to the inflow of freshwater carrying manganese during this season. There was significant negative correlation between manganese and salinity in surface water; but in bottom water significant negative correlation was struck only during monsoon season. The mean concentration of manganese in Chitrapuzha can be compared to concentrations in other major rivers: total dissolved concentration was found higher than the world average of 8.24 µg/l (Table 4.2).

Dissolved iron

Iron the most abundant transition metal, is also probably the most well known metal in biological systems. In estuarine studies iron has received more attention than any other transition metal owing to the possibility of formation of new solid phases during estuarine mixing (Aston, 1978). Recent evidences indicate that iron is an essential nutrient limiting phytoplankton production in ocean (Coale et. al., 1996) as well as in some coastal upwelling environments (Hutchins and Bruland, 1998; Firme et. al., 2001).

A number of studies have been reported on the behaviour of iron in estuaries. The removal of dissolved iron in the early stages of mixing of river and seawater has been established in quite a number of estuaries (Liss, 1976). Bewers and Yeats (1980) studied the behaviour of dissolved iron in St. Lawrence estuary and observed that iron is removed at low salinity. Removal of iron from Savannah estuary was also reported by Windom et. al. (1991). Non-conservative behaviour of dissolved iron due to precipitation and flocculation, in the Lena River was reported by Martin et. al. (1993).

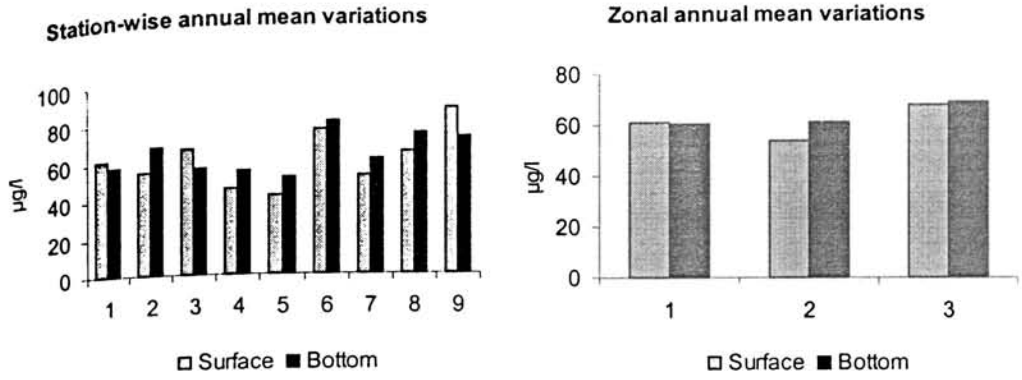
The data revealed the following salient futures with respect to the spatial distribution of dissolved iron. Concentration of iron varied from minimum of 3.33 µg/l to a maximum of 404.58 µg/l in the surface and from 2.46 to maximum of 449.36 µg/l in the bottom waters (Table 4.1). The annual mean concentration of dissolved iron in the surface during the period was 60.89 µg/l and the same in the bottom waters was 63.76 µg/l. The concentration of iron varied over a wide range, which is evident from the large coefficient of variation (133.8 % in surface and 148.9% in bottom). The Station-wise annual mean concentrations of dissolved iron varied from 41.43 µg/l to 87.05 µg/l in surface waters and in bottom waters, the range was 50.89 to 80.00 µg/l (Table 4.6).

Table 4.6 Station - wise summary statistics on dissolved iron distribution (µg/l)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	5.00	278.00	61.23	79.79	130.31	13.65	278.00	57.97	78.75	135.86
2	9.89	178.68	55.07	52.91	96.07	10.55	406.10	67.90	119.12	175.44
3	12.93	404.58	66.21	114.19	172.47	3.53	449.36	56.11	130.81	233.11
4	3.48	275.33	45.42	77.03	169.61	6.68	384.13	54.67	110.85	202.76
5	5.55	129.70	41.43	32.50	78.45	2.46	286.88	50.89	81.33	159.82
6	3.33	310.59	75.65	83.26	110.07	3.63	275.98	80.00	80.89	101.10
7	19.10	213.09	51.90	57.18	110.17	12.47	253.56	60.87	78.29	128.61
8	17.53	344.70	64.05	94.92	148.20	14.78	379.69	73.78	103.64	140.48
9	21.83	395.98	87.05	121.71	139.82	15.65	282.53	71.66	86.62	120.87

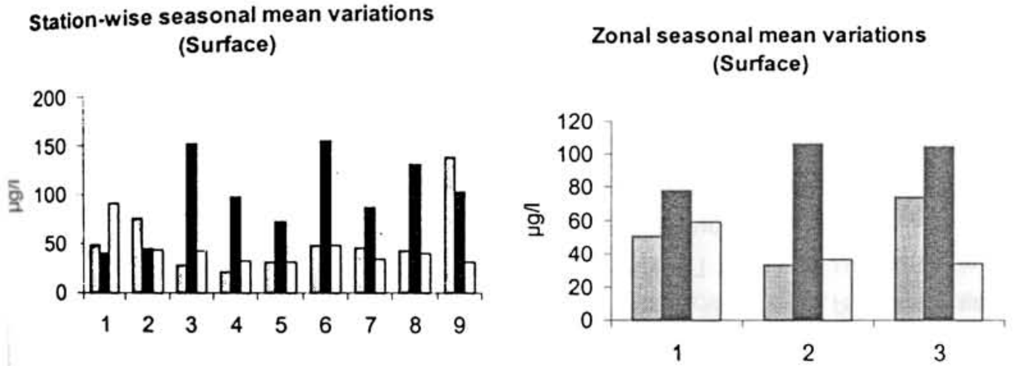
In both surface and bottom waters the lowest annual mean was recorded at Station 5, but highest annual mean values were recorded at Station 9 (in surface) and at Station 6 (in bottom). The annual mean concentrations of iron in Zones 1 and 3 were almost equal, but in Zone 2 the bottom concentration was higher than that of surface. The average concentration of dissolved iron in Chitrapuzha was relatively higher than the world average (Table 4.2); but is comparable to that of Gota and Amazon rivers.

Dissolved iron exhibited pronounced seasonal variations during the period of study. Generally, the monsoon season recorded higher values, but at Stations 2 and 9 pre-monsoon values were higher than monsoon values (Fig. 4.3). At Station 1, post-monsoon recorded the highest value. The concentration of dissolved iron at Station 3 was remarkably high during monsoon season. The highest value of dissolved iron (404.58 µg/l) was recorded at Station 3, during monsoon, which may be due to the discharge of effluents containing iron from the nearby fishing harbour, boat building yards, seaport etc. Wastewater discharged from the heavily populated Cochin city also contributes to the high concentration of iron at this Station. The relatively high concentration of dissolved iron may be due to iron complexation with organic matter (Martin et. al., 1993). Statistical analysis (Table 4.3) revealed a negative correlation between iron and salinity. Correlation was significant during monsoon and post-monsoon periods ($p<0.05$); but not significant during pre-monsoon.



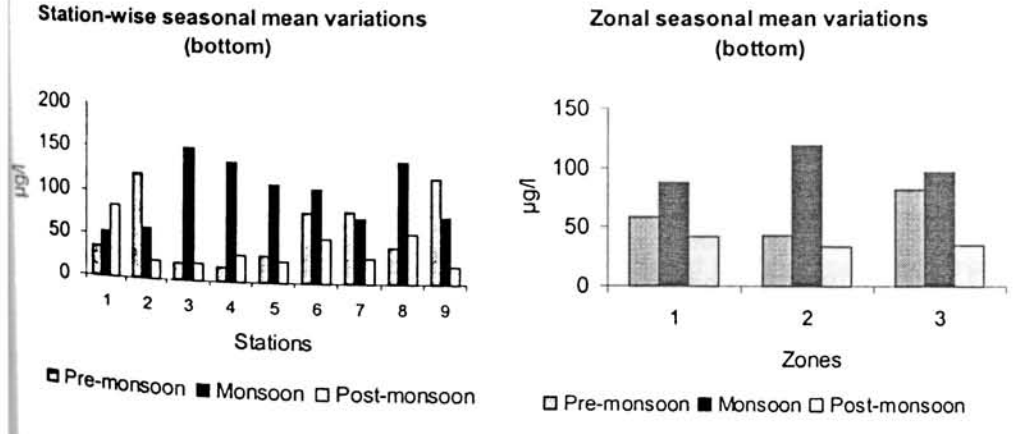
Station-wise annual mean variations

Zonal annual mean variations



Station-wise seasonal mean variations (Surface)

Zonal seasonal mean variations (Surface)



Station-wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Fig. 4.3 Seasonal and spatial variations of dissolved iron in surface and bottom waters

Dissolved cobalt

Cobalt is an essential micronutrient for plants and animals. Cobalt is relatively scarce in the earth's crust, but the human body requires vitamin B_{12}, which is a cobalt (III) complex, cyanocobalamine to form hemoglobin (Forstner and Wittmann, 1979). In fact, cobalt is widely distributed throughout the human body, without any excessive concentration in any particular organ or tissue. Having the ability to occupy low symmetry sites in enzymes, cobalt (II) is an enzyme activator. Burning of fossil fuels constitutes the major source of cobalt and the total environmental flux of cobalt is relatively low compared to most of the trace elements.

In fresh water, the dominant species of cobalt are Co^{2+}, $CoCO_3$, $Co(OH)_3$ and CoS. Although lesser amounts of $CoSO_4$ and $CoCl^+$ may also be detected, chloride complexes dominate in seawater. Published works on the behaviour of cobalt in aquatic systems, especially in estuarine systems are scanty. Windom et. al. (1999) studied the processes affecting cobalt during estuarine mixing in the estuarine region of Patos Lagoon. He observed that concentration of dissolved cobalt increased initially as salinity increased in the low salinity region and then recorded a decline in concentration as the salinity increased. He suggested that the increase in concentration might be due to cation exchange and/or desorption from particles.

Cobalt was the least abundant metal found in Chitrapuzha River. Concentration of dissolved cobalt in the study area was found to vary from 0.83 to 5.23 µg/l in the surface waters and 0.83 to 5.34 µg/l in bottom waters (Table 4.1). The annual mean concentration was 1.77 µg/l in surface and 1.91 µg/l in bottom waters. Zone 2 recorded comparatively low value for annual mean concentrations (Fig 4.4). Station-wise annual mean concentrations of dissolved cobalt were in the range 1.50 to 2.19 µg/l for surface waters and 1.54 to 2.71 µg/l in bottom waters. The lowest and highest annual mean concentrations were observed at Stations 6 and 9 respectively for both surface and bottom waters (Table 4.7).

Table 4.7 Station - wise summary statistics on dissolved cobalt distribution (µg/l)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	1.05	3.34	1.68	0.77	45.56	1.18	2.98	1.91	0.60	31.52
2	0.85	3.55	1.80	0.89	49.34	1.05	4.45	1.92	0.92	47.87
3	1.08	3.22	1.79	0.75	42.08	0.93	2.80	1.76	0.60	33.85
4	0.85	4.12	1.87	1.10	58.87	0.85	2.20	1.60	0.45	28.47
5	0.83	2.55	1.57	0.65	41.17	0.83	5.34	1.65	1.26	76.56
6	0.85	2.60	1.50	0.59	39.48	0.88	2.38	1.54	0.53	34.39
7	0.83	5.23	1.89	1.47	77.95	0.90	3.48	1.90	0.78	41.27
8	0.85	4.34	1.68	1.07	63.77	1.08	3.88	2.23	0.82	36.75
9	1.13	4.56	2.19	1.30	59.70	1.70	3.98	2.71	0.84	30.91

All the Stations except Stations 3 and 4 recorded higher annual mean concentrations in bottom waters (Fig. 4.4). The high bottom values may be the result of geochemical processes involving remobilization from sediments and subsequent diffusion into the overlying waters (Prabhakara Murthy and Satyanarayana, 1999). The Table 4.2 shows that level of dissolved cobalt is much higher when compare to the levels in other rivers and world average.

Dissolved cobalt exhibited distinct seasonal variations with generally higher monsoon values in both surface and bottom waters. The higher concentration during monsoon could be mainly due to land runoff and influx of metal rich fresh water. Cobalt exhibited significant inverse correlation during pre-monsoon and post-monsoon seasons only (Table 4.3).

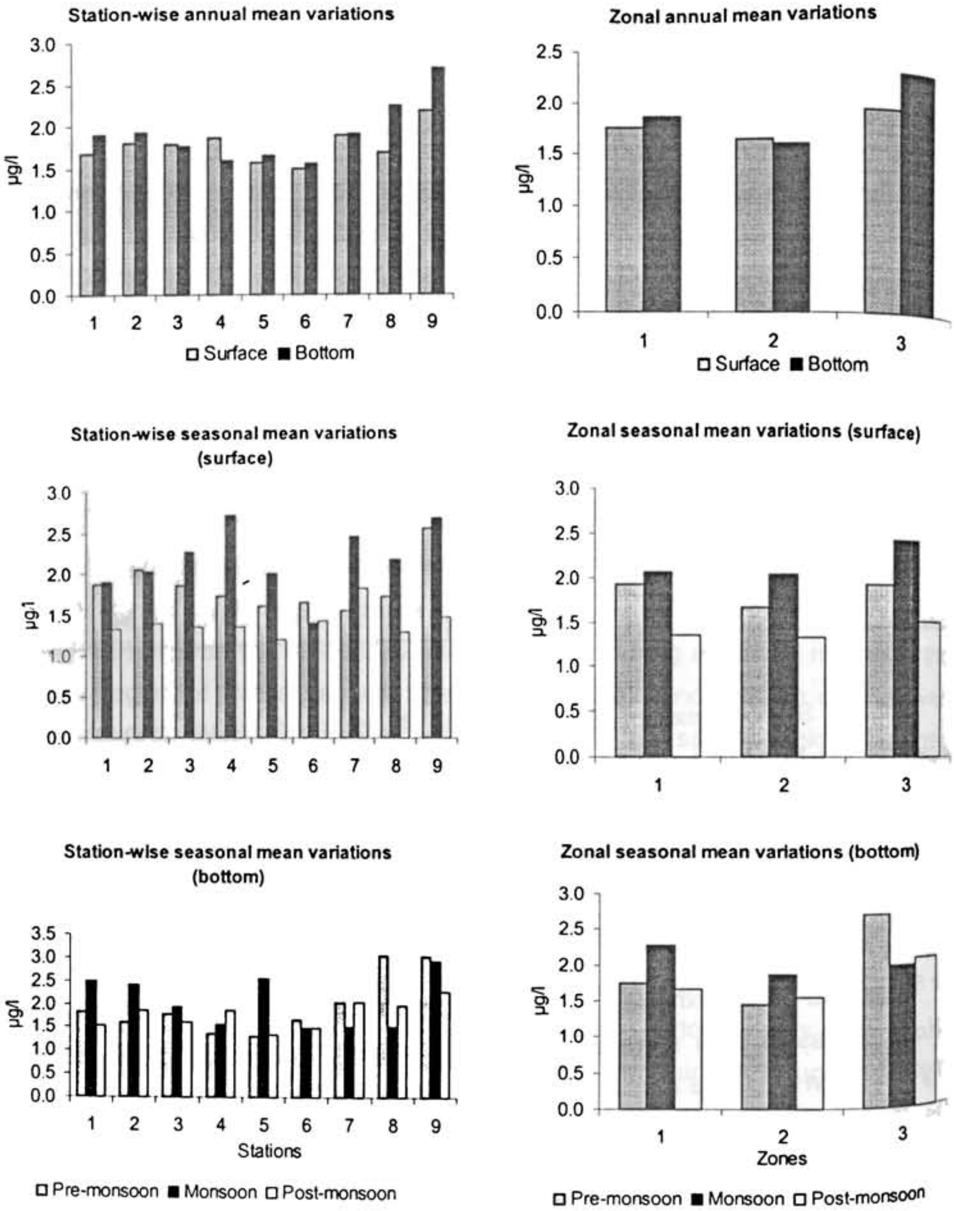


Fig. 4.4 Seasonal and spatial variations of dissolved cobalt in surface and bottom waters

Dissolved nickel

Nickel is essential at trace levels for human health (Moore and Ramamoorthy 1984). Acute toxicity arises from competitive interaction with five major essential elements, calcium, cobalt, iron, copper and zinc. Nickel can replace essential metals in the metallo-enzymes resulting in the disruption of metabolic pathways (McGroth and Smith, 1990). The major source of discharge of nickel is urban wastewater followed by smelting and refining of non-ferrous metals (Nriagu and Pacyna, 1988). The use of fossil fuels, particularly coal, is widely implicated in the release of nickel to the atmosphere and surface waters. The most common oxidation state is Ni (II), which is stable over a wide range of pH. Humic and fulvic acids form moderately strong complexes with nickel. Under reducing conditions in surface water, nickel forms insoluble sulphides, provided that sulphur is present in excess. Under aerobic conditions and pH < 9, nickel complexes with hydroxides, carbonates, sulphates and naturally occurring organic ligands. This has been observed both in fresh waters and saline waters.

Studies on the behaviour of dissolved nickel in estuaries received much attention. Poucot and Wollast (1997) reported that nickel behave conservatively during estuarine mixing. Boyle et. al. (1982) reported conservative behaviour for nickel in Amazon River. Duinker et. al. (1982 a) also reported conservative behaviour for dissolved nickel in Scheldt estuary.

The data revealed the following salient futures with respect to the spatial distribution of dissolved nickel. Concentration of nickel, the forth abundant metal, varied from minimum of 5.83 µg/l to a maximum of 30.53 µg/l in the surface and from 6.12 to maximum of 30.75 µg/l in the bottom waters (Table 4.1). The annual mean concentration of dissolved nickel in the surface during the period was 12.85 µg/l and the same in the bottom waters was 13.79 µg/l. The Station-wise annual mean concentrations of dissolved nickel varied from 9.20 µg/l to 18.24 µg/l in surface waters and in bottom waters the range was 11.34 to 19.21 µg/l (Table 4.8). The lowest annual mean concentrations were recorded at Station 3 and 1, in surface and bottom waters respectively, but highest annual mean values were recorded at Station 9 both in surface and bottom waters. The annual mean concentrations of nickel in bottom waters were slightly higher than those of surfac waters at all the Stations. Statistical analysis (Table 4.3) revealed a negativ correlation between dissolved nickel and salinity. Significant correlation was struc only during pre-monsoon in surface waters and post-monsoon in bottom water (p<0.05). The average concentration of dissolved nickel in Chitrapuzha River wa much higher than the world average (Table 4.2); but is comparable to that o Subarnarekha River, east coast of India.

Table 4.8 Station - wise summary statistics on dissolved nickel distribution (µg/l)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	5.90	19.88	9.86	5.27	53.44	6.45	18.68	11.34	3.94	34.74
2	5.94	20.00	10.50	5.14	48.96	6.25	24.43	12.02	6.43	53.44
3	6.05	14.78	9.20	3.63	39.43	6.28	18.10	12.08	4.70	38.91
4	6.16	22.68	11.04	6.44	58.35	6.12	23.3	11.58	6.67	57.61
5	6.30	23.35	12.92	6.81	52.75	6.49	25.38	13.01	7.28	55.98
6	7.73	22.30	13.21	5.35	40.50	6.98	24.8	13.59	7.26	53.38
7	6.99	24.10	15.05	5.80	38.57	6.20	26.28	15.10	7.50	49.65
8	5.83	25.20	15.65	6.89	44.06	7.00	29.18	16.17	8.04	49.72
9	8.18	30.53	18.24	7.78	42.67	9.50	30.75	19.21	7.19	37.41

Seasonal variations in the dissolved nickel concentrations were significant Unlike other heavy metals studied, nickel exhibited generally higher pre-monsoo values (Fig. 4.5). Desorption from particulate matter when fresh water mixes wit saline water during pre-monsoon may be the reason for higher values. The lowes values were recorded generally during post-monsoon season. There was a stead increase from Zone 1 to Zone 3 during all the seasons in surface waters, but suc a trend was noticed only during pre-monsoon season in bottom waters.

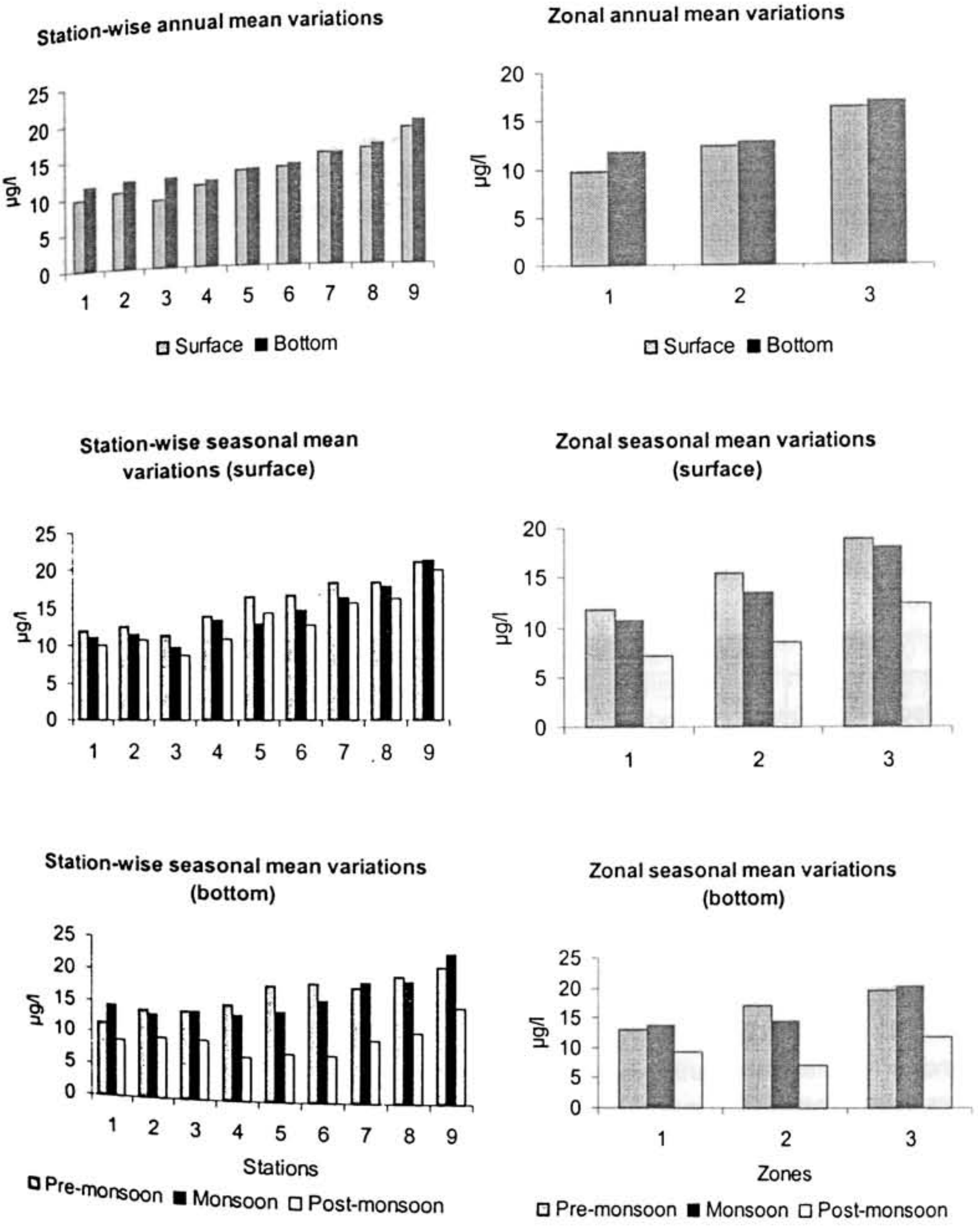


Fig. 4.5 Seasonal and spatial variations of dissolved nickel in surface and bottom waters

Dissolved copper

Copper is an essential micronutrient, which is widely distributed in nature i free state as well as in combined state. It is essential in a number of enzymes Excessive intake of copper results in its accumulation in the liver. Generally copper toxicity is increased by low Mo, Zn, and SO4^{2-} intake, but it is not acutel toxic to humans. This is due to the intermediate coordinate character of coppe between hard and soft acids. It is highly toxic to most aquatic plants. Inhibition c growth generally occurs at ≤ 0.1 mg/l, regardless of test conditions and species Mercury is the only metal which is consistently more toxic to aquatic plants tha copper. The anthropogenic activities by which copper enters the soil, the sedimen and water are the processes of smelting and mining, industrial effluent discharges urban run-off and application of fertilizers and fungicides. The form taken by this metal in natural waters (ionic, complexed or precipitated) and hence its bioavailability, depends on environmental factors such as pH, Eh, soil and sediment type, water hardness, organic content etc. and in estuaries, especially on salinity, freshwater discharge, mean residence time and the suspended solids load These factors influence the environmental setup-giving rise to conditions of coppe deficiency of toxicity. Copper is removed from water into the sediments by natura transformation taking place during chemical complexation, precipitation and adsorption (Salamons and Bacccini, 1986). Copper (II) ion is a strong complexing agent and the stability of complexes depends on the chemical nature of metal ion and the binding energy of the functional groups of the ligands.

Studies on the behaviour of dissolved copper in estuaries received muc attention. Duinker (1983) has reported on the initial removal of copper at low salinit region, while Windom et. al. (1988 & 1999), Guieu et. al. (1998) and Paulson et. a (1989) have reported conservative behaviour of copper during estuarine mixing Vazquez et. al. (1999) reported a positive relationship between dissolve copper and salinity in Terminos lagoon. Several workers have reported mobilization of coppe and its transfer from particulate to dissolved phase when the salinity is increased. has been attributed to the formation of complexes, occurring during the mixing o freshwater with seawater and to the desorption of exchangeable metals due to the increasing concentration of major cations. Muller et. al. (2001) reported the formatio of organic copper complexes in saline waters. The significant relationship betwee dissolved copper and organic carbon established for the Rhone River, Franc

(Dai et. al., 1995), and the Ob and the Yenissei rivers, Russia (Dai and Martin, 1995) suggested that copper is mainly associated with organic matter.

The present investigation brought out the following important futures with respect to the spatial distribution of dissolved copper. Concentration of copper varied from minimum of 3.56 µg/l to a maximum of 12.44 µg/l in the surface and from 4.15 to maximum of 14.67 µg/l in the bottom waters (Table 4.1). The annual mean concentration of dissolved copper in the surface during the period was 5.69 µg/l and the same in the bottom waters was 6.19 µg/l. Zone 2 exhibited comparatively low concentration of dissolved copper in the study area, which may be due to predominantly sandy nature of sediments in this Zone. Such sediment, which lacks metal binding organic carbon content may not be able to supply metals into the overlying waters by remobilization and subsequent diffusion. The Station-wise, the annual mean concentrations of dissolved copper varied from 4.99 µg/l to 7.99 µg/l in surface waters and in bottom waters, the range was 4.94 to 8.39 µg/l (Table 4.9).

Table 4.9 Station - wise summary statistics on dissolved copper distribution (µg/l)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	4.19	6.23	5.11	0.58	11.38	4.38	11.55	5.21	0.56	10.76
2	3.88	7.40	5.70	1.10	19.23	4.56	11.55	7.51	2.70	35.92
3	3.56	6.40	4.99	0.81	16.20	4.44	9.88	6.10	1.71	27.99
4	4.24	6.99	5.09	0.80	15.64	4.15	7.58	5.18	0.97	18.79
5	4.17	6.15	5.18	0.64	12.28	4.15	5.83	4.94	0.56	11.32
6	4.18	6.88	5.01	0.76	15.15	4.38	5.88	5.04	0.66	13.05
7	4.39	6.45	5.16	0.59	11.53	4.25	12.46	6.06	2.62	43.17
8	4.75	9.88	6.97	1.67	23.99	5.04	14.67	7.27	2.73	37.60
9	4.50	12.44	7.99	2.30	28.79	4.72	13.66	8.39	3.06	36.41

The lowest annual mean values were recorded at Station 3 and 5 respectively, but highest annual mean values were recorded at Station 9 both in surface and bottom waters. Generally, no depletion of copper was observed in the surface waters (Fig. 4.6). This behaviour and variations of copper may probably be related to its tendency to complex with dissolved organic matter (Van den Berg et. al., 1987; Paulson et. al., 1993; Gerringa et. al., 1998; Nolting et. al., 1999). The average concentration of dissolved copper in Chitrapuzha is much higher than the world average (Table 4.2); but is comparable to the concentration in Periyar and Muvattupuzha rivers. Subarnarekha River carries more dissolved copper than Chitrapuzha.

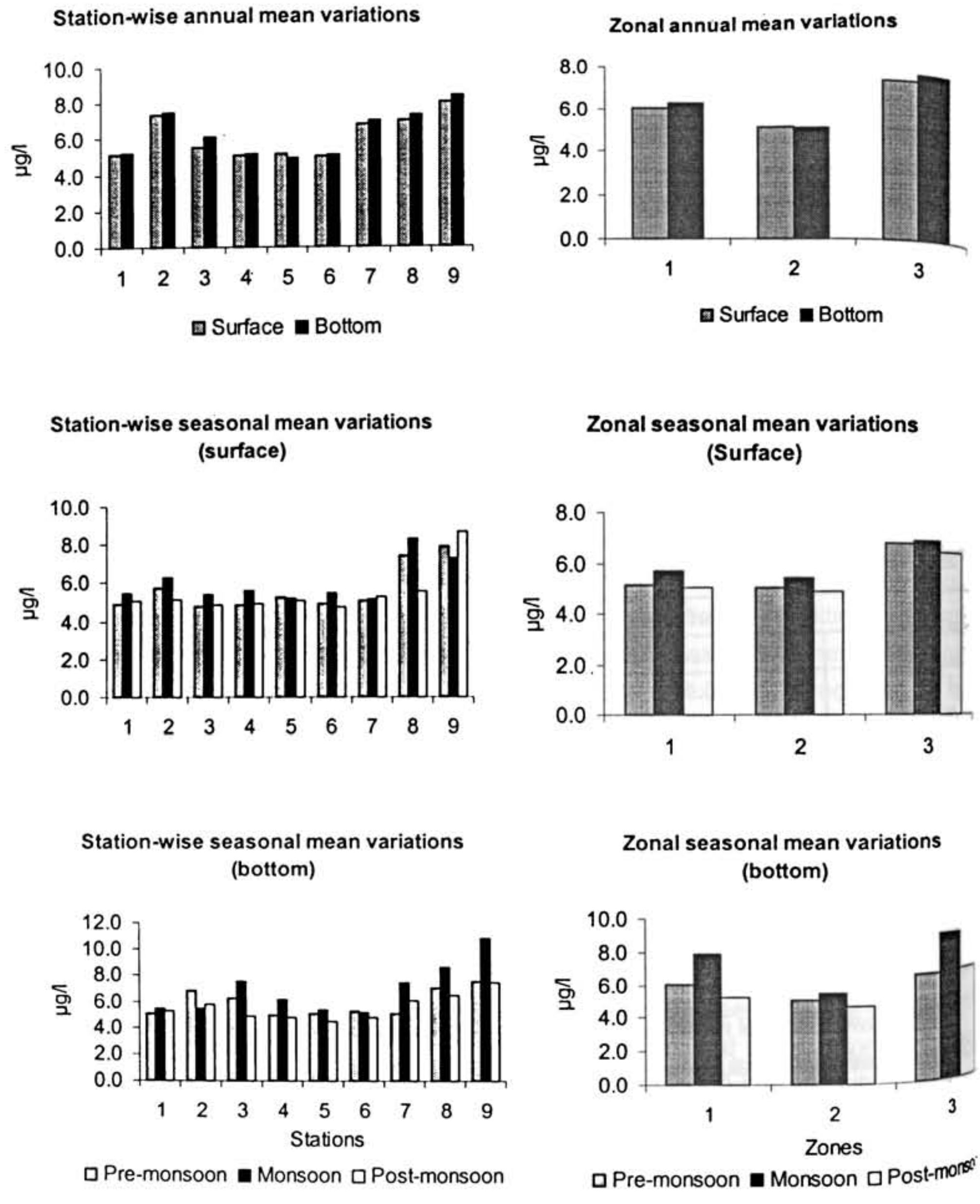


Fig. 4.6 Seasonal and spatial variations of dissolved copper in surface and bottom waters

Seasonal variation in the distribution of dissolved copper is depicted in the Figure 4.6. Distinct seasonal variations could be seen in the seasonal distribution of dissolved copper in surface and bottom waters. Monsoon values were found generally higher than pre and post-monsoon values, which may be due to land runoff and influx of metal rich fresh water. Statistical analysis (Table 4.3) revealed a negative correlation between copper and salinity. Correlation was significant during pre-monsoon and post-monsoon periods ($p < 0.05$); but not significant during monsoon.

Dissolved zinc

Zinc is one of the most abundant essential trace elements in the human body. It is a constituent of all cells and several enzymes depend upon it as a cofactor. The rare toxicity of zinc arises from its synergistic/antagonistic interaction with other heavy metals particularly its homologue cadmium. The non-stoichiometric accumulation of heavy metals by the carrier protein metallothionein could lead to zinc deficiency in humans (Moore and Ramamoorthy 1984). Symptoms of deficiency include delayed healing, suppression of enzymatic activity, and immune response. The main pollutant sources of zinc are metalliferous mining activities, ore-dressing and processing, agricultural use of sewage sludge and composted materials, and the pesticides. In Chitrapuzha River industrial effluents and municipal waste from the city are the main sources of zinc.

There have been a number of studies on the geochemical behaviour of zinc in estuarine waters. The behaviour of the dissolved zinc has been regarded as conservative in large unpolluted estuaries (Danielsson et. al., 1983; Paulson et. al., 1989). But studies of Poucot and Wollast (1997) in Scheldt estuary were contrary to these findings. They observed non-conservative behaviour for dissolved zinc. Dissolved zinc is mobilized in dissolved phase when salinity is increased. Duinker et. al. (1982 a) and Duinker and Nolting (1977) deduced that zinc was removed from solution to particulate matter at low salinities in Rhine and Elbe estuaries respectively. Vazquez et. al. (1999) studied the role of hydrographical parameters on the distribution of heavy metals in Terminos lagoon and observed a positive correlation between dissolved zinc and salinity.

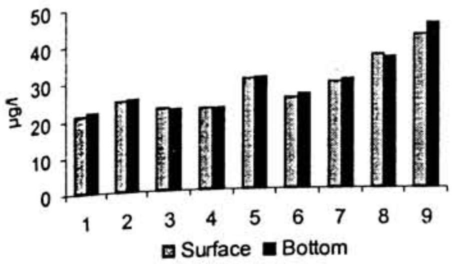
The investigation revealed the following salient futures with respect to the spatial distribution of dissolved zinc. Concentration of zinc, the second abundant metal, varied from minimum of 10.70 µg/l to a maximum of 78.56 µg/l in the surface and from 11.20 to maximum of 88.70 µg/l in the bottom waters (Table 4.1). The annual mean concentration of dissolved zinc in the surface during the period of study was 27.66 µg/l and the same in the bottom waters was 28.17µg/l. The Station-wise annual mean concentrations of dissolved zinc varied from 21.39 µg/l to 40.87 µg/l in surface waters and the range was 21.77 to 43.67 µg/l in bottom waters (Table 4.10).

Table 4.10 Station - wise summary statistics on dissolved zinc distribution (µg/l)

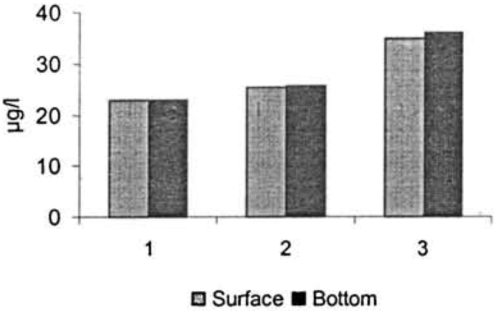
Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	10.70	32.66	21.39	6.58	30.74	11.68	30.45	21.77	5.84	26.82
2	11.98	66.58	24.74	15.06	60.87	11.34	66.58	24.91	15.66	62.87
3	11.30	29.80	22.36	5.76	25.78	11.3	29.80	22.06	5.34	24.22
4	11.20	31.18	22.05	6.72	30.50	11.2	31.18	21.85	6.75	30.90
5	11.34	77.13	29.52	21.62	73.23	12.88	77.13	29.93	21.28	71.08
6	12.34	68.68	24.20	16.20	66.95	12.34	78.55	25.32	18.88	74.57
7	14.80	74.18	28.27	16.31	57.68	14.80	74.18	29.07	16.21	55.78
8	13.00	74.75	35.55	21.45	60.32	13.00	74.75	34.96	21.61	61.80
9	24.68	78.56	40.87	18.58	45.46	24.68	88.68	43.67	20.74	47.49

The lowest and highest annual mean concentrations were recorded at Stations 1and 9 respectively, in surface and bottom waters. Dissolved zinc showed lower values at the bar-mouth (Station 1), which may be due to the dilution of metal rich river water with metal impoverished seawater. This may also be attributed to flushing activity by tides along with the impact of waves which removes the finer fractions of the sediments from the bar-mouth (Sunil Kumar, 1996). Such sandy sediments in this Zone, which lacks metal binding organic content may not be able to supply zinc into the overlying waters by remobilization and subsequent diffusion The annual mean concentrations of zinc in surface and bottom waters were same in Zones 1 and 2; but in Zone 3, bottom values were slightly higher. An increasing trend from Stations 1 to 9 can be noted in the distribution of zinc (Fig. 4.7).

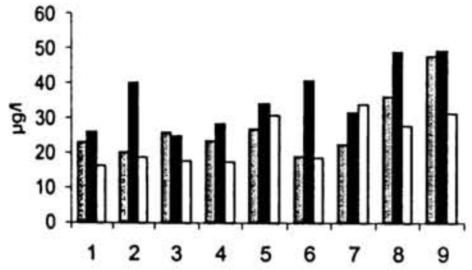
Station-wise annual mean variations



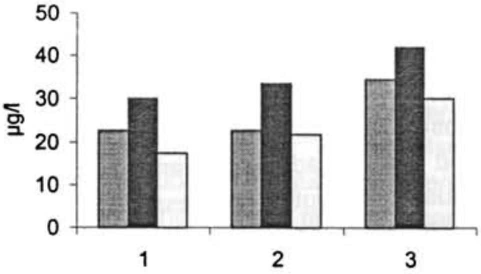
Zonal annual mean variations



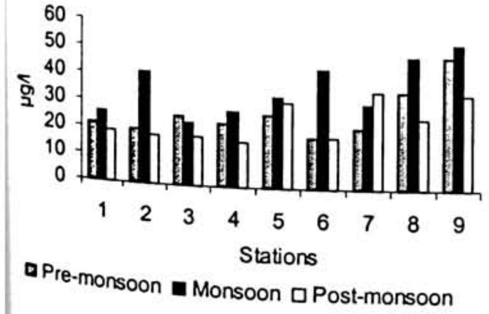
Station-wise seasonal mean variations (surface)



Zonal Seasonal mean variations (surface)



Station-wise seasonal mean variations (bottom)



Zonal seasonal mean variations (bottom)

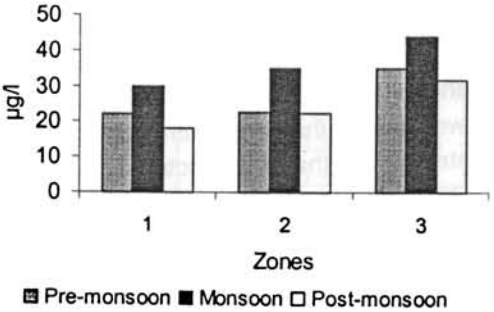


Fig. 4.7 Seasonal and spatial variations of dissolved zinc in surface and bottom waters

Distribution of dissolved zinc exhibited pronounced seasonal variations with generally higher values during monsoon. At Station 3, pre-monsoon recorded highest value whereas at Station 7 post-monsoon value was the highest. The higher concentration during monsoon could be mainly due to land runoff and influx of metal rich fresh water. Salinity plays an important role in the distribution of dissolved zinc in Chitrapuzha River. Statistical analysis (Table 4.3) revealed a negative correlation between dissolved zinc and salinity. Significant correlation was found during all seasons except during monsoon in surface waters. ($p<0.05$). The average concentration of dissolved zinc in Chitrapuzha River was much higher than the world average (Table 4.2); but it falls within the range for Periyar, Muvattupuzha and Subarnarekha rivers.

Dissolved cadmium

Cadmium is a highly toxic non-essential metal. The stable state of cadmium in the natural environment is Cd (II) and has moderate covalency in bonds and high affinity for sulfhydryl groups, leading to increased lipid solubility, bioaccumulation and toxicity. Cadmium accumulates in liver and kidney through its strong binding with cysteine residues of metallothionein. Since the metabolism of cadmium is closely related to that of zinc, metallothionein binds and transports both cadmium and zinc. Cadmium seems to displace zinc in many vital enzymatic reactions, causing disruption or cessation of activity. There is no known mechanism for controlling cadmium levels in humans, which may therefore accumulate following intake. This fact, together with relatively longer half-life (10 – 30 days) in biological systems makes cadmium one of the most toxic metals (Craig, 1986). It occurs in the earth's crust at concentrations between 0.1 to 0.5 µg/g, whereas the average concentration in natural waters is 0.4 µg/l. Although its concentration in the aqueous environment, both in water and sediment are low, several fold enrichment is observed in the aquatic biota. The anthropogenic sources of cadmium in the environment includes the primary uses of cadmium in electroplating other metals or alloys for protection from corrosion, in photographic industry and in the manufacture of storage batteries, pigments, glass ceramics and plastic stabilizers. It was found that cadmium content is high in rock phosphate, which is the raw material, for the manufacture of phosphate fertilizers (Forstner and Wittmann, 1979). As far as Chitrapuzha River is concerned, the major point source is the fertilizer-manufacturing unit on its banks.

Considerable information is available on the behaviour of cadmium in the aquatic environment (Jouanneau et. al., 1983; Elbaz-Poulichet et. al., 1987; Windom et. al., 1988 and 1991; Forstner et. al., 1990). Removal of cadmium from Scheldt estuary at low salinity was reported by Duinker et. al. (1982 a) and

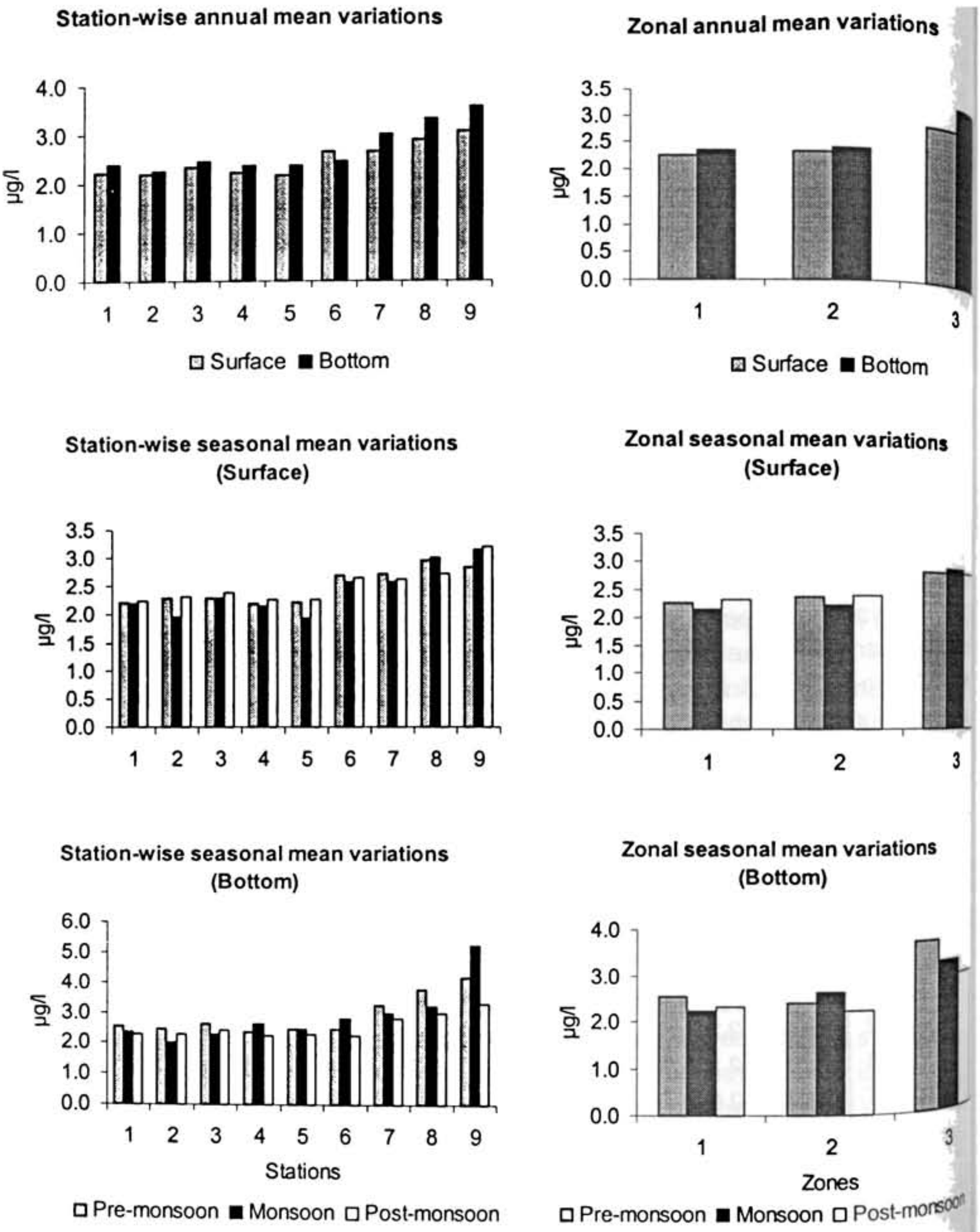
Zwolsman et. al. (1990). But several workers have reported mobilization of cadmium during estuarine mixing. Studies of Poucot and Wollast (1997) in Scheldt estuary were contrary to these studies. They observed an important mobilization from particulate phase to dissolved phase when the salinity is increased. Mobilization of cadmium was also observed in other estuaries (Elbaz-Poulichet et. al., 1987; Windom et. al., 1991; Chiffoleau et. al., 1994; Dai et. al., 1995). Cadmium is relatively mobile in aquatic systems and exists as Cd $^{2+}$, Cd(OH)$_2$ (aq), Cd(OH)$_4$ $^{2-}$, CdCO$_3$ and in various other organic and inorganic complexes (Moore, 1991). In many fresh waters, the affinity of ligands to complex with cadmium follows the order: humic acids, CO$_3$ $^{2-}$, OH$^-$, Cl$^-$, SO4 $^{2-}$ (Moore, 1991).

The concentration levels in the estuarine Zone were in agreement with earlier studies of Nair et. al. (1990), Shibu et. al. (1990) and Babukutty (1991) in the Cochin estuary. Concentration of dissolved cadmium in the study area was found to vary from 1.73 to 4.65 µg/l in the surface waters and 1.96 to 7.95 µg/l in bottom waters (Table 4.1). The annual mean concentration was 2.49 µg/l in surface and 2.69 µg/l in bottom waters. The dissolved concentration of cadmium showed minimum variability, which is evident from the low coefficient of variation. The percentage coefficient of variation for the distribution of cadmium in surface waters (17.47%) was the lowest among the nine metals studied (Table 4.1). Station-wise annual mean concentrations were in the range 2.16 to 3.05 µg/l for surface waters and 2.26 to 3.56 µg/l in bottom waters. The lowest and highest annual mean concentrations were observed at Stations 5 and 9 respectively for surface waters and at Stations 2 and 9 respectively for bottom waters (Table 4.11).

Table 4.11 Station - wise summary statistics on dissolved cadmium distribution (µg/l)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	2.03	2.63	2.22	0.21	9.34	2.09	2.92	2.39	0.29	12.34
2	1.88	3.00	2.21	0.34	15.28	1.96	2.95	2.26	0.31	13.70
3	2.03	2.75	2.33	0.24	10.50	2.04	2.98	2.46	0.30	12.38
4	2.02	2.95	2.21	0.26	11.65	2.02	2.78	2.37	0.28	11.91
5	1.73	2.70	2.16	0.25	11.53	1.98	2.75	2.38	0.30	12.45
6	2.37	3.03	2.65	0.18	6.83	2.03	2.93	2.46	0.31	12.44
7	2.52	3.13	2.65	0.18	6.76	2.62	3.58	3.01	0.32	10.57
8	2.58	3.39	2.88	0.27	9.41	2.62	4.63	3.33	0.51	15.28
9	2.62	4.65	3.05	0.63	20.63	2.63	7.95	3.56	1.64	45.91

All the Stations except Station 6 recorded higher annual mean concentrations in bottom waters (Fig. 4.8).



Station-wise annual mean variations

Zonal annual mean variations

Station-wise seasonal mean variations (Surface)

Zonal seasonal mean variations (Surface)

Station-wise seasonal mean variations (Bottom)

Zonal seasonal mean variations (Bottom)

Fig. 4.8 Seasonal and spatial variations of dissolved cadmium in surface and bottom waters

The high bottom values may be the result of geochemical processes involving remobilization from sediments and subsequent diffusion into the overlying waters (Prabhakara Murthy and Satyanarayana, 1999). This may also be due to biological uptake and bottom water remobilization (Paulson et. al., 1993). In surface and bottom waters the annual mean concentrations generally showed an increasing trend from Stations 1 to 9. This may be due to discharge of effluents containing cadmium from the chemical industries situated in the Ambalamugal industrial area.

Seasonal variations were observed (Fig. 4.8) and it can be seen that in surface waters, the higher seasonal values were recorded in pre-monsoon and post-monsoon seasons, but in Zone 3, monsoon season recorded slightly higher value. In Zone 3 the seasonal trend expected, is often disturbed by the discharge of industrial effluents. In bottom waters pre-monsoon recorded higher values in Zones 1 and 3 but in Zone 2, monsoon season recorded higher value. The increase in concentration of dissolved cadmium during pre-monsoon and post-monsoon seasons may be attributed to the formation of chloride complexes, occurring during the mixing of fresh water with seawater and to the desorption of exchangeable metals due to the increasing concentration of major cations (Poucot and Wollast, 1997; Elbaz-Poulichet et. al., 1987; Windom et. al., 1991; Chiffoleau et. al., 1994; Dai et. al., 1995). A comparison of average concentrations of dissolved cadmium in Chitrapuzha River with other major rivers is represented in the Table 4.2. It was found that the level of cadmium is much higher than the world average, but is comparable to that of Periyar and Muvattupuzha rivers.

Dissolved lead

Lead, one of the most abundant toxic pollutants in the environment, becomes a real concern as a contaminant because of its constant and continuous release into air, water and soil in appreciable amounts (Branica, 1980). Lead toxicity appears to cause brain damage, mental deficiency and serious behavioural problems generally known as "plumbism". Another consequence is the kidney disorder known as "nephritis". Lead exists mainly in carbonate, sulphide and oxide forms in the earth's crust and the average concentration is approximately 13 µg/g (Craig, 1986). The average concentrations of lead in river and ocean waters are

0.1 and 0.003 µg/l respectively (Martin and Whitefield, 1983) although rivers flowing adjacent to industrialized centres may contain upto 100 µg/l. Sources of lead contamination to the environment include fairly localized impacts such as disposal of lead-acid batteries, lead based paint wastes in landfills, fillings from the processing of lead minerals etc. More widespread occurrences of lead contamination have been associated with aerosols from leaded gasoline and smelters lead based paintings and sewage sludge applied to agricultural fields. Since lead continues to be used as antiknocking agent in gasoline in many nations, residues are correspondingly elevated in urban air. Total lead in surface water is highly variable but is typically <50 µg/l (Moore, 1991). Although maximum residues are often associated with poorly treated industrial or mining effluents, the input of lead into remote waters is primarily due to atmospheric deposition. Considerable atmospheric addition of lead has been reported from various parts of the world (Alloway, 1990).

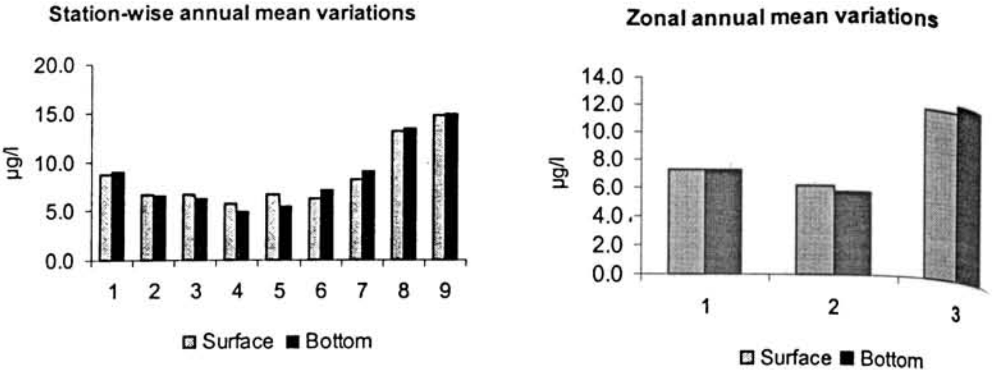
A major form of lead is the organo-metallic form whereas most of the other metals are released in the inorganic form. Lead is a non-essential and a potentially toxic element. Therefore, an accurate assessment of the lead concentration and its physico-chemical partitioning in the aquatic environment would be of importance. Lead resembles the divalent alkaline earth group metals in chemical behaviour more than its own Group IV metals. It differs from the poor solubility of lead salts such as hydroxides sulphides, halids and phosphates. Lead has stable +2 and +4 oxidation states. In fresh water, lead forms a number of complexes of low solubility with many of the major anions including hydroxides, carbonates sulphides. Lead also partitions favourably with humic and fulvic acids forming moderately strong chelates (Moore, 1991). Speciation shifts to favour chlorides and hydroxide complexes in salt water.

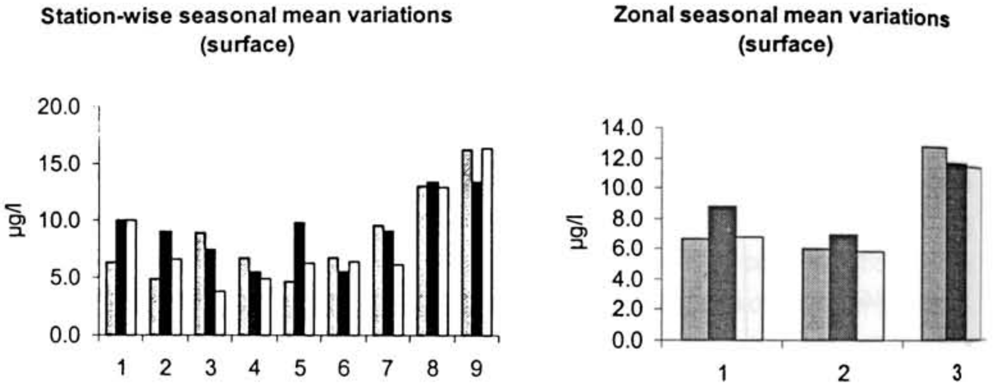
Lead emerged as the fifth most abundant of the metals estimated in Chitrapuzha River during the study. Concentration of dissolved lead in the study area was found to vary from 2.25 to 19.45 µg/l in the surface waters and 2.00 to 19.78 µg/l in bottom waters (Table 4.1). The annual mean concentrations were almost equal both in surface and bottom waters, 8.47 µg/l in surface and 8.48 µg/l in bottom waters. The annual mean concentration of dissolved lead was in the order Zone 2 < Zone 1< Zone 3. The high concentration of lead in Zone 3 may be attributed to the discharge of effluents from nearby petrochemical industries, fertilizer factory and oil refinery. The low level of lead in Zone 2 may be due to the predominantly sandy sediments in this Zone, which lacks metal binding organic content. Such sediment may not be able to supply metals into the overlying waters by remobilization and subsequent diffusion. Station-wise annual mean concentrations of dissolved lead were in the range 5.70 to 14.64 µg/l for surface waters and 4.89 to 14.81 µg/l in bottom waters (Table 4.12).

Table 4.12 Station - wise summary statistics on dissolved lead distribution (µg/l)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	3.40	17.34	8.65	5.19	15.00	3.40	17.34	9.03	5.47	60.56
2	2.25	16.55	6.64	4.73	17.82	2.25	14.98	6.56	4.39	66.83
3	2.50	13.54	6.61	3.61	13.63	2.50	13.54	6.21	3.26	52.59
4	3.00	11.56	5.70	3.25	14.24	2.70	11.56	4.89	2.75	56.26
5	2.53	12.98	6.60	4.00	15.14	2.00	12.78	5.41	3.49	64.50
6	3.15	12.78	6.22	3.56	14.33	3.15	12.98	7.09	4.06	57.27
7	2.50	19.44	8.11	5.48	16.89	3.40	19.44	8.96	5.09	56.87
8	3.20	18.68	13.03	5.37	10.30	3.50	18.78	13.32	5.45	40.93
9	3.18	19.45	14.64	5.70	9.73	4.25	19.78	14.81	5.54	37.39

The lowest and highest annual mean concentrations were observed at Stations 4 and 9 respectively for both surface and bottom waters. Table 4.2 shows that concentration of lead is much higher than world average, but less, when compared to concentration of lead in Subarnarekha River, east coast of India and the Gota River, Sweden. An inverse relationship was found between dissolved lead and salinity (Table 4.3), which was significant only during pre-monsoon and post-monsoon seasons ($p < 0.05$). A remarkable seasonal variation was not observed in the distribution of lead, but a steady estuarine removal from the dissolved phase is evident (Fig. 4.9).





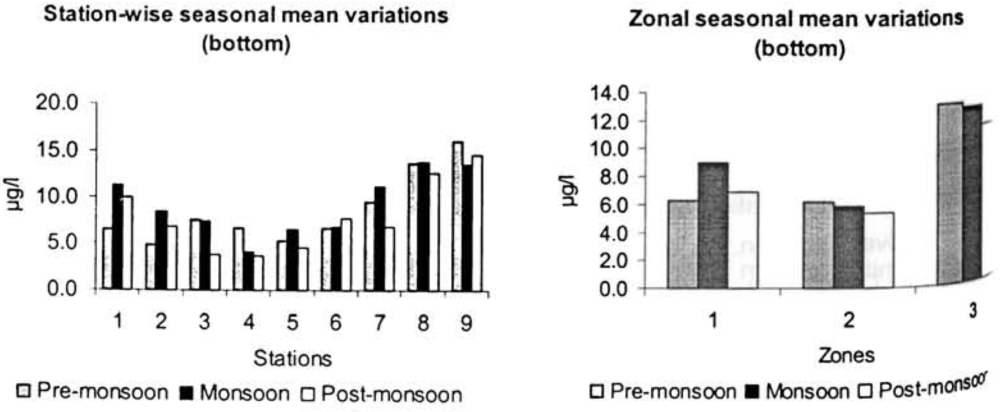


Fig. 4. 9 Seasonal and spatial variations of dissolved lead in surface and bottom waters

Enrichment ratio

The quantification of trace metal enrichment in waters of Chitrapuzha River was attempted by calculating the enrichment ratio (Forstner and Wittmann, 1979; Senapati and Sahu, 1996). The concentration of dissolved metals from a far upstream site, which is free from industrial pollution (Station R), was considered for calculation of enrichment ratio (Tables 4.13a to 4.13i).

Table 4.13a. Enrichment ratios of dissolved chromium

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	2.26	2.49	3.33	3.09	2.55	2.58
2	3.04	3.06	3.77	3.52	2.83	2.77
3	2.56	2.66	3.64	3.52	2.35	2.43
4	2.48	2.59	3.10	3.26	2.50	2.54
5	2.54	2.70	2.63	2.74	2.35	2.44
6	2.79	2.78	2.34	2.67	2.33	2.57
7	2.46	2.71	2.43	2.51	2.50	2.52
8	2.71	3.03	2.75	2.74	2.57	2.78
9	3.19	3.33	2.61	2.92	3.24	3.23

Table 4.13b. Enrichment ratios of dissolved manganese

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	1.80	2.43	2.06	2.65	1.78	2.26
2	1.80	2.08	2.34	2.34	2.07	2.07
3	1.86	2.48	3.01	3.01	2.22	2.22
4	1.92	2.53	2.73	2.73	2.51	2.51
5	1.75	2.11	2.09	2.09	1.80	1.80
6	2.43	2.50	2.77	2.77	2.01	2.01
7	2.00	2.97	3.12	3.12	2.33	2.33
8	2.39	2.99	2.91	2.91	3.15	3.15
9	2.67	2.97	3.19	3.19	3.20	3.20

Table 4.13c. Enrichment ratios of dissolved iron

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	1.14	0.83	0.94	1.25	2.13	1.99
2	1.77	2.85	1.06	1.38	1.02	0.53
3	0.66	0.48	3.54	3.60	0.99	0.46
4	0.51	0.40	2.26	3.24	0.75	0.72
5	0.72	0.75	1.66	2.64	0.72	0.58
6	1.10	1.92	3.58	2.55	1.13	1.20
7	1.07	1.95	2.01	1.76	0.80	0.68
8	1.00	1.00	3.01	3.26	0.91	1.35
9	3.18	2.83	2.35	1.81	0.73	0.47

Table 4.13d. Enrichment ratios of dissolved cobalt

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	1.12	1.09	1.13	1.49	0.79	0.92
2	1.22	0.96	1.21	1.44	0.83	1.12
3	1.11	1.07	1.35	1.16	0.81	0.96
4	1.04	0.81	1.62	0.93	0.81	1.11
5	0.96	0.78	1.19	1.52	0.72	0.79
6	0.98	0.99	0.84	0.88	0.85	0.88
7	0.92	1.22	1.46	0.91	1.09	1.22
8	1.02	1.82	1.30	0.91	0.76	1.17
9	1.52	1.80	1.59	1.74	0.87	1.35

Table 4.13e. Enrichment ratios of dissolved nickel

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	3.59	3.48	3.34	4.27	3.04	2.68
2	3.73	4.12	3.45	3.96	3.23	2.84
3	3.39	4.09	2.93	4.10	2.61	2.81
4	4.13	4.49	3.94	4.02	3.24	2.06
5	4.88	5.39	3.82	4.17	4.21	2.23
6	4.93	5.48	4.36	4.74	3.77	2.18
7	5.41	5.35	4.80	5.58	4.62	2.93
8	5.41	5.88	5.24	5.61	4.74	3.26
9	6.19	6.27	6.22	6.89	5.84	4.42

Table 4.13f. Enrichment ratios of dissolved copper

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	2.49	2.55	2.41	3.19	2.57	2.64
2	2.93	3.48	3.20	3.19	2.61	2.89
3	2.43	3.19	2.74	3.81	2.46	2.44
4	2.46	2.49	2.85	3.10	2.49	2.40
5	2.67	2.58	2.64	2.69	2.56	2.28
6	2.51	2.64	2.78	2.60	2.39	2.42
7	2.55	2.55	2.59	3.78	2.68	3.05
8	3.74	3.56	4.21	4.36	2.81	3.28
9	4.00	3.79	3.67	5.48	4.37	3.78

Table 4.13g. Enrichment ratios of dissolved zinc

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	1.06	0.99	1.21	1.22	0.76	0.87
2	0.93	0.92	1.83	1.90	0.85	0.84
3	1.18	1.18	1.14	1.06	0.81	0.83
4	1.06	1.06	1.28	1.28	0.79	0.76
5	1.22	1.22	1.54	1.54	1.39	1.44
6	0.86	0.86	1.84	1.99	0.84	0.87
7	1.01	1.01	1.42	1.42	1.52	1.62
8	1.63	1.63	2.20	2.20	1.25	1.18
9	2.15	2.19	2.21	2.41	1.40	1.57

Table 4.13h. Enrichment ratios of dissolved cadmium

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	4.96	5.26	6.21	6.40	5.30	5.33
2	5.03	5.51	5.74	6.45	5.43	5.35
3	5.22	5.76	5.99	6.40	5.35	5.44
4	5.18	5.53	5.98	6.48	5.35	5.21
5	5.21	5.75	4.90	6.37	5.34	5.33
6	6.32	5.74	6.39	6.61	6.25	5.23
7	6.41	7.59	6.38	7.01	6.20	6.64
8	6.96	8.87	7.38	7.56	6.40	6.98
9	6.69	9.79	7.71	12.31	7.50	7.74

Table 4.13i. Enrichment ratios of dissolved lead

Station	Pre-monsoon		Monsoon		Post-monsoon	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
1	2.80	2.89	4.47	4.98	4.42	4.42
2	2.18	2.18	4.00	3.77	2.93	3.02
3	3.93	3.38	3.32	3.32	1.67	1.72
4	2.97	2.97	2.43	1.84	2.17	1.63
5	2.04	2.35	4.33	2.93	2.77	2.07
6	2.97	2.97	2.44	3.03	2.80	3.42
7	4.22	4.22	4.04	4.92	2.70	3.04
8	5.77	6.09	5.93	6.14	5.71	5.58
9	7.13	7.13	5.93	6.00	7.20	6.46

The calculations showed that enrichment of metals was high in the Zone 3. Enrichment of metals in water was found to be high during monsoon, but nickel showed high enrichment during pre-monsoon period. Iron is depleted in the Stations 3, 4 and 5 during pre-monsoon and post-monsoon periods while zinc showed depletion in Zones 1 and 2 during pre and post-monsoon. Enrichment ratios proved that Cadmium was the only metal that is enriched to very high level in the study area.

4.2 DISTRIBUTION OF HEAVY METALS IN THE PARTICULATE PHASE

4.2.1 Introduction

The distribution of particulate metals in water is basically controlled by the relative proportions of the inorganic and organic constituents of the suspended matter, and their respective affinity for these metals (Windom et. al. 1989). In aquatic systems, most contaminants especially trace metals show a high affinity for particulate matter and preferentially for the fine-grained fraction of suspended solids (Regnier and Wollast, 1993). Thus, for a realistic and complete assessment of river fluxes and potential pollution, the composition of suspended particulate matter is obligatory in addition to the concentration of dissolved elements (Wollast, 1982; Church, 1986). Luoma (1983 & 1989) had shown that metals present in the particulate form in the aqueous phase are more bio-available to the aquatic organisms than those in the dissolved form. Particulate matter exhibits strong changes in chemical composition in the tidal Zone, indicating mixing c contaminated particles of continental origin with less contaminated marine particles. The composition and variability of particulate matter in an estuary are affected by many complex geochemical processes such as precipitation and flocculation, desorption/adsorption, river flow, tidal energy, etc. and are therefore often difficult to interpret (Morris et. al., 1978; Turner et. al., 1991 & 1994). During estuarine mixing the trace metals in the particulate forms can behave either conservatively or non-conservatively depending on various physico-chemical factors such as pH, Eh and suspended solids. When river water mixes with saline water desorption and solubilization of particulate metals may occur. As pointed out by Zwolsman et. al. (1993), there is overwhelming evidence, both from laboratory experiments and field investigations, that heavy metals bound on to suspended matter is partially desorbed when river water mixes with seawater.

A number of studies have been carried out on the behaviour of particulate metals in rivers and estuaries. Some of the recent works include those by Sfriso et. al. (1995) on the Lagoon of Venice, Moran and Woods (1997) on Ob-Irtysh Rivers, Russia. Particulate heavy metal data on Indian waters are relatively less. The available literature include data on particulate metals by Sanzgiry and Braganca (1981) from Andaman Sea, particulate metals from harbour and coastal environment of Visakhapatnam by Sathyanarayana et. al. (1985). This section focuses on the spatial and seasonal variations of heavy metals associated with particulate matter in the waters of Chitrapuzha River.

4.2.2 Results And Discussion

The overall summary statistics on particulate metals is given in Table 4.14. The Station-wise summary statistics showing the minimum and maximum values, mean, standard deviations and %CV of particulate metals are furnished in the Tables 4.17 to 4.25. The concentration levels of metals, chromium, cobalt. copper, zinc, cadmium and lead in the estuarine Zone (Zone 1) were in agreement with earlier studies of Nair et. al. (1990) in the Cochin estuary, but iron, nickel and manganese were found to have substantially increased in the estuarine Zone in a decade. The data revealed the following salient futures with respect to the spatial and seasonal distribution of particulate heavy metals. The concentration of these metals varied over a wide interval; iron was the most abundant and cadmium was the least abundant metal in the study area (Table 4.14).

Table 4.14 Overall summary statistics on particulate metal distribution (n=99) Concentration (mg/kg)

Metal	Surface					Bottom				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Cr	6.51	1209.95	213.50	223.00	104.45	3.97	1241.69	214.81	256.53	119.42
Mn	11.87	11918.6	2254.7	2.57	0.11	34.24	16660	1792	2.41	0.13
Fe	1376.45	195450	56231.25	43.32	77.03	126.19	177723	50804	32.70	64.37
Co	0.56	611.34	111.39	128.09	115.00	3.77	502.41	106.58	115.36	108.23
Ni	2.84	900.26	221.40	205.22	95.38	13.49	1314.78	215.17	192.77	89.59
Cu	0.68	353.24	101.02	66.18	65.51	8.91	360.82	97.92	79.30	80.99
Zn	65.58	6508.43	1142.84	1205.66	105.50	116.54	6486.68	1121.20	1201.42	107.15
Cd	0.59	532.61	61.67	46.69	75.72	7.40	273.86	46.50	54.57	117.34
Pb	25.18	1271.33	270.73	237.59	87.76	26.18	1281.33	278.72	237.77	85.31

The observed order of abundance which differs from that of dissolved metals, was iron > manganese > zinc > lead > nickel > chromium > cobalt > copper > cadmium in both surface and bottom particulates. The spatial variations of particulate metals generally followed the trend found in dissolved metals. When chromium, iron, nickel, copper, zinc, cadmium and lead exhibited higher values in Zone 3, manganese and cobalt recorded higher values in the Zone 2. Comparison of particulate metal levels in Chitrapuzha River with other rivers indicated higher concentrations of all metals except iron and copper (Table 4.15).

As in the case of dissolved metals, salinity plays an important role in the distribution of particulate metals also, in the study area. The relationship between metal levels in particulate matter and salinity (Table 4.16) was found to be negative. The sharp change in salinity as the fresh water mixes with seawater would result in the precipitation and coagulation of colloidal clay particles and co precipitation of metal with/or adsorption on to the particles resulting in the removal of considerable amount of metals from the solution phase (Regnier and Wollast, 1993; Bryan and Langston 1992). No significant correlation was struck between the particulate metals and the hydrographic parameters pH, dissolved oxygen and suspended solids.

***Table 4.15* Comparison of average concentration of particulate metals (mg/kg) of the Chitrapuzha River with other river/estuaries**

Location	Cr	Mn	Fe (mg/g)	Co	Ni	Cu	Zn	Cd	Pb	Reference
Chitrapuzha *	214.15	2023.58	53.52	108.99	218.29	99.47	1132.02	54.09	274.73	Present study
Periyar, India	-	-	62.17	-	113.33	91.00	290.00	4.13	94.33	Ouseph (1992)
Lena, Russia	-	-	-	-	31.00	28.00	143.00	-	23.00	Martin et al. (1993)
Amazon, S. America	193.00	1030.00	55.00	41.00	105.00	266.00	426.00	-	105.00	Martin and Meybeck (1979)
Mississippi, N. America	72.00	1300.00	47.40	21.00	55.00	42.00	184.00	1.4	45.00	Martin and Meybeck (1979)
Rhone, France	71 - 120	-	-	3.8 - 8.3	17 - 56	33 - 70	152 - 241	0.90-1.70	45 - 63	Paucot and Wollast 1997
Scheldt, Netherlands	150 - 220	-	-	5.8-20	33 - 67	125 - 192	540 - 1133	6.2-12.7	125 - 132	Paucot and Wollast 1997
Danube, Austria	-	1704.00	36.00	25.60	106.00	115.00	248.00	1.14	84.00	Guieu et al. (1998)
Ob – Irtysh, Russia	49.80		-	-	28.80	25.80	-	0.58	14.90	Moran and Woods (1997)
Tay, Scotland	-	0.24 - 3.74	-	-	9.0 - 63.0	12 - 133	53 - 470	0.02 - 3.99	18 - 191	Owens et al. (1997)
Ganges, India	71.00	1000.00	37.00	14.00	80.00	30.00	163.00	-	32.00	1) Martin and Meybeck (1979) 2) Subramanian et al. (1988)
World average	100.00	1050.00	48.00	20.00	90.00	100.00	250.00	1.20	35.00	1) Guieu et al. (1998) 2) Paucot and Wollast (1997)

* Average of surface and bottom values

Table 4.16 Correlation coefficient (r) between particulate metal concentration and salinity (n = 36)

Metal	Surface			Bottom		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
Cr	-0.3598*	-0.2855	-0.4522***	-0.3020	-0.3464*	-0.2525
Mn	-0.2653	-0.3252*	-0.0417	-0.0325	-0.3248*	-0.3067
Fe	-0.3088	-0.4964***	-0.6197***	-0.2256	-0.3867**	-0.6022***
Co	-0.1534	0.1444	-0.0783	-0.2103	-0.1021	-0.3524*
Ni	-0.2648	-0.0135	-0.2116	0.0020	-0.2111	-0.2399
Cu	-0.3366*	-0.3528*	-0.2346	-0.2368	-0.2815	-0.3508*
Zn	-0.4226***	-0.3354*	-0.0597	-0.3730*	-0.3597*	-0.03038
Cd	-0.5468***	-0.1558	-0.3254*	-0.3755*	-0.2472	-0.4714***
Pb	-0.3573*	-0.2128	-0.3093	-0.3580*	-0.2039	-0.3558*

The seasonal variations of particulate metals in the study area are depicted in Figures 4.10 to 4.18. Unlike dissolved metals, particulate metals follow considerable variations seasonally. While chromium, iron, manganese and nickel recorded higher values during the monsoon season, cadmium and cobalt showed higher values in post-monsoon season. When zinc recorded higher values during pre-monsoon season, copper and lead recorded no significant seasonal variations.

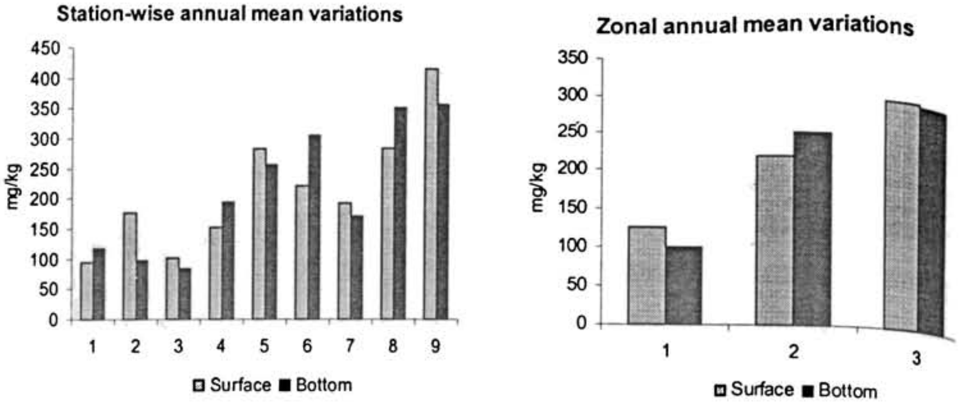
Particulate chromium

Concentration of chromium varied from a minimum of 6.51 mg/kg to a maximum of 1209.95 mg/kg in the surface and from 3.97 to maximum of 1241.69 mg/kg in the bottom waters (Table 4.14). The annual mean concentration of particulate chromium in the surface during the period was 213.50 mg/kg and in the bottom waters was 214.81 mg/kg. The Station-wise annual mean concentrations of particulate chromium varied from 95.92 to 417.17 mg/kg in surface waters and the range was 84.84 to 356.85 mg/kg in bottom waters (Table 4.17). The lowest and highest annual mean concentrations were recorded at Station 1and 9 respectively in surface waters and the same for bottom waters were at Stations 3 and 9 respectively. Concentration of particulate chromium recorded a steady increase from Zone 1 to Zone 3.

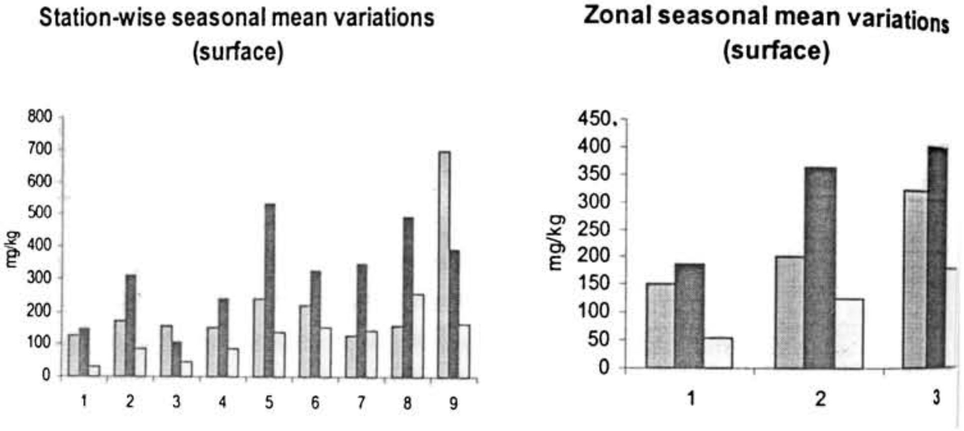
Table 4.17 Station-wise summary statistics on particulate chromium distribution (mg/kg)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	12.62	186.94	95.92	57.90	60.36	27.20	241.17	117.89	65.56	55.61
2	6.51	458.36	177.33	156.15	88.06	4.86	259.24	97.10	82.55	85.02
3	10.45	285.72	101.90	77.29	75.85	11.35	207.77	84.84	59.49	70.13
4	16.38	368.66	152.29	108.13	71.00	14.78	630.66	193.77	178.65	92.20
5	11.97	1178.89	281.93	320.56	113.70	35.25	1185.45	255.63	337.34	131.96
6	25.99	796.55	221.23	251.73	113.79	4.63	903.78	304.70	370.41	121.56
7	34.45	498.86	191.32	138.95	72.63	37.64	498.86	170.93	120.53	70.52
8	75.00	693.61	282.41	184.15	65.21	39.06	1082.57	351.58	311.21	88.52
9	61.20	1209.95	417.17	362.64	86.93	3.97	1241.69	356.85	368.40	103.24

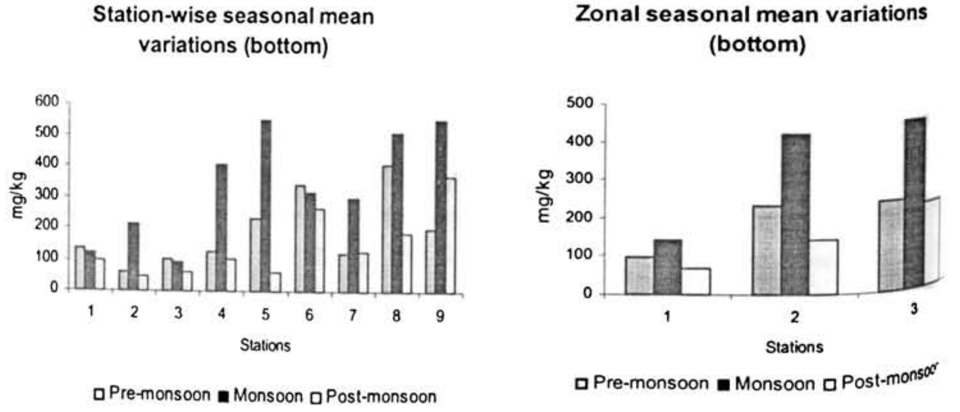
Chromium exhibited significant seasonal variations with higher values during monsoon except at Stations 3 and 9 in surface waters (Fig. 4.10). In bottom waters also monsoon values were generally higher. The lower values during pre-monsoon and post-monsoon may be attributed to the dilution of metal-rich fresh water by metal impoverished seawater, which occurs to maximum extent during pre-monsoon and post-monsoon. The high sedimentation processes in the estuary also promotes removal of chromium from particulate phase (Paucot and Wollast, 1997). Table 4.15 represents the comparison of particulate chromium level in the study area with other major rivers. Though the overall annual mean concentration of particulate chromium in the Chitrapuzha River was more than double the world average, it conforms to the range observed for other large rivers such as Amazon and Scheldt.


Station-wise annual mean variations

Zonal annual mean variations


Station-wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)


Station-wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Fig. 4.10 Seasonal and spatial variations of particulate chromium in surface and bottom waters

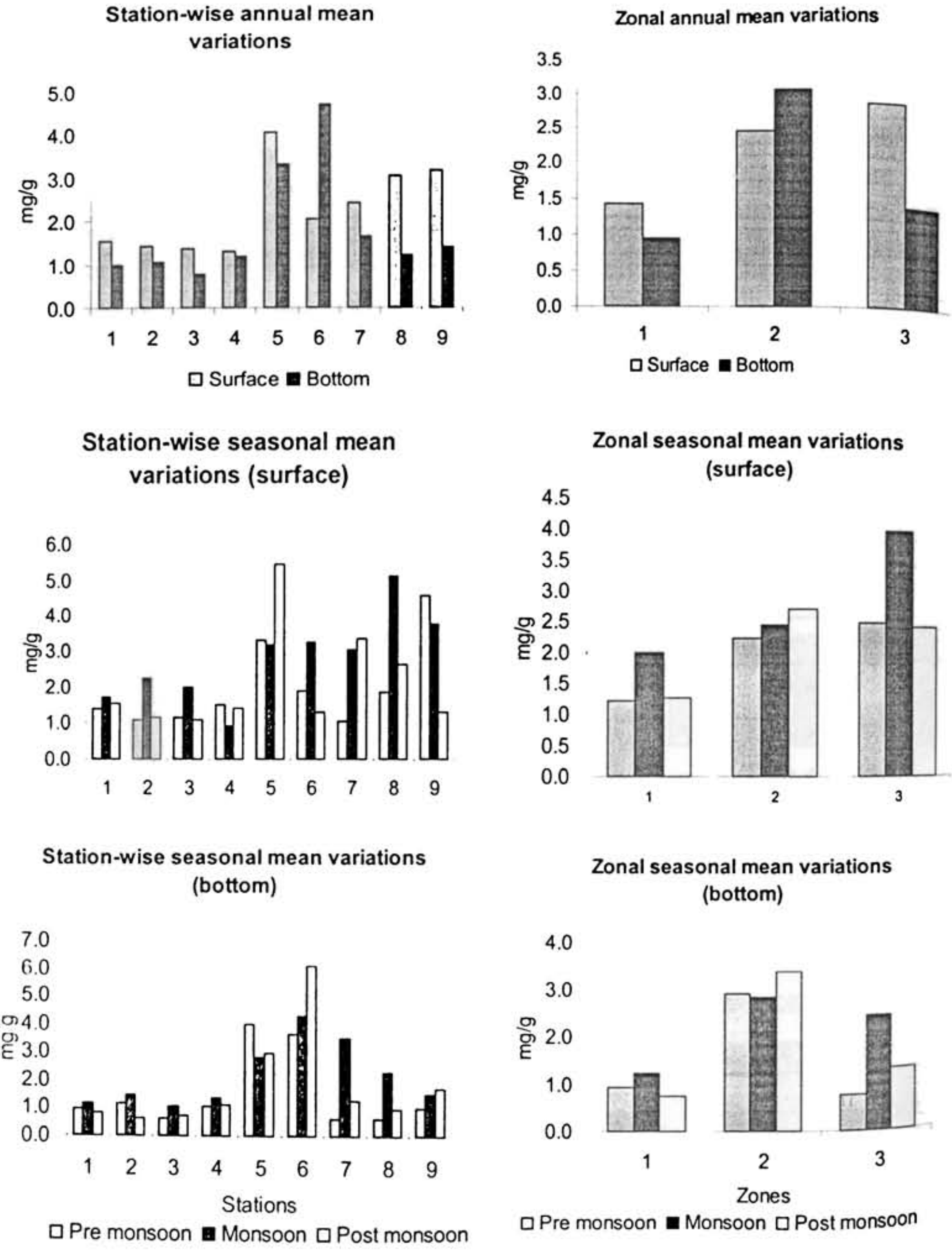
particulate manganese

The concentration of particulate manganese, the second most abundant metal in particulate matter, ranged from 11.87 to 11918 mg/kg in the surface waters and from 34.24 to 16660 mg/kg in the bottom waters (Table 4.14). The annual mean concentrations during the study period were 2254.7 mg/kg and 1792 mg/kg in surface and bottom waters respectively. Station-wise annual mean concentrations in surface waters varied from 1.30 to 4.04 mg/g and in bottom waters it ranged from 0.78 to 4.69 mg/g (Table 4.18). The lowest and highest annual mean values in surface waters were recorded at Stations 4 and 5. The lowest and highest values for bottom waters were recorded at Stations 3 and 6 respectively. Surface annual mean concentrations were higher than bottom annual mean values except at Station 6.

Table 4.18 Station-wise summary statistics on particulate manganese distribution (mg/g)

	Surface					Bottom				
Station	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	0.01	4.40	1.53	1.48	96.58	0.15	2.22	0.99	0.73	73.59
2	0.14	4.29	1.42	1.19	83.51	0.10	3.58	1.05	1.00	95.50
3	0.04	3.14	1.35	1.18	87.45	0.06	1.99	0.78	0.70	89.86
4	0.03	3.79	1.30	1.10	84.45	0.17	2.89	1.16	0.86	74.34
5	0.93	10.33	4.04	3.11	76.91	1.07	12.01	3.30	3.15	95.46
6	0.06	8.73	2.04	2.57	125.78	0.38	16.66	4.69	4.84	103.28
7	0.15	10.89	2.42	3.18	131.30	0.05	6.09	1.64	1.83	111.81
8	0.01	11.92	3.03	3.47	114.83	0.03	3.96	1.22	1.15	94.45
9	0.46	9.75	3.16	3.39	107.30	0.18	2.87	1.39	0.98	70.62

Seasonal variations observed in the distribution of manganese are represented in Figure 4.11. In Zone 1, monsoon values are higher than pre-monsoon and post-monsoon values whereas; in Zones 2 and 3 no significant seasonal trend could be noticed. The average concentration reported in the present study (2023.58 mg/kg) is remarkably higher than the world average concentration of 1050 mg/kg and values reported for other rivers (Table 4.15).



Station-wise annual mean variations

Zonal annual mean variations

Station-wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station-wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Fig. 4.11 Seasonal and spatial variations of particulate manganese in surface and bottom waters

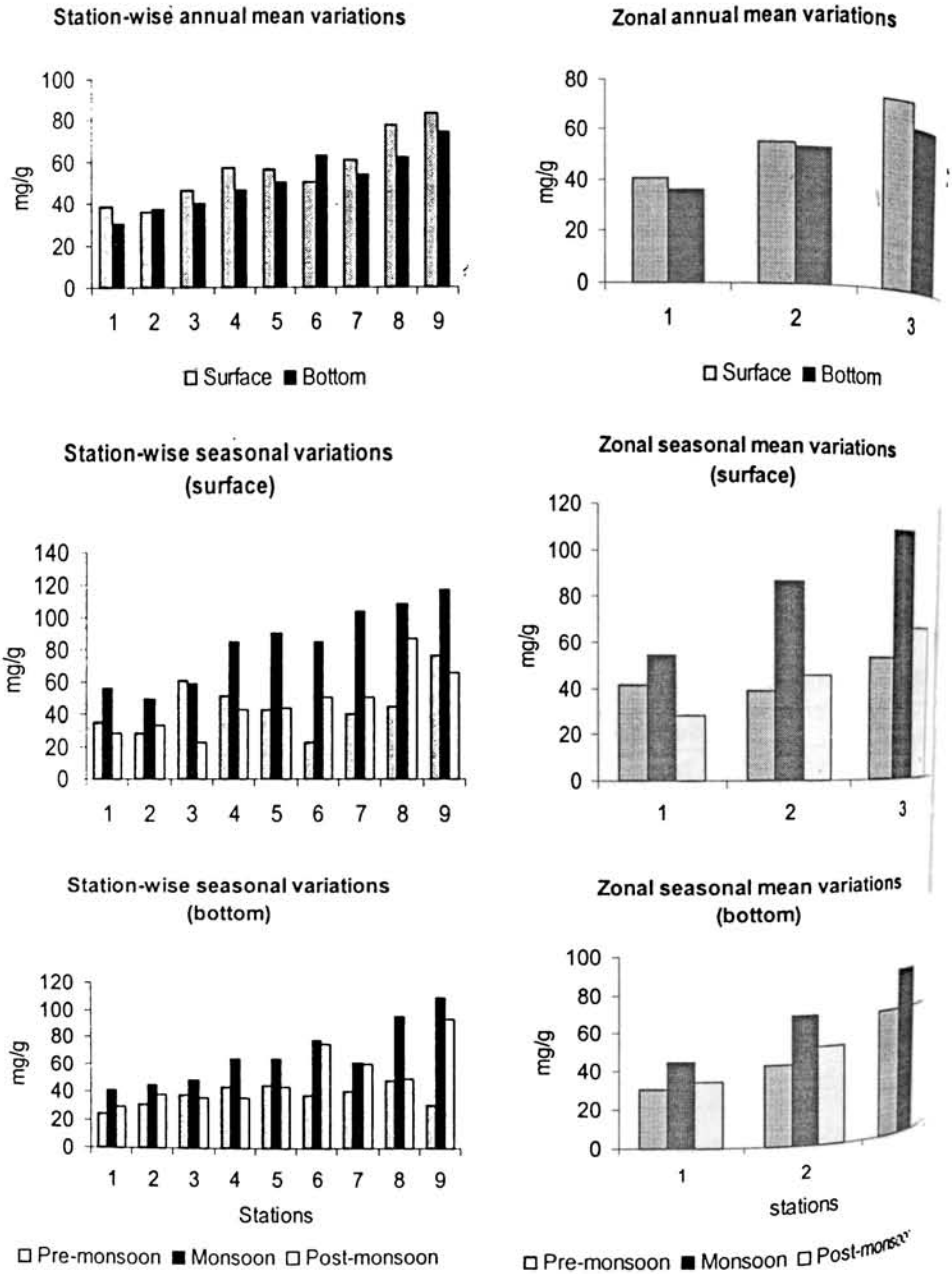
Particulate iron

The data revealed the following salient futures with respect to the spatial distribution of particulate iron. Concentration of iron, the most abundant metal, varied from a minimum of 1.376 mg/g to a maximum of 195.45 mg/g in the surface and from 0.126 mg/g to a maximum of 177.72 mg/g in bottom waters (Table 4.14). The annual mean concentration of particulate iron in the surface was 56.23 mg/g and the same in the bottom waters was 50.80 mg/g. The Station-wise annual mean concentrations of particulate iron (Table 4.19) varied from 35.71mg/g (Station 2) to 83.61 mg/g (Station 9) in surface waters and the range was from 30.61 mg/g (Station 1) to 74.99 mg/g in bottom waters (Station 9). The particulate concentrations of iron in surface waters were higher than that of bottom waters except at Stations 2 and 6. Salinity plays an important role in the distribution of particulate iron. There was a steady increase in concentration from Zones 1 to 3 (Fig. 4.12). The average concentration of particulate iron in Chitrapuzha was comparatively higher than the world average but it was lower than that of rivers, Amazon and Periyar (Table 4.15).

Table 4.19 Station-wise summary statistics on particulate iron distribution (mg/g)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	2.03	100.04	38.52	33.42	86.76	4.89	55.58	30.61	15.80	51.61
2	13.82	67.06	35.71	15.01	42.03	0.13	57.58	37.03	16.25	43.88
3	1.38	195.45	46.46	54.41	117.11	24.17	65.58	40.43	12.55	31.04
4	10.28	124.78	57.25	39.34	68.72	7.57	109.59	46.44	30.30	65.24
5	12.53	111.86	56.24	37.18	66.11	23.10	88.06	49.68	18.97	38.19
6	3.41	133.16	49.84	45.23	90.76	19.17	177.72	62.55	48.63	77.74
7	2.72	148.81	60.85	39.52	64.94	12.34	100.47	53.63	28.79	53.69
8	1.57	184.45	77.61	48.24	62.15	19.01	145.32	61.87	39.08	63.17
9	17.52	169.10	83.61	53.95	64.53	28.89	156.56	74.99	45.52	60.70

Seasonal variations were observed and are represented in Figure 4.12. Monsoon season recorded higher seasonal average values in surface and bottom waters. High monsoon values may be attributed to the inflow of freshwater carrying iron rich suspended matter during this season. This may also be due to desorption of iron from particulate matter resulting from the sharp change in salinity when fresh water mixes with seawater.



Station-wise annual mean variations

Zonal annual mean variations

Station-wise seasonal variations (surface)

Zonal seasonal mean variations (surface)

Station-wise seasonal variations (bottom)

Zonal seasonal mean variations (bottom)

Fig. 4.12 Seasonal and spatial variations of particulate iron in surface and bottom waters

Particulate cobalt

The distribution of cobalt in the particulate phase was found to fall within the range 0.56 to 611.34 mg/kg in the surface waters and between 3.77 to 502.41 mg/kg in bottom waters (Table 4.14). The annual mean concentration was 111.39 mg/kg in surface and 106.58 mg/kg in bottom waters. Zone 2 recorded comparatively higher values for annual mean concentrations, which may be partially due to local discharge of cobalt-containing effluents (Fig. 4.13). Surface annual mean values were higher than that of bottom in Zones 1 and 2 whereas in Zone 3, bottom values were comparatively higher than surface values. Station-wise annual mean concentrations of particulate cobalt were in the range 40.75 to 160.31 mg/kg for surface waters and 40.51 to 184.89 mg/kg in bottom waters (Table 4.20). The lowest annual mean concentrations for surface and bottom waters were observed at Stations 1 and 2 respectively, but Station 6 recorded highest value in surface and bottom waters.

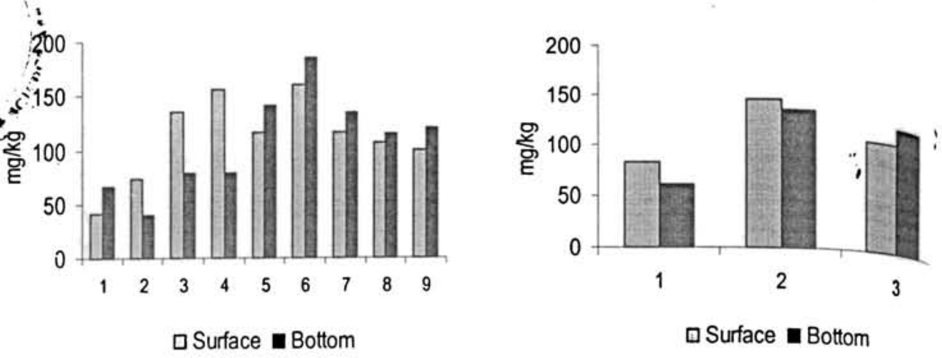
Table 4.20 Station-wise summary statistics on particulate cobalt distribution (mg/kg)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	4.29	149.25	40.75	46.51	114.12	4.34	188.89	66.47	62.80	94.47
2	2.64	164.71	73.09	50.54	69.16	4.61	143.56	40.51	40.56	100.11
3	0.56	384.99	135.71	118.35	87.21	10.73	332.29	78.86	90.44	114.68
4	7.02	611.34	155.56	192.61	123.82	5.61	287.67	78.89	83.07	105.29
5	4.37	533.45	116.21	162.63	139.95	3.77	317.29	140.92	104.69	74.29
6	21.74	475.31	160.31	152.19	94.94	8.27	475.31	184.89	152.80	82.65
7	10.24	424.67	115.55	124.16	107.45	36.46	424.67	133.80	114.33	85.45
8	22.06	471.74	106.04	126.53	119.33	16.34	471.74	114.61	132.56	115.66
9	2.18	392.00	99.28	105.69	106.46	6.47	502.41	120.28	165.52	137.61

Particulate cobalt exhibited significant seasonal variations. In Zone 1 high values were recorded during monsoon while in Zones 2 and 3 no such trend could be seen. The low values during pre-monsoon and post-monsoon in Zone 1 may be due to the desorption of metal from the particulate matter when fresh water mixes with highly saline seawater in the estuary. There was a negative correlation between particulate cobalt and salinity (Table 4.16). The average concentration of cobalt in the particulates of Chitrapuzha River was found to be surprisingly higher than any other major rivers and world average reported (Table 4.15).

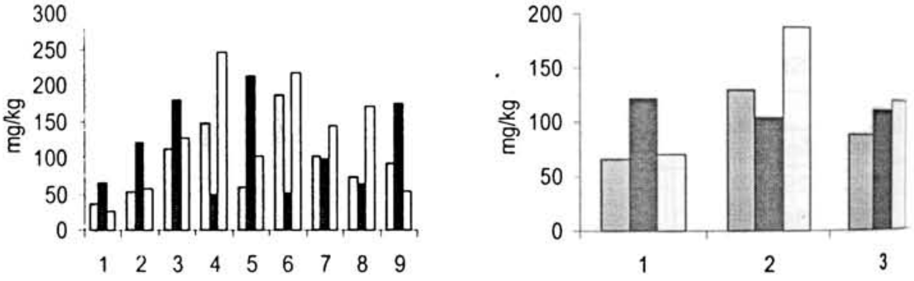
Station-wise annual mean variations

Zonal annual mean variations



Station-wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)



Station-wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

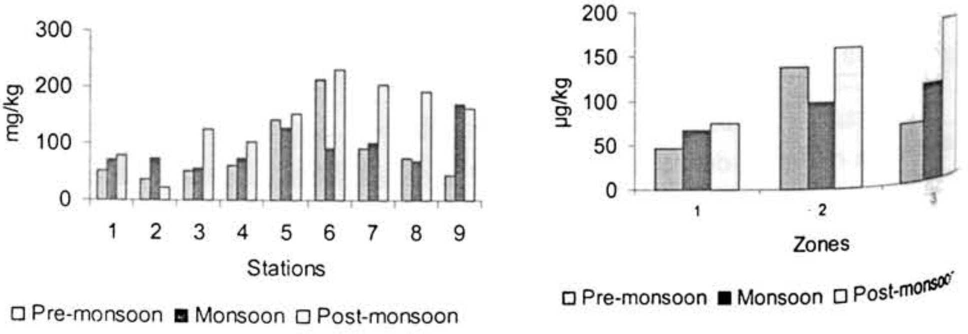


Fig. 4.13 Seasonal and spatial variations of particulate Cobalt in surface and bottom waters

Particulate nickel

Concentration of nickel, the fifth abundant metal, varied from minimum of 2.84mg/kg to a maximum of 900.26 mg/kg in the surface and from 13.49 to maximum of 1314.78 mg/kg in the bottom waters (Table 4.14). The annual mean concentration of particulate nickel in the surface was 221.40 mg/kg and the same in the bottom waters was 215.17 mg/kg. The Station-wise, the annual mean concentrations varied from 126.71 mg/kg to 321.97 mg/kg in surface waters and in bottom waters, the range was 154.01 to 326.69 mg/kg (Table 4.21). The lowest and highest annual mean concentrations were recorded at Stations 4 and 6 in surface waters. In bottom waters, the lowest and highest were at Stations 2 and 6 respectively.

Table 4.21 Station-wise summary statistics on particulate nickel distribution (mg/kg)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	33.02	388.56	137.57	116.46	84.65	62.43	312.52	159.59	83.93	52.59
2	2.84	676.56	176.62	235.46	133.32	60.53	263.07	154.01	62.79	40.77
3	19.88	519.64	194.82	204.23	104.83	60.44	288.78	169.43	82.38	48.62
4	8.89	485.73	126.71	130.17	102.73	54.45	441.57	164.24	100.08	60.93
5	8.48	589.62	260.48	197.92	75.98	65.27	580.99	260.85	179.90	68.97
6	35.21	900.26	321.97	280.54	87.13	13.49	1314.78	326.69	422.31	129.27
7	15.00	576.56	244.86	223.41	91.24	51.33	784.50	243.66	225.95	92.73
8	52.34	886.68	316.33	255.83	80.87	42.42	551.87	218.67	159.95	73.14
9	83.51	350.88	213.26	88.76	41.62	47.62	581.40	239.39	142.02	59.32

Statistical analysis (Table 4.16) revealed an overall negative correlation between particulate nickel and salinity, but significant correlation was not struck during any particular season. Particulate nickel showed pronounced seasonal variations. Monsoon values were distinctly higher than pre-monsoon and post-monsoon seasons both in surface and bottom waters (Fig. 4.14). The high monsoon values observed in Chitrapuzha River may be due to the inflow of fresh water carrying nickel rich suspended solids. The average concentration of particulate nickel in Chitrapuzha River was much higher than the world average concentration (Table 4.15).

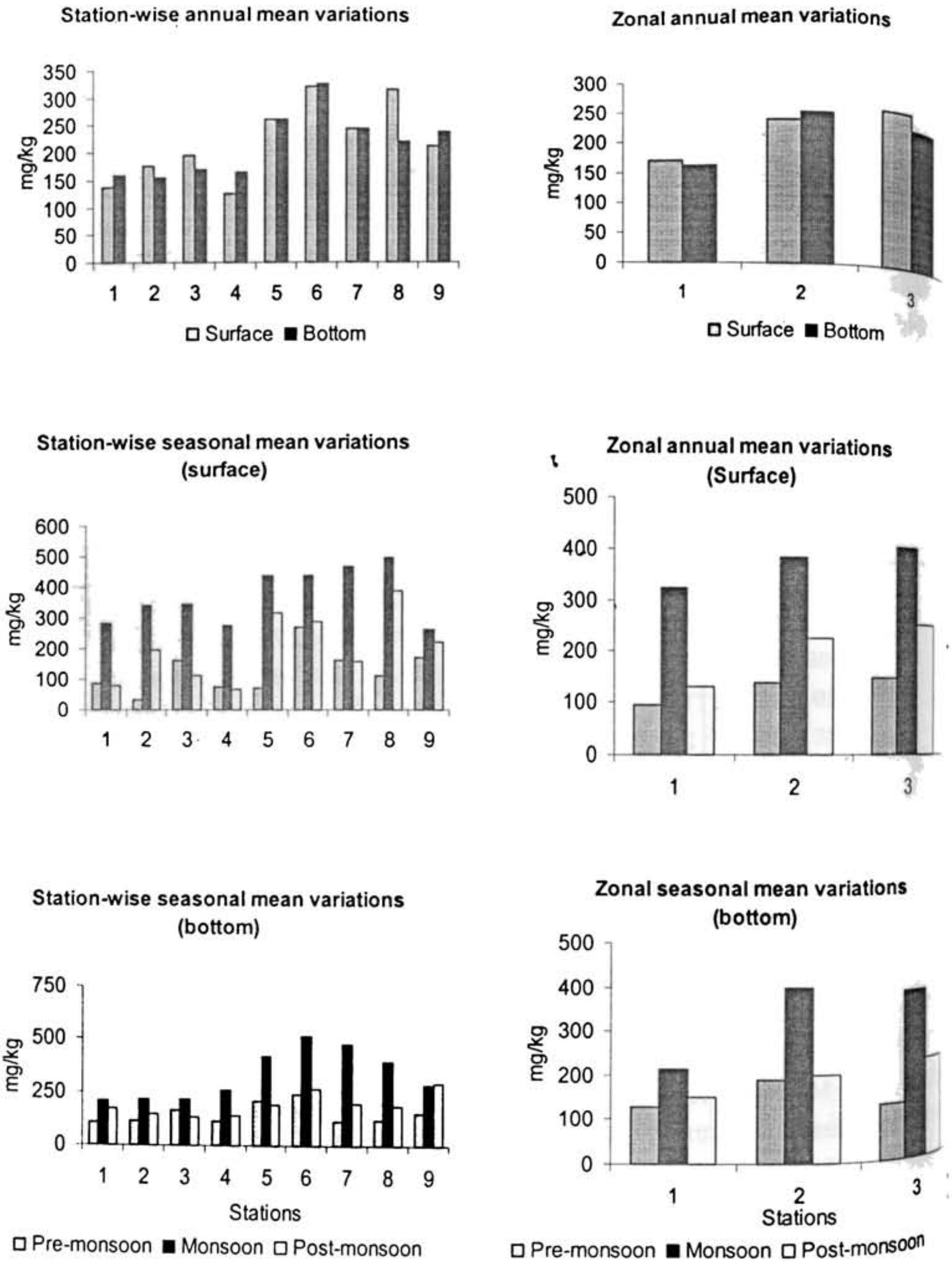


Fig. 4.14 Seasonal and spatial variations of particulate nickel in surface and bottom waters

Particulate copper

The distribution of copper in the particulate phase ranged from 0.68 to 353.24 mg/kg with a mean concentration of 101.02 mg/kg whereas in bottom waters it varied from 8.91 to 360.82 mg/kg with a mean value of 97.92 mg/kg. The surface annual mean values were generally higher than bottom waters in Zones 1 and 2 but in Zone 3, the bottom recorded higher values. The Station-wise annual mean values ranged from 66.29 mg/kg (at Station 1) to 141.09 mg/kg (at Station 9) in surface waters (Table 4.22). In bottom waters annual mean values ranged from 53.43 (at Station 3) to 152.01 mg/kg (at Station 8).

Table 4.22 Station-wise summary statistics on particulate copper distribution (mg/kg)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	0.68	156.45	66.29	49.65	74.90	17.83	147.45	69.48	45.73	65.81
2	23.58	102.34	68.36	21.04	30.78	28.80	181.71	80.93	59.76	73.83
3	2.21	145.68	73.83	46.64	63.18	19.25	127.41	53.43	35.24	65.97
4	24.45	145.45	84.82	37.51	44.23	14.03	126.68	69.60	35.71	51.30
5	30.34	291.57	114.16	79.63	69.75	19.05	169.75	92.18	57.92	62.83
6	9.09	218.26	97.20	74.41	76.56	16.46	194.78	83.54	56.27	67.36
7	14.53	230.00	123.79	68.49	55.33	8.91	307.18	138.21	100.00	72.35
8	55.00	353.24	139.64	81.70	58.51	34.95	319.90	152.01	95.95	63.12
9	50.74	274.44	141.09	73.50	52.10	23.66	360.82	141.90	126.74	89.31

No significant seasonal variation could be observed in the distribution of particulate copper in Chitrapuzha River during the study (Fig. 4.15). Correlation between copper and salinity indicated a negative relationship (Table 4.16). The average concentration of particulate copper found in the Chitrapuzha River during the study conformed to world averáge and the range observed for other rivers (Table 4.15).

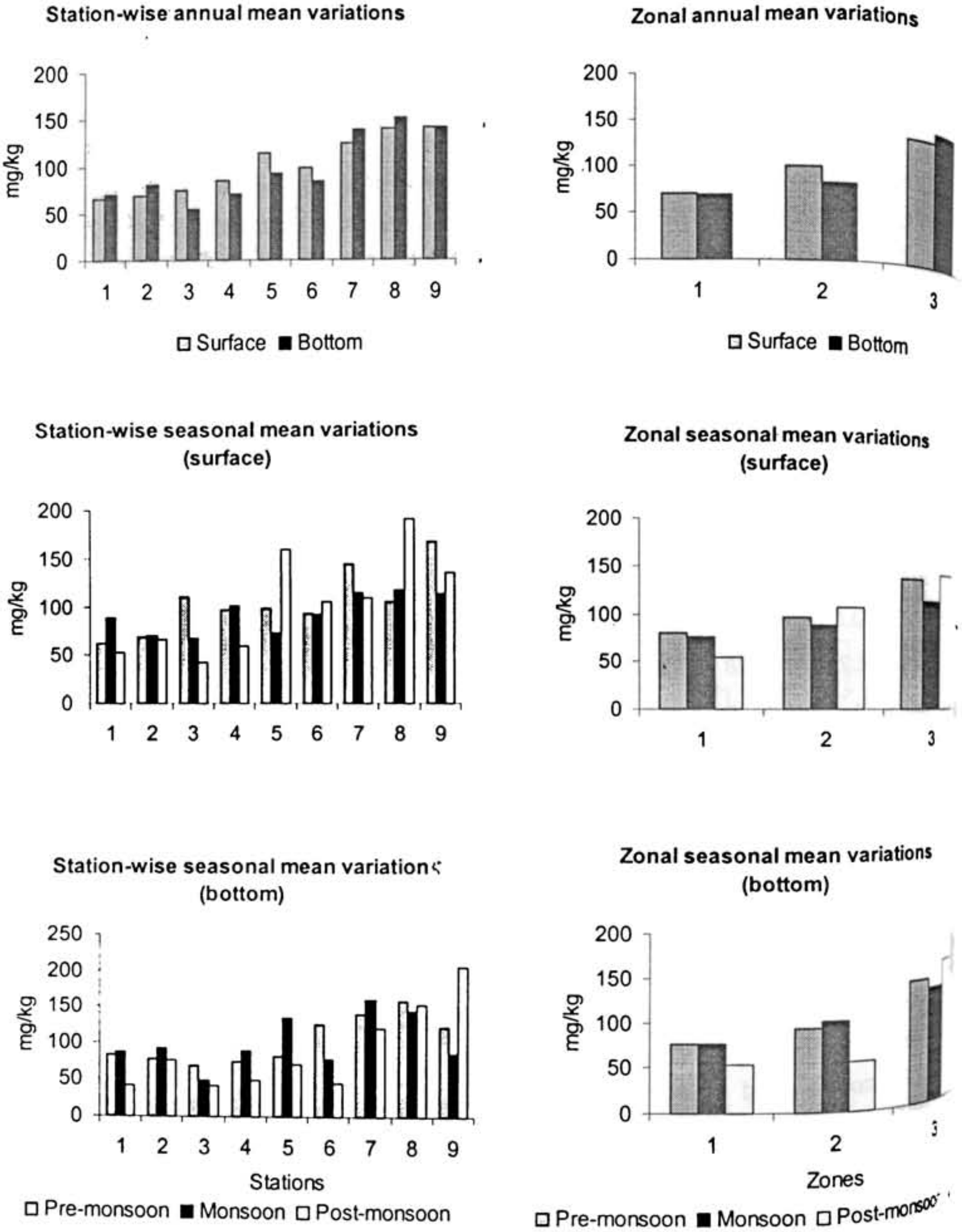


Fig. 4. 15 Seasonal and spatial variations of particulate copper in surface and bottom waters

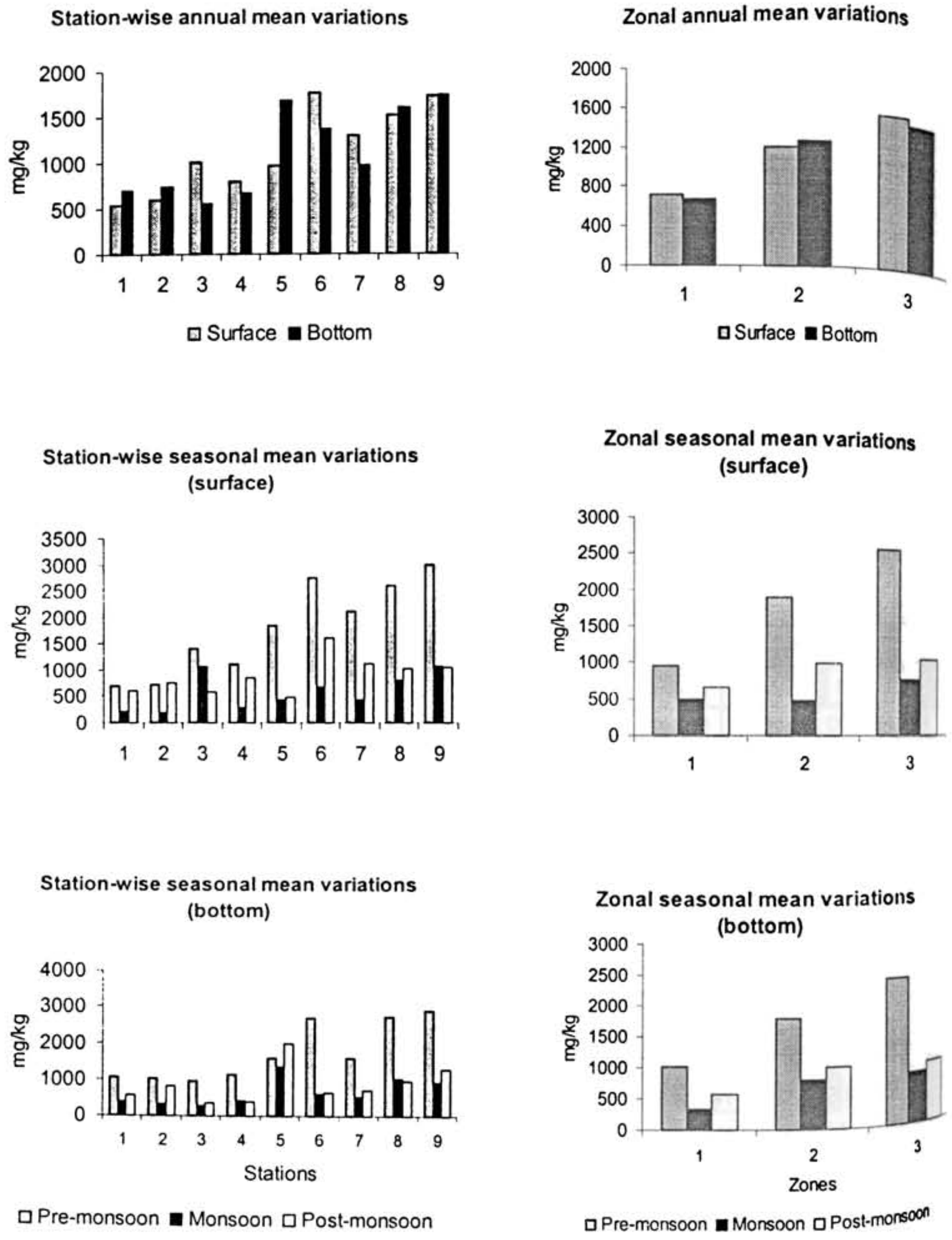
Particulate zinc

The data revealed the following salient features with respect to the spatial distribution of particulate zinc. Concentration of zinc, the third abundant metal, varied from a minimum of 65.58 mg/kg to a maximum of 6508.43 mg/kg in the surface and from 116.54 mg/kg to maximum of 6486.68 mg/kg in the bottom waters (Table 4.14). The annual mean concentration of particulate zinc in the surface during the period was 1142.84 mg/kg and the same in the bottom waters was 1121.20 mg/kg. The concentration of metals in particulate matter varied over a wide range, which is evident from the large percentage coefficients of variations. The Station-wise, the annual mean concentrations of zinc varied from 535.83 mg/kg to 1773.46 mg/kg in surface waters and in bottom waters, the range was 558.48 to 1769.90 mg/kg (Table 4.23). The lowest and highest annual mean concentrations were recorded at Stations 1and 6 in surface waters while Stations 3 and 9 recorded the lowest and highest values in bottom waters. An increasing trend from Station 1 to 9 can be noted in the distribution of zinc (Fig. 4.16).

Table 4.23 Station-wise summary statistics on particulate zinc distribution (mg/kg)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	81.90	1318.11	535.83	398.91	74.45	142.68	1750.66	698.80	527.37	75.47
2	87.66	1232.69	595.47	492.69	82.74	256.52	1237.13	747.10	457.40	61.22
3	65.58	2563.46	1019.68	913.10	89.55	118.43	1980.93	558.48	556.86	99.71
4	133.65	2035.34	800.40	636.47	79.52	196.98	1925.74	674.27	572.23	84.87
5	306.15	2698.93	971.65	915.98	94.27	198.23	4959.15	1680.27	1357.13	80.77
6	88.64	5263.03	1773.46	1688.28	95.20	116.54	5254.78	1367.75	1503.04	109.89
7	220.00	4017.68	1301.30	1257.65	96.65	204.17	2642.80	977.21	816.74	83.58
8	243.80	6508.43	1534.10	1793.75	116.93	354.46	6486.68	1617.03	1775.38	109.79
9	328.56	5400.78	1753.71	1469.51	83.79	429.82	5398.78	1769.90	1736.52	98.11

Particulate zinc recorded significant seasonal variations in Chitrapuzha River during the study. The pre-monsoon and monsoon values were the highest and lowest respectively, in all the Zones. Higher pre-monsoon and post-monsoon concentrations may be attributed to transfer of zinc from dissolved phase to particulate phase when fresh water mixed with saline water. The concentration of zinc in Chitrapuzha River (1132 mg/kg) is surprisingly high when compare to world average of 250 mg/kg and the values reported from other rivers (Table 4.15).



Station-wise annual mean variations

Zonal annual mean variations

Station-wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station-wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Fig. 4.16 seasonal and spatial variations of particulate zinc in surface and bottom waters

Particulate Cadmium

Cadmium was the least abundant among the metals studied. Its concentration varied from 0.59 kg/kg to 532.61 mg/kg in the surface waters and 7.40 mg/kg to 273.86 mg/kg in bottom waters (Table 4.14). The annual mean concentration was 61.67 mg/kg in surface and 46.50 mg/kg in bottom waters. Station-wise annual mean concentrations were in the range 19.91 mg/kg to 120.71mg/kg for surface waters and 19.49 mg/kg to 82.03 in bottom waters (Table 4.24). The lowest and highest annual mean concentrations were observed at Stations 1 and 6 both in surface and bottom waters. All the Stations except Station 3 recorded higher annual mean concentrations in surface waters (Fig. 4.17).

Table 4.24 Station-wise summary statistics on particulate cadmium distribution (mg/kg)

Metal	Surface					Bottom				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
1	1.55	69.82	19.91	21.79	109.45	7.40	44.86	19.49	13.96	71.64
2	1.29	88.32	33.27	30.14	90.59	8.70	47.48	26.34	16.99	64.51
3	0.59	80.29	20.75	22.15	106.74	7.73	53.68	26.44	15.69	59.35
4	0.93	126.40	30.64	41.35	134.96	7.45	71.33	25.93	20.17	77.78
5	9.79	218.53	73.82	76.16	103.18	11.87	88.16	45.60	33.21	72.83
6	3.23	532.61	120.71	167.89	139.08	12.62	273.86	82.03	79.91	97.42
7	2.59	280.00	79.93	89.10	111.47	10.71	250.79	64.48	71.46	110.82
8	11.87	397.06	100.31	127.04	126.65	12.03	242.46	59.14	64.48	109.03
9	8.58	187.50	75.65	61.51	81.30	9.17	260.81	69.09	81.57	118.07

Seasonal variations observed in the distribution of particulate cadmium are illustrated in Figure 4.17. Cadmium exhibited seasonal variations with relatively higher values during post-monsoon season in Zone 2 and 3. In Zone 1, pre-monsoon and post-monsoon values were lower than monsoon value. This lowering in concentration may be due to the desorption and solubilization of particulate cadmium as salinity increased. As pointed out by Zwolsman et. al. (1993), there is overwhelming evidence, both from laboratory experiments and field investigations, that cadmium bound to suspended matter is desorbed (partially) when river water mixes with seawater. Speciation studies suggest that desorption of particulate cadmium during estuarine mixing is due to the formation of chlorocomplexes (Turner et. al., 1981; comans and Van Dijk, 1988; Elbaz-Poulichet et. al., 1987; Windom et. al., 1991; Chiffoleau et. al., 1994; Dai et. al., 1995). Station 6 recorded remarkably high concentration during post-monsoon season, which may due, in part, to the local input of contaminated wastewater of industrial origin during this season (Fig. 4.17).

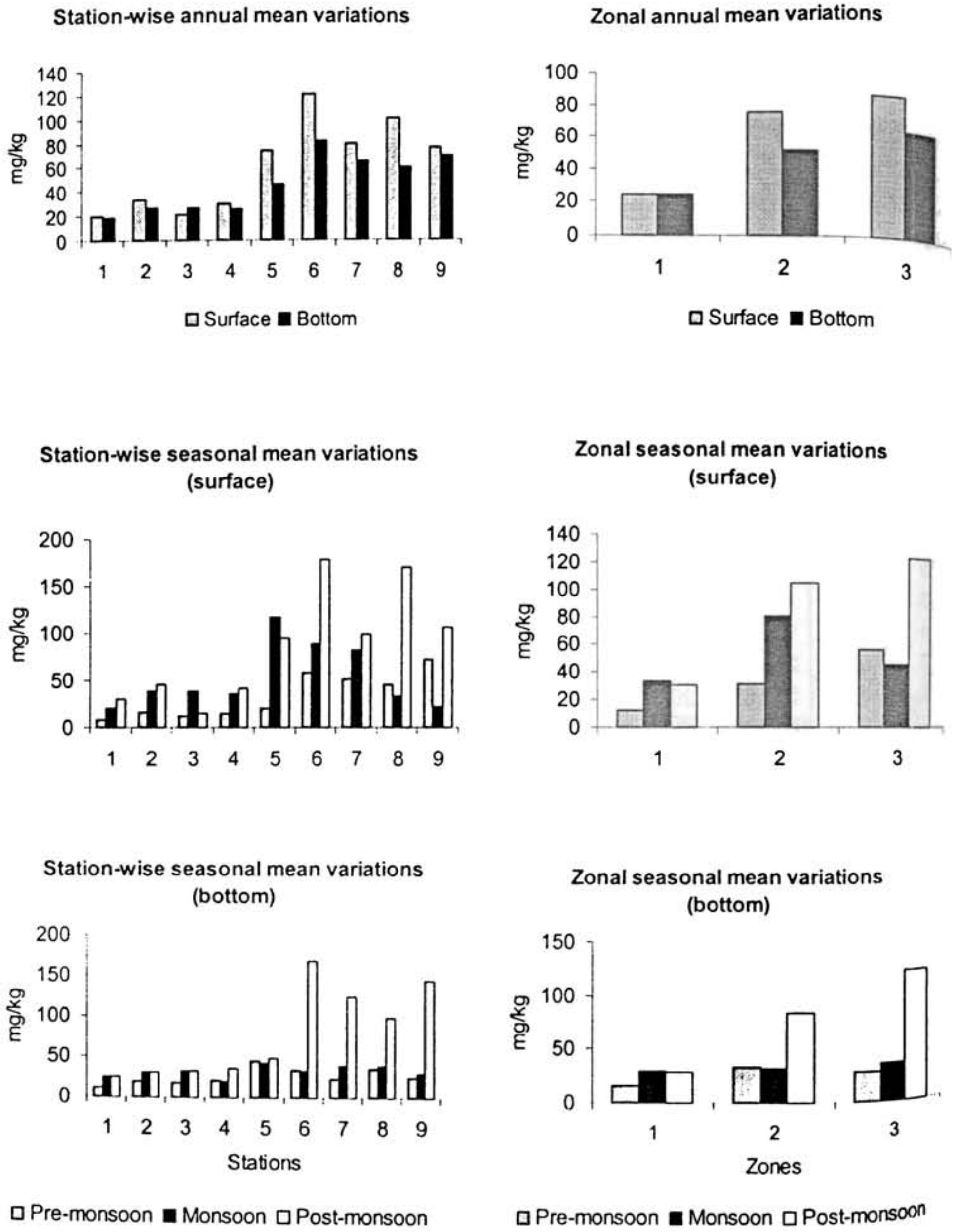


Fig. 4.17 Seasonal and spatial variations of particulate cadmium in surface and bottom waters

In surface and bottom waters the annual mean concentrations generally showed an increasing trend from Stations 1 to 9. This may be due to discharge of effluents containing cadmium from the petrochemical and fertilizer industries situated in Ambalamugal industrial area. The concentration of cadmium in the particulates of Chitrapuzha (54 mg/kg) was surprisingly higher than the concentrations of cadmium in other rivers and the world average (1.2 mg/kg).

Particulate lead

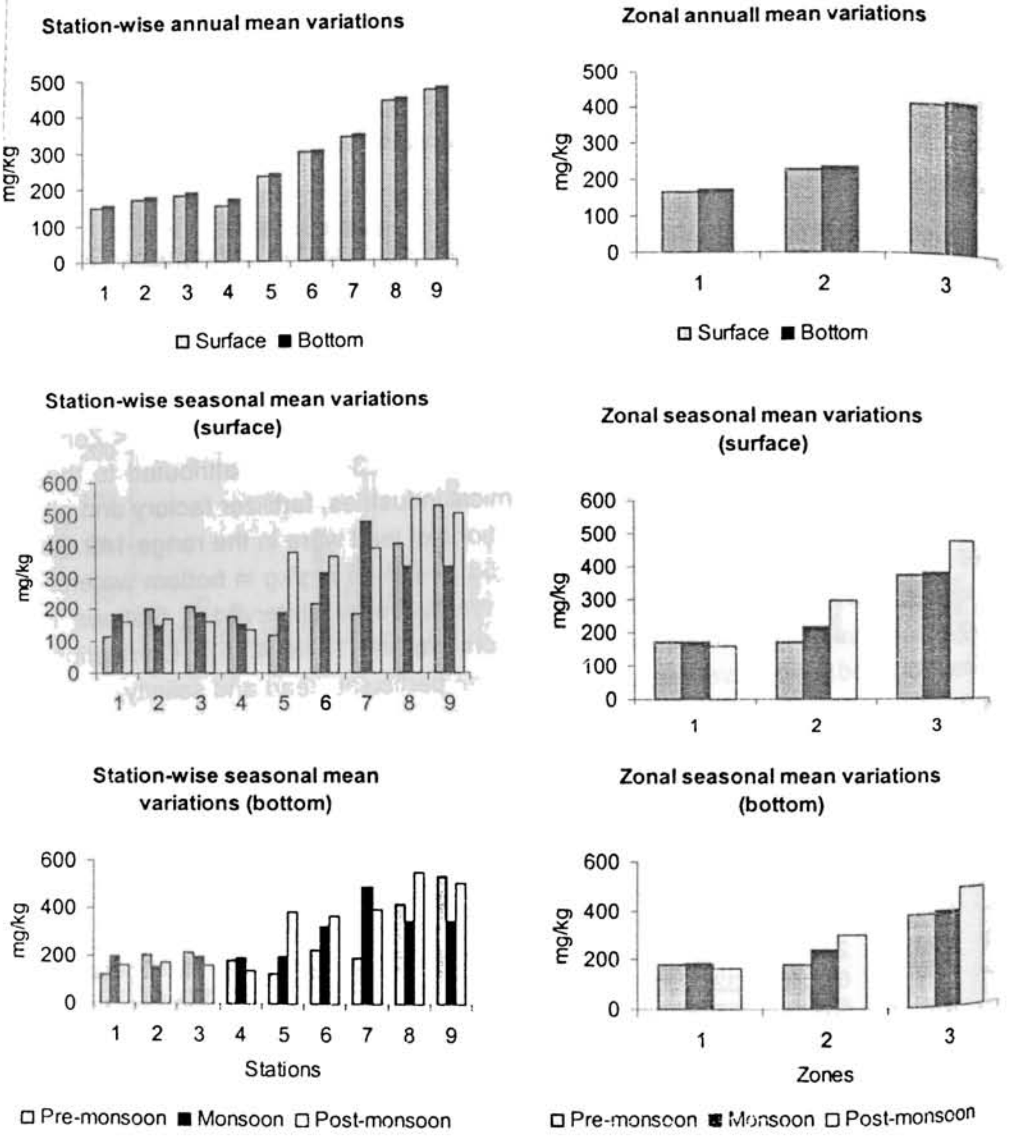
Lead was the fourth abundant of the metals estimated in Chitrapuzha River. Concentration of particulate lead in the study area was found to vary from 25.18 to 1271.33 mg/kg in the surface waters and 26.18 to 1281.33 mg/kg in bottom waters (Table 4.14). The annual mean concentrations were almost equal both in surface and bottom waters, 270.73 mg/kg in surface and 278.72 mg/kg in bottom waters. The annual mean concentration of particulate lead was in the order Zone 1 < Zone 2 < Zone 3. The high concentration of lead in Zone 3 may be attributed to the discharge of effluents from nearby petrochemical industries, fertilizer factory and oil refinery. Station-wise annual mean concentrations of lead were in the range 149.65 to 466.54 mg/kg for surface waters and 156.56 to 473.45 mg/kg in bottom waters. The lowest and highest annual mean concentrations were observed at Stations 1 and 9 respectively for both surface and bottom waters (Table 4.25). Correlation studies indicated a negative relationship between particulate lead and salinity, but it was significant only during pre-monsoon and post-monsoon seasons (Table 4.16).

Table 4.25 Station-wise summary statistics on particulate lead distribution (mg/kg)

Station	Surface					Bottom				
	Min	Max	Mean	SD	CV %	Min	Max	Mean	SD	CV %
1	33.61	373.13	149.65	111.02	74.19	37.61	386.13	156.56	112.20	71.66
2	53.42	283.02	172.67	79.79	46.21	61.42	295.02	180.46	80.73	44.74
3	25.18	292.85	183.01	80.28	43.86	26.18	302.85	189.92	82.53	43.46
4	59.49	273.97	154.91	81.39	52.54	67.98	284.74	170.67	75.41	44.19
5	72.41	611.46	232.22	175.27	75.48	77.41	621.46	239.13	174.48	72.97
6	88.10	652.17	297.73	175.64	58.99	96.10	653.17	304.64	175.49	57.61
7	77.16	1021.28	340.41	301.35	88.52	82.16	1033.28	347.32	302.43	87.08
8	71.23	1271.33	439.45	365.59	83.19	76.23	1281.33	446.36	367.47	82.33
9	107.30	1020.55	466.54	322.86	69.20	105.30	1030.55	473.45	325.38	68.73

Significant seasonal variations could not be observed in the distribution of particulate lead (Fig. 4.18). In Zone 1 all the seasons recorded almost equal mean concentrations whereas in Zones 2 and 3, post-monsoon recorded comparatively higher values. Similar trend was noted in the distribution of bottom waters also. Table 4.15 represents the comparison of particulate cadmium in the waters of

Chitrapuzha River with other rivers, and it indicate that the level of particulate lead is about eight times greater than the world average.



Station-wise annual mean variations

Zonal annuall mean variations

Station-wise seasonal mean variations (surface)

Zonal seasonal mean variations (surface)

Station-wise seasonal mean variations (bottom)

Zonal seasonal mean variations (bottom)

Fig. 4.18 Seasonal and spatial variations of particulate lead in surface and bottom waters

4.3 DISTRIBUTION OF HEAVY METALS IN THE SEDIMENT PHASE

4.3.1 Introduction

Heavy metal contamination in sediment is one of the largest threats to environmental quality and human health. The distribution of heavy metals in sediments is thus an important area of research in environmental studies. Several studies, which recognized the adverse effects of heavy metals on health, have suggested that water quality standards should account for the accumulation and release of toxic metal compounds. Generally, as metals enter a coastal environment, they are transferred to the sediments by various processes, that is, adsorption on to particle surfaces and co-precipitation with solid phases (Karickhoff, 1984; Santchi et. al., 1990; Daskalakis and O'Conor, 1995; Lee et. al., 1998). These sediments become an important reservoir for metals and provide input records of metals to the ecosystem (Salamons and Forstner, 1984; Zwolsman et. al., 1996). However, some of the sediment-bound metals may remobilize and be released back to waters with a change of environmental conditions, and impose adverse effects on living organisms. Sediments have thus proved to be excellent indicators of environmental pollution, as they accumulate pollutants to the levels that can be measured reliably by a variety of analytical techniques. The concentration of heavy metals in surficial sediments may be elevated above background levels due to anthropogenic activities such as industrial and agricultural runoff. This section focuses on the spatial and seasonal variations of heavy metals associated with surficial sediments of Chitrapuzha River.

There have been a number of studies on the distribution of heavy metals in sediments of Cochin estuary. Some of the earlier investigations carried out in the heavy metal distribution in the sediments of Cochin estuary were Murty and Veerayya (1981), Venugopal et. al.'(1982), Ouseph (1987), Nair et. al. (1990) and Jayasree and Nair (1995). None of the above studies have determined metal distribution in the surficial sediments of Chitrapuzha River, though it is flowing through a large industrial area.

4.3.2 Results And Discussion

The overall summary statistics showing the minimum and maximum values, mean, standard deviations and percentage coefficient of variation of total metals studied in the sediments of Chitrapuzha River are furnished in the Table 4.26. Seasonal variations of total metals in sediment are depicted in Figures 4.19 to 4.27. The data revealed the following salient futures with respect to the spatial and distribution of total metals in the surficial sediments of Chitrapuzha River. The concentration of total metals in the surficial sediments in the Cochin estuary has increased two fold within the last decade based on the observations of Nair et. al. (1990) and Nair (1992). The concentration of these metals varied over a wide interval. The large variations in trace metal distribution observed were primarily due to the variations in particle size, organic matter content, net deposition rates and sediment mixing. Iron was the most abundant (annual mean 25.56 mg/g) and cadmium (annual mean 12.87 mg/kg) was the least abundant metal in the study area. The observed order of abundance was iron > manganese > zinc > chromium > nickel > copper > lead > cobalt > cadmium (Table 4.26).

Table 4.26 Overall summary statistics on total metals in sediments (n=99)

(mg/kg)

Metal	Min	Max	Mean	SD	CV %
Cr	8.27	285.00	101.00	60.94	60.34
Mn	14.74	868.92	245.18	188.08	76.71
Fe	1260.00	57672.00	25559.00	12.21	47.78
Co	1.25	33.33	16.39	7.94	48.45
Ni	5.30	116.73	62.60	28.96	46.25
Cu	2.92	68.24	28.47	16.77	58.89
Zn	7.13	1029.18	177.01	148.99	84.17
Cd	2.29	34.47	12.87	7.43	57.75
Pb	0.93	41.91	22.40	9.77	43.60

All the metals showed a decreasing tendency towards the bar-mouth, which may be due to the tidal flushing and the impact of waves, which remove the finer fractions of the sediments from the bar-mouth (Sunil Kumar 1996). A decrease in the content of copper, lead and cadmium in the estuarine sediments under the marine influence was reported by Forstner et. al. (1990) for Elbe estuary and observed that the same corresponded with an increase in marine borne sediments, which diluted the contaminated sediments. The decrease in concentration of sediment metals from estuary to the marine region was reported in the Cochin estuary previously by Nair (1992). Except iron and lead, all other metals recorded higher concentration in Zone 3. Discharge of effluents containing heavy metals from various industries including fertilizer and petrochemical units may be the major reason for it. The chemical substances such as rock phosphate, phosphoric acid and sulphur falling into water while transferring them from cargo barges to the fertilizer firm may also contribute to high level of metals in the sediments in this Zone. Other factors that may contribute are the high concentration of organic carbon, phosphorus and fine grains in the sediments (Owen and Sandhu 2000). Clay minerals and organic matter are important carriers of heavy metals in sediments (Brook and Moore, 1988; Stone and Droppo, 1996; Murray et. al., 1999). All the metals recorded their minimum values in Zone 2, which was a result of the predominantly sandy nature of the sediment at this Station. Another striking observation was that the spatial distribution pattern of the heavy metals cobalt, nickel and lead is quite similar. At all the Stations, their annual mean variation was found to be analogous. The uniformity in spatial variation of metals in the sediment suggests similarity in estuarine mixing behavior and occurrence of sources of metals. Comparison of total metals in the sediments of Chitrapuzha River with other rivers indicated lower concentration of metals in Chitrapuzha River (Table 4.27).

Table 4.27 Comparison of average concentration of sediment metals of the Chitrapuzha River with other major rivers (mg/kg)

Location	Cr	Mn	Fe (mg/g)	Co	Ni	Cu	Zn	Cd	Pb	Reference
Chitrapuzha	101.00	245.18	25.56	16.39	62.60	28.47	177.01	12.87	22.40	Present study
Subarnarekha, India	69.81	0.07	2.29	9.94	23.13	12.90	42.56	-	6.25	Senapati and Sahu 1996
Vellar, India	252.00	3545.00	18.47	19.00	110.00	7.00	117.00	5.00	-	Mohan, P.M (1995).
Narmada, India	55.00	514.00	31.40	36.00	23.00	46.00	50.00		-	Mohan, P.M (1995).
Krishna, India	82.00	906.00	25.10	32.00	32.00	35.00	26.00		-	Mohan. P.M (1995).
Cauvery, India	54.00	212.00	12.60	15.00	12.00	3.00	13.00		-	Mohan, P.M (1995).
Tees, England	224.00	-	-	34.00	41.00	103.00	392.00	5.90	307.00	Jones and Turky (1997)
Indian average	87.00	605.00	29.00	31.00	37.00	28.00	16.00		-	Mohan, P.M (1995).
Average Shale	100.00	-	-	20.00	80.00	50.00	90.00	0.30	20.00	Turekian and Wedepohl (1961)
World average	100.00	1050.00	48.00	20.00	90.00	100.00	350.00		-	Mohan. P.M (1995).

Chromium

The concentration of total chromium in the sediments of Chitrapuzha River varied from 8.27 to 285 mg/kg during the period of investigation with a mean concentration of 101 mg/kg (Table 4.26). The level of chromium in the study area conformed to world average, but it is higher than Indian average (Table 4.27). The Station-wise annual mean concentrations ranged from 26.45 mg/kg at Station 5 to 189.87 mg/kg at Station 8 (Table 4.28). The level of chromium in the Zone 3 was almost double when compare to that in Zone 1 (Fig. 4.19). This high concentration in the sediments of Zone 3 especially at Station 8 may be due to the discharge of effluents from industries, mainly from the fertilizer-manufacturing unit located on the banks of the river near Zone 3. The lowest annual mean concentration in Zone 2, especially at Stations 4 and 5 may be attributed to the low clay-silt content and sediment organic carbon of this region. Distribution of chromium essentially followed the distribution of organic carbon and fine grains in the sediments. The ability of fine particles and organic materials to scavenge trace metal effectively has been discussed by several authors (Olsen et. al., 1982; Brook and Moore, 1988; Perez et. al., 1991; Izquierdo et. al., 1997).

Table 4.28 Station-wise summary statistics on total chromium in sediments (mg/kg)

Station	Min	Max	Mean	SD	CV %
1	53.96	150.77	77.91	27.10	34.78
2	56.15	127.39	94.32	20.97	22.23
3	81.95	124.88	99.88	11.12	11.14
4	51.78	93.35	74.60	11.50	15.41
5	8.27	47.69	26.45	10.11	38.20
6	13.88	108.66	47.18	29.79	63.14
7	40.31	178.56	127.90	35.03	27.39
8	104.38	285.00	189.87	54.98	28.96
9	31.66	279.96	170.86	64.54	37.78

Chromium exhibited significant seasonal variations in the study area during the investigation with higher pre-monsoon values at all Stations (Fig. 4.19). The pre-monsoonal maxima coinsided with salinity maximum of water, increase organic carbon and fine grains in sediments. It is postulated that, during periods of low riverine flow, the longer residence times of water and suspended matter would result in an enhancement of metal scavenching, coagulation and settling, resulting in higher content of metal in sediments.

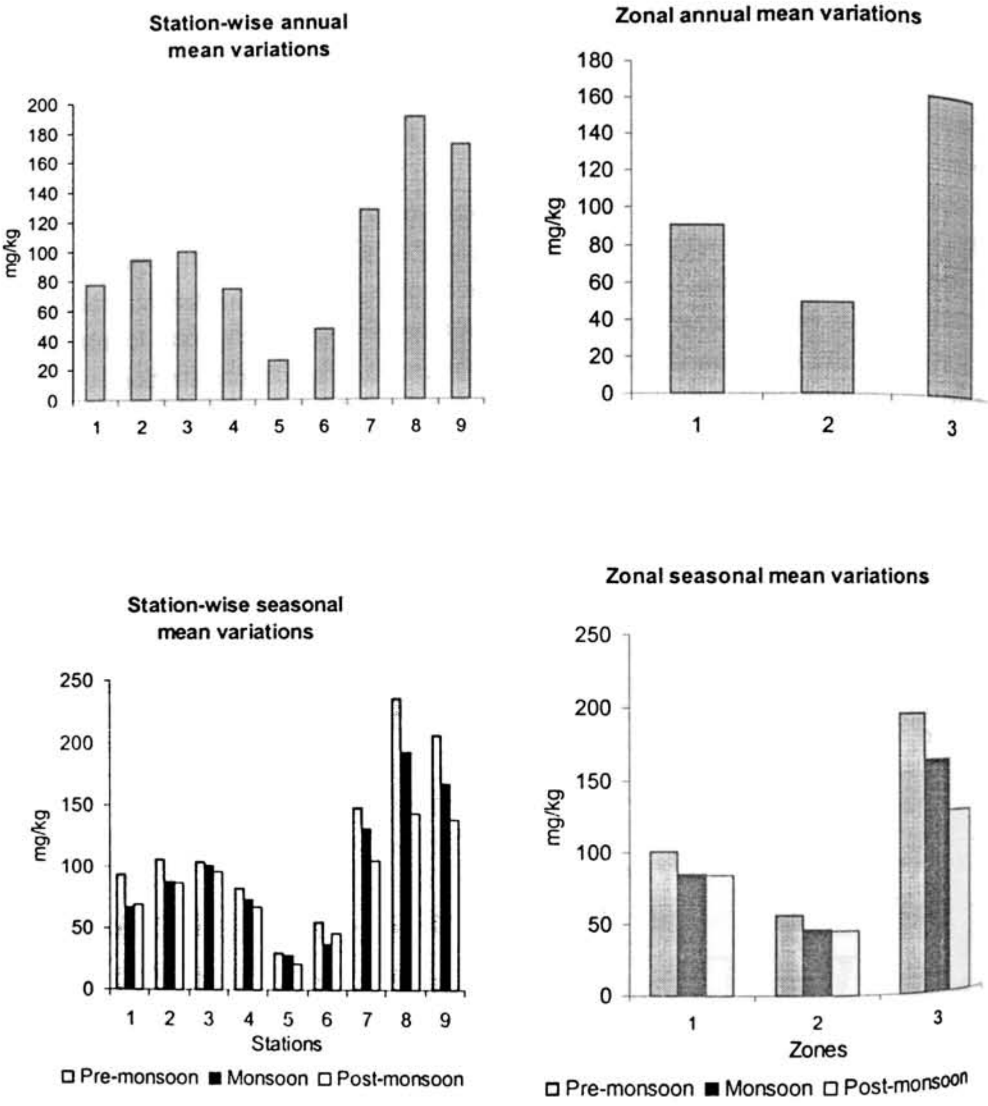


Fig. 4.19 Seasonal and spatial variations of total chromium in sediments

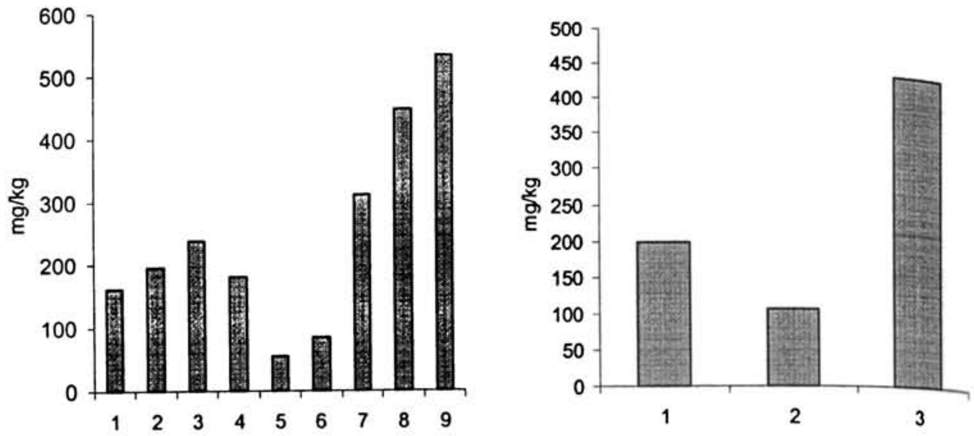
Manganese

Manganese was the second most abundant heavy metal found in the surficial sediments of the study area. The concentration of total manganese varied from a minimum of 14.74 to a maximum of 868.92 mg/kg with an overall mean concentration of 245.18 mg/kg. The lowest and highest values were recorded at Stations 5 and 9 respectively. The Station-wise annual mean concentrations ranged from 54.33 at Station 5 to 532.83 mg/kg at Station 9 (Table 4.29). The concentration increased from Station 1 to 3, reached its minimum at Station 5 and then recorded a sharp increase to Station 9 (Fig. 4.20). The mean concentration of manganese in the industrial Zone (Zone 3) is more than double than the concentration in the Zone 1. The average level of manganese (245 mg/kg) in the study area was well below the Indian average of 605 mg/kg and world average of 1050 mg/kg (Table 4.27).

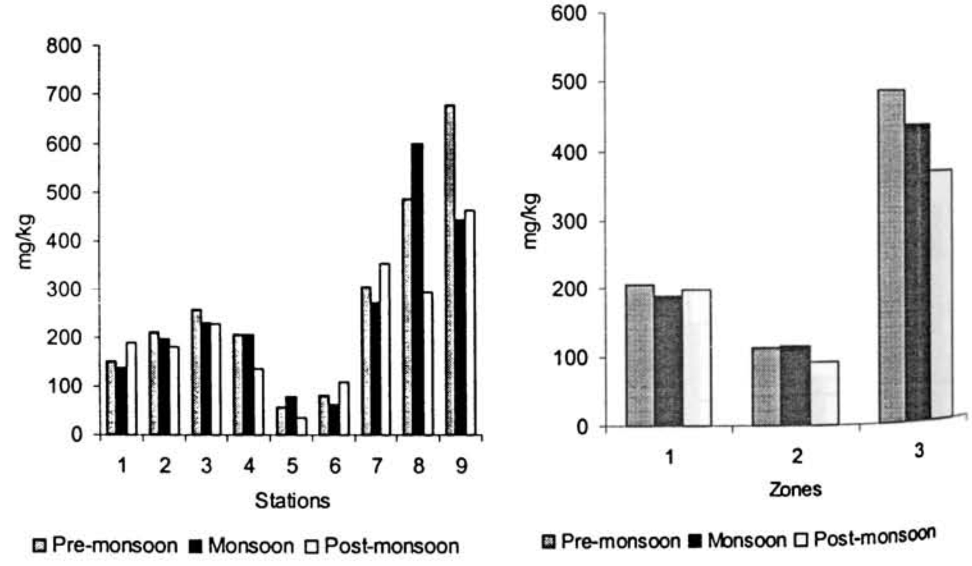
Table 4.29 Station-wise summary statistics on total manganese in sediments (mg/kg)

Station	Min	Max	Mean	SD	CV %
1	99.64	275.05	162.12	63.96	39.45
2	49.88	310.64	196.01	69.99	35.71
3	184.07	316.41	238.66	41.56	17.41
4	44.36	250.37	180.62	55.20	30.56
5	14.74	103.12	54.33	28.36	52.21
6	21.19	289.56	85.51	75.89	88.75
7	240.99	465.36	311.65	64.02	20.54
8	89.90	700.13	444.92	204.75	46.02
9	105.52	868.92	532.83	239.88	45.02

The seasonal distribution of manganese in the surficial sediments is represented in Figure 4.20. As in the case of chromium, manganese also exhibited high pre-monsoon values for the same reasons as mentioned for chromium. The relatively higher concentration of manganese during the post-monsoon at Station 7 may be due to higher level of sediment organic carbon at that Station.


Station-wise annual mean variations

Zonal annual mean variations


Station-wise seasonal mean variations

Zonal seasonal mean variations

Fig. 4.20 Seasonal and spatial variations of total manganese in sediments

Iron

Iron was the most abundant metal studied in Chitrapuzha River. The overall annual mean concentration and range of sediment total iron in the study area are furnished in the Table 4.26. The concentration of iron varied from 1.26 mg/g (at Station 5) to 57.67 mg/g at (Station 2) with a mean concentration of 25.56 mg/g. The lowest and highest Station-wise annual mean concentrations were recorded at Station 5 (12.32 mg/g) and at Station 3 (36.46 mg/g) respectively (Table 4.30). Iron content was found to be the highest among all the metals at all the Stations. Unlike most of the other metals studied, iron recorded higher values in Zone 1 (Fig. 4.21), which may be due to its proximity to Cochin shipyard, oil tanker berth, fishing harbour and Cochin port. Wastewater discharged from the densely populated Cochin city also contributes to the high concentration of iron in this Zone. Nair et. al. (1990) had reported high concentration of iron in Cochin estuary. The average concentration of iron in the sediments of Chitrapuzha River (25.56 mg/g) was found lower than the Indian average (29 mg/g) and the world average of 48 mg/g (Table 4.27).

Table 4.30 Station-wise summary statistics on total iron in sediments (mg/g)

Station	Min	Max	Mean	SD	CV %
1	22.64	54.81	30.78	9.05	29.41
2	13.60	57.67	33.20	11.23	33.82
3	28.01	40.19	36.46	6.11	16.76
4	7.96	47.50	30.60	9.54	31.18
5	1.26	27.32	12.32	8.04	65.26
6	2.88	35.51	16.70	9.97	59.72
7	11.90	45.97	29.69	10.48	35.31
8	3.88	33.26	21.11	10.72	50.77
9	5.32	35.35	19.18	10.90	56.81

The seasonal variation of sediment total iron is illustrated in the Figure 4.21. Iron exhibited significant seasonal variations with higher values during pre-monsoon and lower values during monsoon; but in Stations 5, 6 and 8 monsoon values are higher than post-monsoon values. Comparatively higher concentration of iron during post-monsoon at Station 7 may be attributed to exceptionally high organic carbon content at this Station.

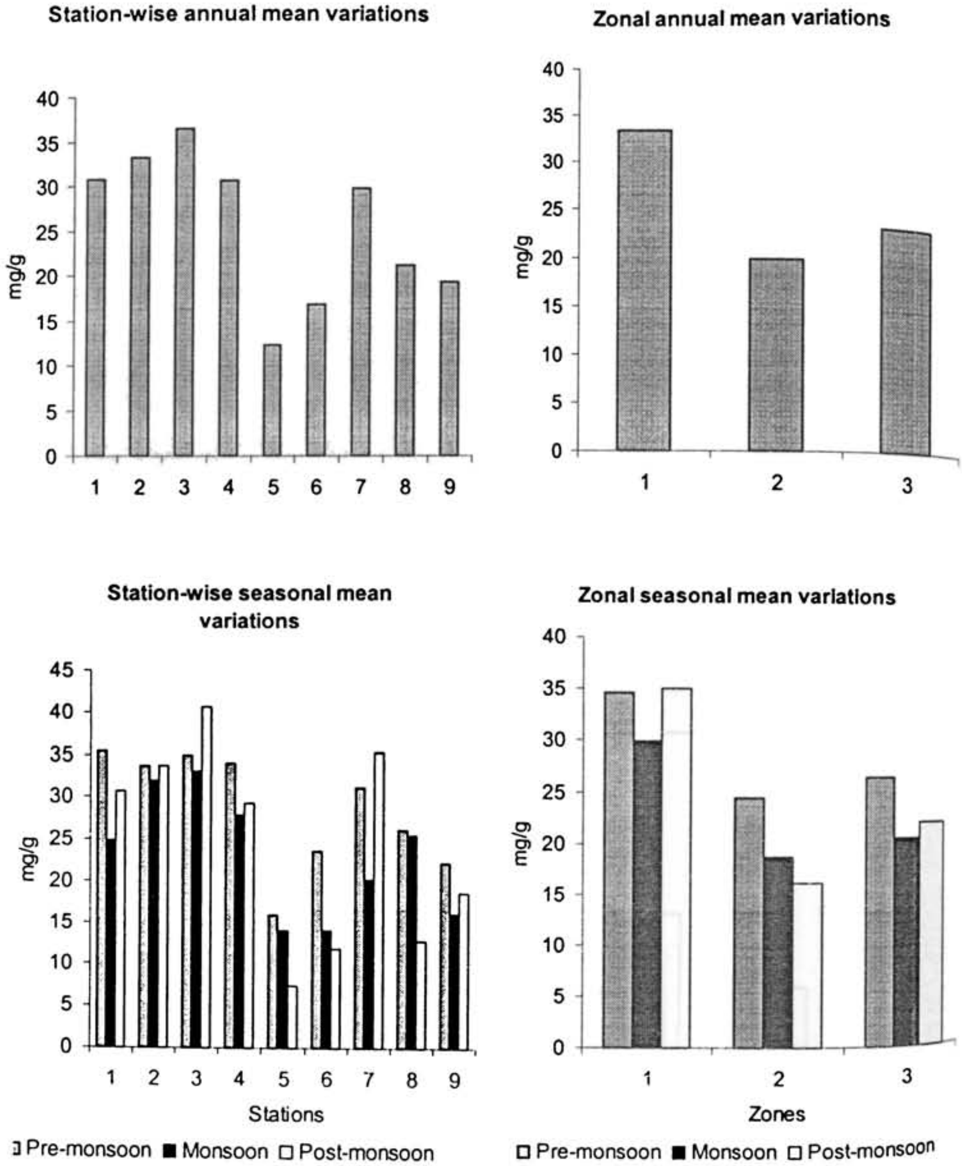


Fig. 4.21 Seasonal and spatial variations of total iron in sediments

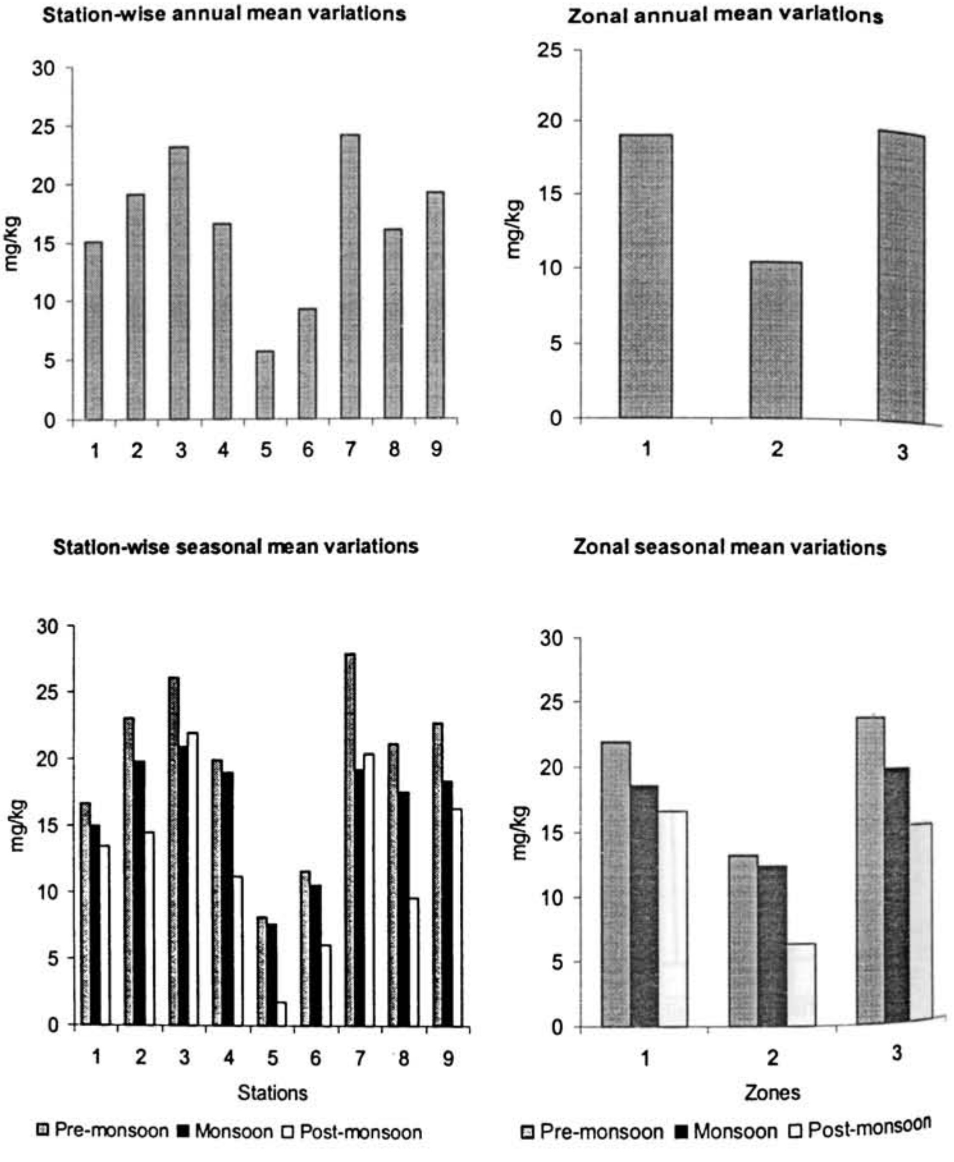
Cobalt

The concentration of total cobalt in the study area ranged from a minimum of 1.25 (Station 5) to a maximum of 33.33 mg/kg (Station 7) with annual mean concentration of 16.39 mg/kg (Table 4.26). The Station-wise annual mean values varied from 5.66 to 23.93 mg/kg (Table 4.31). Zones 1 and 3 possessed almost equal concentrations during the study, which indicated the absence of source of cadmium in Zone 3. The average concentration reported in this study (16.39 mg/kg) was less than the values reported for many Indian rivers (Table 4.27). The level of cobalt in the sediments of River Cauvery was almost equal to the value reported in this study.

Table 4.31 Station-wise summary statistics on total cobalt in sediments (mg/kg)

Station	Min	Max	Mean	SD	CV %
1	6.70	20.92	15.03	4.49	29.86
2	8.44	29.60	19.04	6.02	31.62
3	17.19	29.10	23.13	3.94	17.03
4	3.25	25.46	16.47	6.86	41.63
5	1.25	13.94	5.66	4.71	83.22
6	2.84	16.23	9.25	5.17	55.88
7	6.66	33.33	23.93	7.35	30.69
8	2.88	24.63	15.91	7.21	45.32
9	7.54	29.18	19.11	5.58	29.19

Cobalt exhibited significant seasonal variations during the investigation with high pre-monsoon values at all Stations (Fig. 4.22). The pre-monsoonal maxima in cobalt content could be related to the biogeochemical changes occurring in the river itself and also to the hydrological and sedimentological character, which vary along with reduced discharge rate conditions during these months.


Station-wise annual mean variations

Zonal annual mean variations

Station-wise seasonal mean variations

Zonal seasonal mean variations

Fig. 4.22 Seasonal and spatial variations of total cobalt in sediments

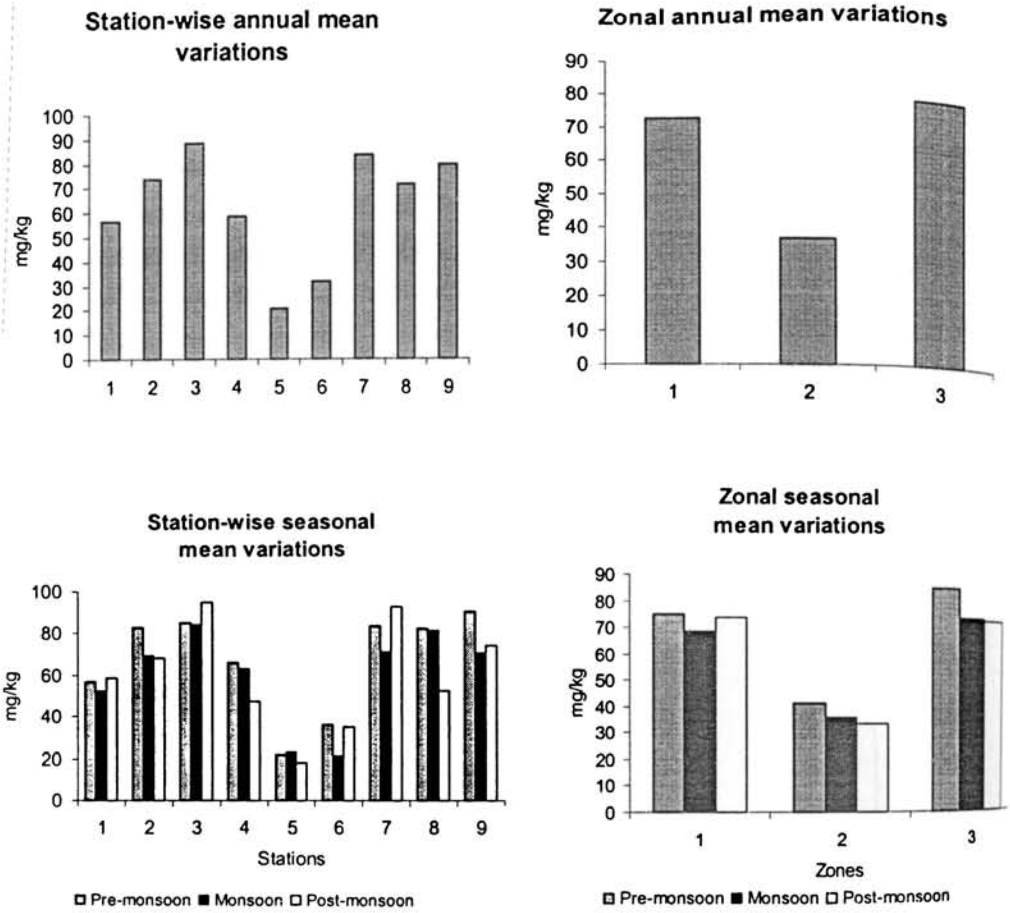
Nickel

The concentration of nickel recorded its minimum of 5.30 mg/kg at Station 5 and maximum of 116.73 mg/kg at Station 2. The annual mean concentration during this study period was 62.60 mg/kg. The concentration of nickel in Zone 1 and 3 were almost equal. The lowest and highest Station-wise annual mean values were 20.92 mg/kg (at Station 5) and 88.41 mg/kg (at Station 3) respectively (Table 4.32). The average concentration of total nickel in Chitrapuzha River was higher than Indian average (37 mg/kg), but it was less than world average as well as average shale concentration.

Table 4.32 Station-wise summary statistics on total nickel in sediments (mg/kg)

Station	Min	Max	Mean	SD	CV %
1	38.54	92.70	56.37	17.74	31.47
2	21.89	116.73	73.86	25.88	35.04
3	59.78	109.55	88.41	13.84	15.66
4	12.26	76.30	58.52	17.59	30.06
5	5.30	45.33	20.92	12.63	60.38
6	8.75	76.72	31.66	22.77	71.92
7	55.26	116.48	83.51	19.83	23.75
8	38.95	105.16	71.10	22.23	31.27
9	35.45	113.94	79.06	20.23	25.59

The seasonal variations of sediment nickel in the study area are depicted in Figure 4.23. Nickel recorded higher values during pre-monsoon and generally low values during monsoon season, but at Stations 4, 5 and 8 post-monsoon concentration recorded low values. Higher values during post-monsoon than pre-monsoon at Stations 3 and 7 may be due to the high organic and fine grain content in the sediments of these Stations. The ability of fine particles and organic materials to scavenge trace metal effectively has been discussed by several authors (Olsen et. al., 1982; Brook and Moore, 1988; Perez et. al., 1991; Izquierdo et. al., 1997).


Station-wise annual mean variations

Zonal annual mean variations

Station-wise seasonal mean variations

Zonal seasonal mean variations

Fig. 4.23 Seasonal and spatial variations of total nickel in sediments

Copper

Another important heavy metal, copper varied from a minimum of 2.92 mg/kg at Station 6 to a maximum of 68.24 mg/kg at Station 9 (Table 4.26). The annual mean concentration of copper during the study period in Chitrapuzha was 28.47 mg/kg. The lowest (8.08 mg/kg) and highest (46.75 mg/kg) annual mean concentrations of copper were recorded at Stations 5 and 8 respectively (Table 4.33). Station 8 is in a region where organic carbon content was very high and Station 5 is in a region, which is very poor in organic content. The annual mean concentration of copper in Zone 3 was almost double than that in Zone 1 (Fig. 4.24). The distribution of copper in the sediments depends to a great extent on the distribution of organic matter and total phosphorus in the sediments. The high level of copper in the Zone 3 may be due to the formation of organic bound and phosphate bound compounds (Fernandes, 1997; Zhou et. al., 1998; Ramos et. al., 1999; Xiangdong Li et. al., 2001). Speciation studies of Roux et. al. (1998) and Jones and Turki (1997) also proved that dominant portion of copper is associated with organic fraction of the sediment. The studies conducted by Morrison et. al. (2001) in Laucala Bay, Fiji showed the strong correlation between sediment copper and organic content. A gradual decline in concentration towards bar-mouth is evident from the graph.

Table 4.33 Station-wise summary statistics on total copper in sediments (mg/kg)

Station	Min	Max	Mean	SD	CV %
1	11.88	37.09	21.52	6.97	32.36
2	6.93	36.14	24.27	10.81	44.54
3	26.99	36.39	31.36	2.96	9.44
4	6.88	32.30	21.69	6.74	31.07
5	2.99	16.17	8.08	3.98	49.25
6	2.92	34.16	13.81	9.43	68.31
7	31.80	53.31	45.46	5.94	13.06
8	6.92	63.54	46.75	18.89	40.41
9	9.62	68.24	43.32	16.90	39.02

Copper showed significant seasonal variation with higher values during pre-monsoon and comparatively lower values during monsoon and post-monsoon seasons (Fig. 4.24). The higher content of copper during pre-monsoon season may be due to high saline conditions, which might cause the dissolved copper to precipitate and flocculate. The concentration of copper can be compared with that of other major rivers (Table 4.27). The average concentration of copper (28.47 mg/kg) in Chitrapuzha River conformed to Indian average (28 mg/kg), but it was less than average shale (50 mg/kg) and world average (100 mg/kg).

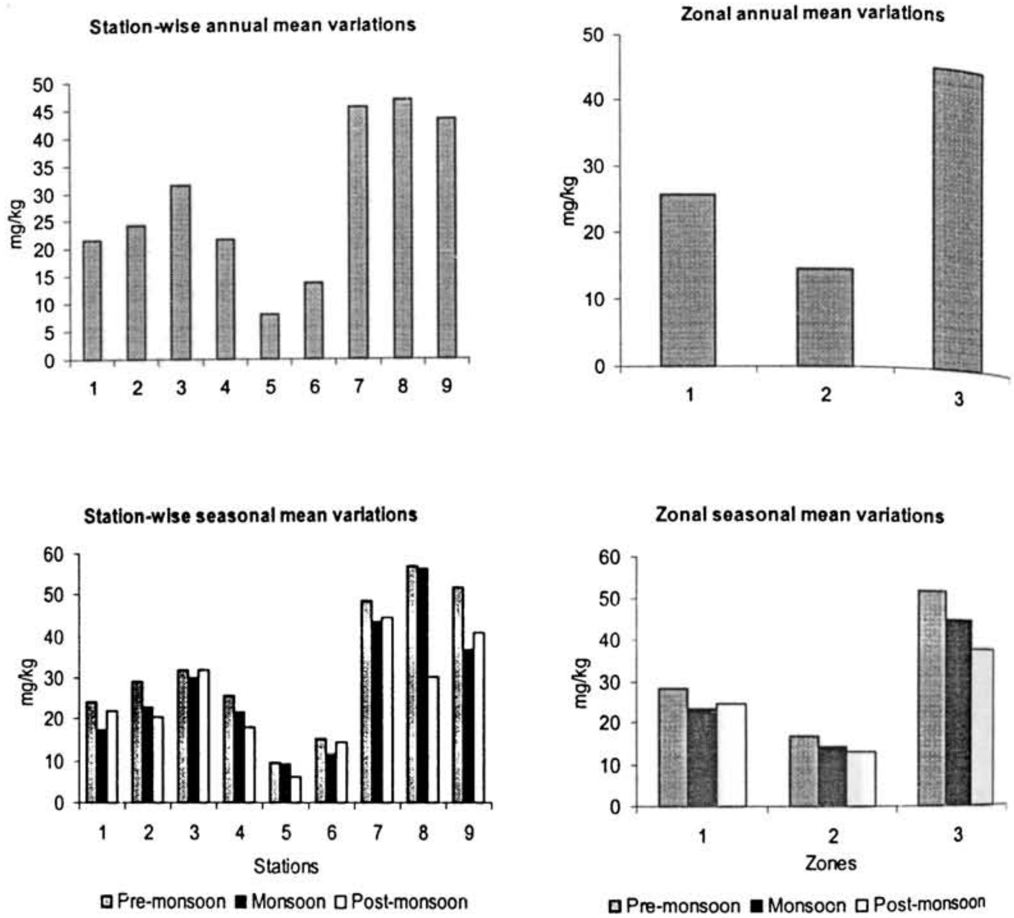


Fig. 4.24 Seasonal and spatial variations of total copper in sediments

Zinc

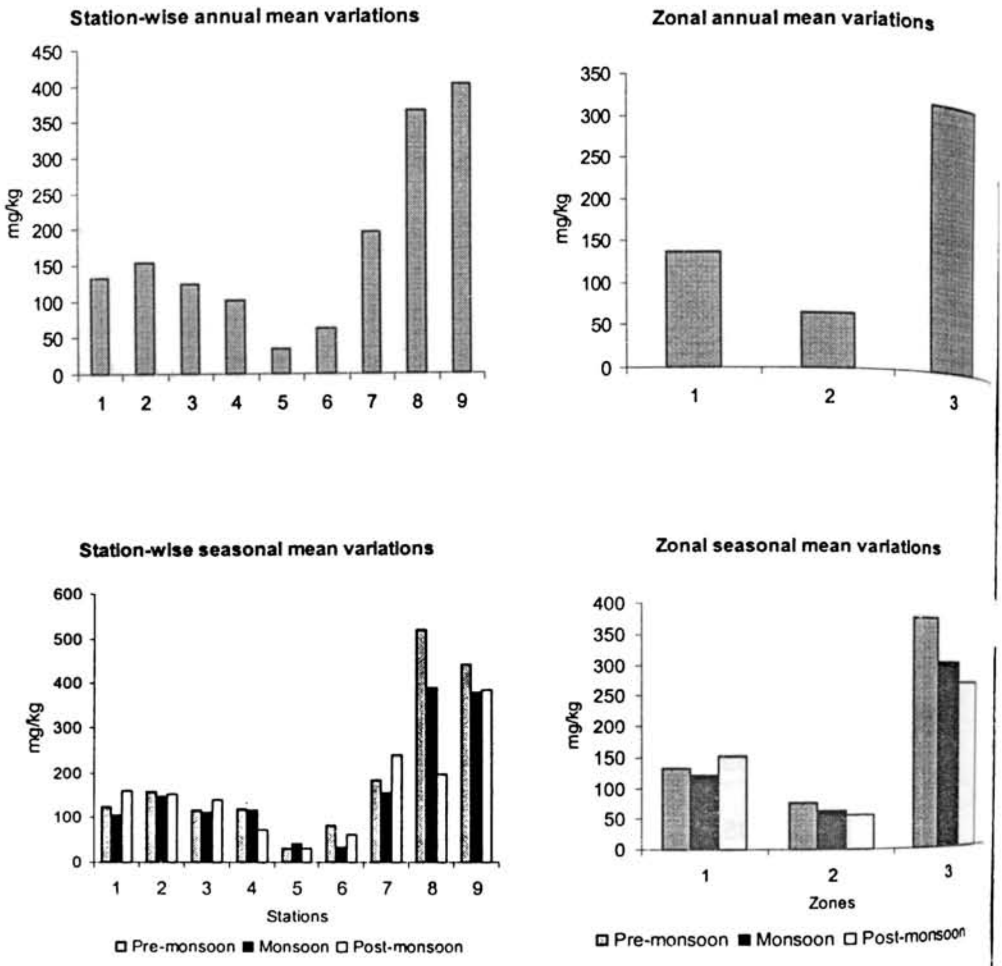
The concentration of the third abundant metal, zinc in Chitrapuzha River ranged from 7.13 to 1029.18 mg/kg. The overall annual mean concentration during the investigation was found to be 177 mg/kg (Table 4.26). The concentration of zinc varied over a wide range that is evident from the high coefficient of variation. The lowest and highest Station-wise annual mean concentrations were

31.83 mg/kg (at Station 5) and 426.27 mg/kg (at Station 9) respectively (Table 4.34). Concentration of zinc in the Zone 3 was found twice greater than that in Zone 1 (Fig.4.25). The Zone 2 recorded minimum level of zinc due to the sandy nature of sediments.

Table 4.34 Station-wise summary statistics on total zinc in sediments (mg/kg)

Station	Min	Max	Mean	SD	CV %
1	23.52	271.25	131.75	71.84	54.53
2	82.32	209.23	145.73	46.21	31.71
3	93.60	170.74	119.18	22.20	18.62
4	11.66	159.71	102.12	40.37	39.53
5	7.13	74.72	31.83	20.93	65.74
6	24.83	131.60	53.27	36.56	68.64
7	137.89	352.10	193.62	62.64	32.35
8	126.85	1029.18	389.35	248.81	63.90
9	311.76	535.04	426.27	75.14	17.63

The seasonal variations of total zinc in Chitrapuzha River are illustrated in the Figure 4.25. Zinc recorded significant seasonal variations with generally higher pre-monsoon values in Zones 2 and 3, but in Zone 1 post-monsoon recorded higher values. Comparatively higher concentration of zinc during post-monsoon at Station 7 may be attributed to exceptionally high organic carbon content at this Station.


Station-wise annual mean variations

Zonal annual mean variations

Station-wise seasonal mean variations

Zonal seasonal mean variations

Fig. 4.25 Seasonal and spatial variations of total zinc in sediments

Cadmium

Cadmium, the least abundant metal in the sediments of Chitrapuzha River ranged from 2.29 to 34.47 mg/kg with an overall mean concentration of 12.87mg/kg (Table 4.26). The lowest (7.71 mg/kg) and highest (23.82 mg/kg) annual mean values were recorded at Stations 5 and 9 respectively (Table 4.35). Distribution of cadmium was found almost uniform through out the Zones 1 and 2 (Fig 4.26)

Zone 3 recorded very high concentration of cadmium. Many reasons can be quoted for the abnormal cadmium level in this Zone. It was found that cadmium content is high in rock phosphate, which is the row material, used for the manufacture of phosphate fertilizers (Forstner and Wittmann, 1979). Rock phosphate and phosphoric acid falling into water while transferring them from the cargo barge to fertilizer manufacturing firm contribute to the very high cadmium level in Zone 3. As far as Chitrapuzha River is concerned, the major point source is the fertilizer-manufacturing unit on the banks of Chitrapuzha River.

Table 4.35 Station-wise summary statistics on total cadmium in sediments (mg/kg)

Station	Min	Max	Mean	SD	CV %
1	3.65	13.11	9.06	3.47	38.25
2	3.05	12.67	9.06	3.59	39.63
3	4.15	13.48	9.46	3.23	34.13
4	3.54	12.64	9.47	3.06	32.30
5	2.29	11.49	7.71	3.07	39.88
6	4.00	11.94	8.49	2.60	30.61
7	10.98	20.58	15.53	3.18	20.50
8	7.95	30.70	23.23	7.42	31.93
9	7.45	34.47	23.82	7.05	29.60

Cadmium exhibited significant seasonal variations in its distribution in Chitrapuzha River. Cadmium was the only metal that recorded distinctly lower values during pre-monsoon and post-monsoon seasons than monsoon values at all Stations (Fig. 4.26). The decrease in concentration of total cadmium during pre-monsoon and post-monsoon seasons may be attributed to the formation of chloride complexes, occurring during the mixing of fresh water with seawater and to the desorption of exchangeable metals due to the increasing concentration of major cations (Poucot and Wollast, 1997; Elbaz-Poulichet et. al. 1987; Windom et. al. 1991; Chiffoleau et. al. 1994; Dai et. al. 1995).

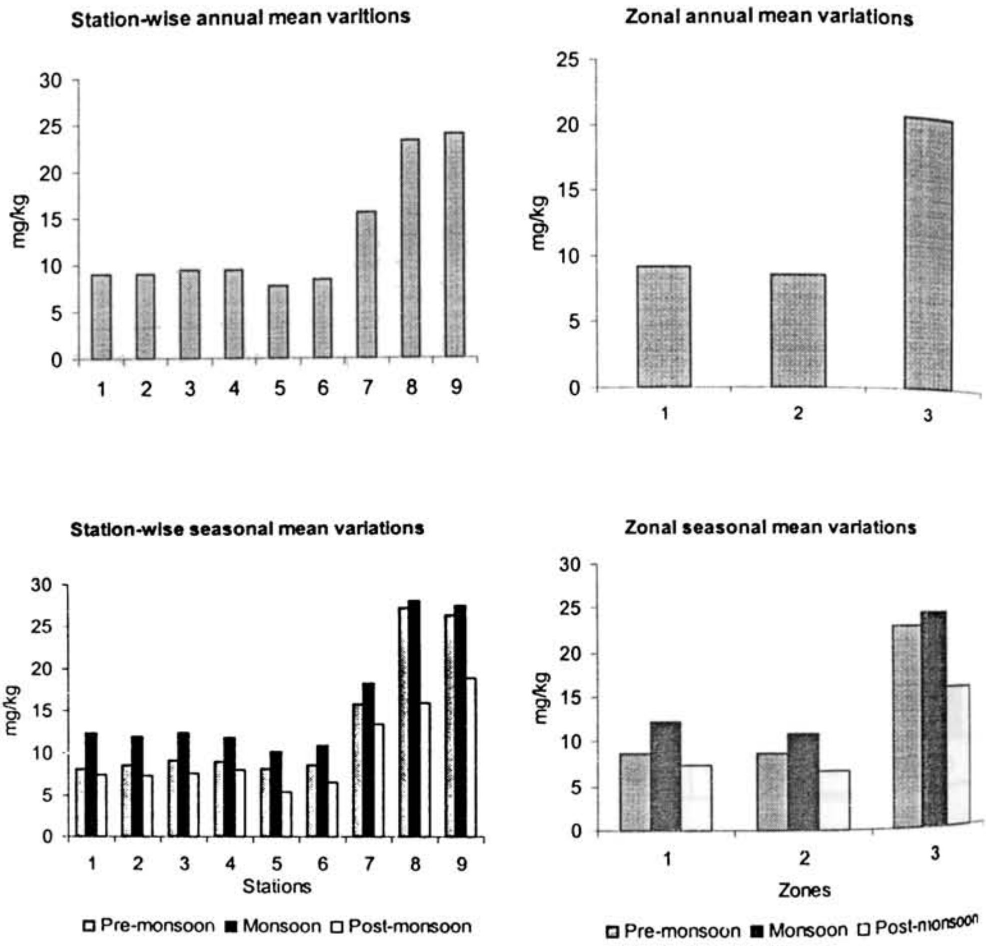


Fig. 4.26 Seasonal and spatial variations of total cadmium in sediments

Lead

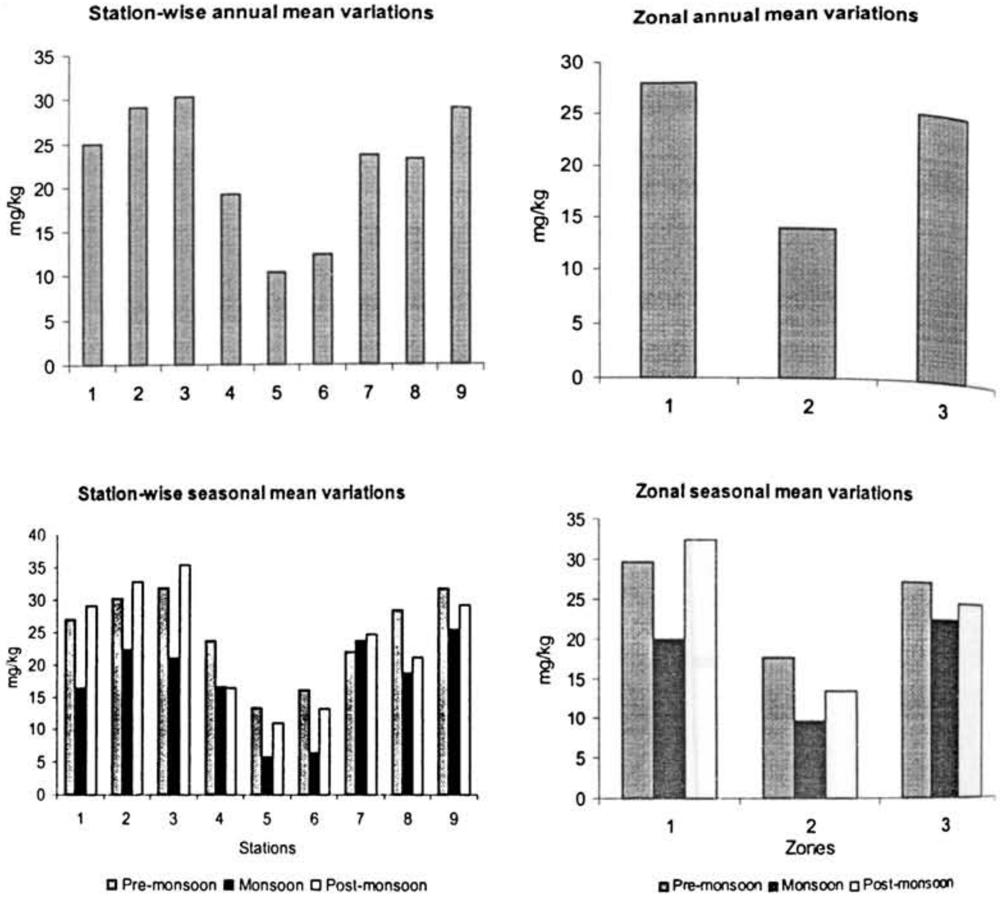
The distribution of lead in the surficial sediments during the period of study was found to fall within the range 0.93 to 41.91 mg/kg with an annual mean concentration of 22.40 mg/kg. The Station-wise annual mean values varied from

10.39 (at Station 5) and 30.18 mg/kg (at Station 3) (Table 4.36). Unlike most other metals studied, lead recorded higher concentration in Zone 1 rather than in Zone 3. The precipitation and settling of particulate matter while river water mixes with saline water in Zone 1 may be the main reason for high level of lead in Zone 1. Automobile emission, waste from ship building yard, fishing harbour and seaport may also contribute to the relatively higher values in Zone 1.

Table 4.36 Station-wise summary statistics on total lead in sediments (mg/kg)

Station	Min	Max	Mean	SD	CV %
1	14.21	40.23	24.88	8.37	33.65
2	18.49	40.69	28.99	8.53	29.44
3	17.04	37.74	30.18	7.12	23.58
4	11.18	30.50	19.16	5.72	29.84
5	0.93	19.94	10.39	5.76	55.42
6	3.86	26.42	12.37	6.11	49.36
7	12.72	31.93	23.49	5.85	24.92
8	12.70	41.91	23.11	8.89	38.50
9	10.16	39.33	29.00	8.54	29.43

Lead exhibited pronounced seasonal variations with comparatively higher values during pre-monsoon and post-monsoon seasons (Fig. 4.27). The higher content of lead during pre-monsoon and post-monsoon seasons may be due to high saline conditions, which might cause the dissolved lead to precipitate and flocculate. High content of organic carbon and fine particles in the surficial sediments during these seasons contribute to relatively higher concentration of lead.


Station-wise annual mean variations

Zonal annual mean variations

Station-wise seasonal mean variations

Zonal seasonal mean variations

Fig. 4.27 Seasonal and spatial variations of total lead in sediments

Metal enrichment in sediments

The quantification of trace metal enrichment in the sediments of Chitrapuzha River was attempted by calculating the enrichment factor. In this study Fe was selected as a normalization constituent and enrichment factor calculated using the equation:

Enrichment Factor = $(X/Fe)_{sample}$ / $(X/Fe)_{Ref}$, where $(X/Fe)_{sample}$ is the ratio of the concentration of element 'X' to that of iron in the sample sediment, and $(X/Fe)_{Ref}$ is the same ratio in the sediment from a far upstream Station (Station R, Fig. 2.1), which is free from industrial pollution (Lee et. al., 1998; Tanner et. al., 2000; Tuncer et. al., 2001). Seasonal enrichment factors of various heavy metals studied are shown in the Table 4.37.

Table. 4.37 Enrichment Factors for total metals in surficial sediments

Pre-monsoon

Station	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
1	1.93	0.73	0.72	1.18	1.03	2.53	1.38	1.18
2	2.24	1.05	1.05	1.79	1.30	3.41	1.53	1.38
3	2.10	1.24	1.14	1.77	1.37	2.43	1.56	1.40
4	1.73	1.02	0.90	1.42	1.13	2.53	1.60	1.08
5	1.37	0.60	0.79	1.02	0.92	1.38	3.07	1.30
6	1.66	0.57	0.75	1.11	0.97	2.56	2.20	1.05
7	3.38	1.63	1.37	1.95	2.32	4.28	3.01	1.09
8	6.37	3.11	1.23	2.29	3.25	14.32	6.20	1.67
9	6.58	5.10	1.56	2.96	3.48	14.28	7.04	2.20

Monsoon

Station	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
1	1.92	0.94	0.92	1.53	1.05	3.06	2.95	1.02
2	1.96	1.04	0.95	1.58	1.08	3.34	2.25	1.08
3	2.16	1.17	0.97	1.86	1.38	2.44	2.24	0.99
4	1.87	1.24	1.04	1.65	1.16	3.02	2.53	0.92
5	1.44	0.94	0.83	1.20	1.00	2.17	4.29	0.63
6	1.88	0.76	1.15	1.12	1.22	1.79	4.60	0.70
7	4.61	2.26	1.46	2.56	3.23	5.60	5.38	1.81
8	5.35	3.94	1.05	2.31	3.31	10.99	6.53	1.13
9	7.45	4.64	1.76	3.22	3.42	17.07	10.23	2.45

Post-monsoon

Station	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
1	1.62	1.04	0.67	1.39	1.08	3.78	1.47	1.46
2	1.83	0.90	0.66	1.47	0.91	3.27	1.30	1.49
3	1.68	0.95	0.83	1.70	1.18	2.52	1.12	1.34
4	1.63	0.78	0.58	1.18	0.92	1.76	1.66	0.86
5	1.98	0.77	0.36	1.76	1.24	3.11	4.40	2.26
6	2.81	1.53	0.78	2.16	1.82	3.86	3.34	1.71
7	2.11	1.68	0.88	1.91	1.89	4.86	2.26	1.08
8	7.99	3.87	1.15	2.99	3.54	11.17	7.44	2.56
9	5.30	4.19	1.34	2.91	3.28	14.98	6.07	2.41

It was found that all the trace metals were enriched in Chitrapuzha River to varying extents. The enrichment factors showed no significant seasonal variation except in the case of lead. Enrichment Factors for lead exhibited seasonal variation with higher values during pre-monsoon and post-monsoon seasons. The depletion of cobalt at Stations 1 to 6 during all the seasons may be attributed to absence of contributing sources. The contamination was found severe in Zone 3. Zinc, chromium and cadmium showed strong enrichment when compare to other metals in Chitrapuzha River especially at Stations 8 and 9.

Multiple regression analysis on sediment metal distribution

In order to gain understanding about variables which influence the distribution pattern of total metals during different seasons, a number of sediment parameters were examined. These factors exhibited considerable seasonal and spatial variations due to changes in environmental conditions from estuarine to riverine environments. The sediment parameters considered were sediment organic carbon, total phosphorus, total iron and clay content. The importance of these factors in determining binding and remobilizing of trace metals in sediments has been extensively discussed (Calmano et. al., 1993). Multiple regression analysis was performed on the total metal concentrations considering these variables as independent. The regression models were generally found fit for all metals and the combination of four factors explained between 46% to 91% of variations in the distribution of total metals in the sediments irrespective of seasons, except lead for which this combination could explain only 32% during pre-monsoon. The analysis has categorically proved the existence of a patent relationship between total phosphorus and metal distribution. The identified models are discussed below.

The identified model for total chromium in the sediment during the pre-monsoon was

$$\text{Cr} = 0.94639\ \text{OC} + 1.30655^{**}\ \text{TP} + 1.89653\ \text{Fe-T} + 1.58202\ \text{Clay\%} - 34.0492$$

$$(R^2 = 0.8251^{***})$$

This model explains 83% of variations in the distribution of total chromium in the surficial sediments of Chitrapuzha River. Though the model is significant, the variables OC (organic carbon), Fe-T (total iron) and clay percentage do not have significant contributions during the pre-monsoon period of analysis. But during monsoon period all the parameters except clay percentage have significant contribution.

The regression model for monsoon season was

$$Cr = 1.28082^{***}\ OC + 1.23463^{***}\ TP + 1.75751^{*}\ Fe\text{-}T + 1.04109\ Clay\% - 22.775$$
$$(R^2 = 0.9136^{***})$$

The model for monsoon accounts for 91% of variations in the distribution of chromium during monsoon.

The regression model of Chromium for post-monsoon was

$$Cr = 0.14547\ OC + 1.15346^{***}\ TP + 0.649896\ Fe\text{-}T + 1.17115^{*}\ Clay\% + 18.5343$$
$$(R^2 = 0.5793^{***})$$

During post-monsoon total phosphorus plays the most important role in determining the distribution of chromium. The model explains 58% of the variations in the distribution of chromium during the post-monsoon period.

The identified model for total manganese during the pre-monsoon was

$$Mn = 1.87139\ OC + 1.34006\ TP - 0.51727\ Fe\text{-}T + 8.94864^{**}\ Clay\% - 85.9106$$
$$(R^2 = 0.7994^{***})$$

The model, which accounts for 80% variations, indicated that the only relevant parameter in the distribution of total manganese during pre-monsoon was the clay percentage. The other factors have not much significance during this period. Unlike the pre-monsoon, total phosphorus and total iron in the sediment have significant part in the distribution of total manganese during the monsoon season.

The identified regression model for manganese for monsoon during the study period was

$$Mn = 2.03175\ OC + 4.586220^{***}\ TP + 6.50478^{*}\ Fe\text{-}T + 3.38233\ Clay\% - 127.751$$
$$(R^2 = 0.8689^{***})$$

The model furnished below shows the contribution of sediment parameters in determining the distribution of manganese during post-monsoon.

$$\text{Mn} = 0.66948\ \text{OC} + 4.86930^{***}\ \text{TP} + 5.92958^{***}\ \text{Fe-T} + 2.52760\ \text{Clay\%} - 78.6421$$
$$(R^2 = 0.7624^{***})$$

As the model shows the total phosphorus has significant role during monsoon as well as post-monsoon periods.

Except organic carbon content, all other parameters have significant role in determining the distribution of cobalt during pre-monsoon.

$$\text{Co} = 0.16065\ \text{OC} - 0.21904^{**}\ \text{TP} + 0.06232\ \text{Fe-T} + 0.49880^{***}\ \text{Clay\%} + 0.8539$$
$$(R^2 = 0.6779^{***})$$

Distribution of cobalt was found to depend largely on clay content. The model explains 68% of the variations in the distribution of cobalt during the season.

The identified model for distribution of cobalt during monsoon was

$$\text{Co} = 0.17629^{*}\ \text{OC} + 0.08958\ \text{TP} + 0.53984\ {}^{**}\text{Fe-T} - 0.13322\ \text{Clay\%} + 1.7880$$
$$(R^2 = 0.5611^{***})$$

This regression model explains 56% variability, which indicates that these four parameters are not sufficient for explaining the distribution of cobalt during monsoon.

The fitted model for the distribution of cobalt during post-monsoon was as follows:

$$\text{Co} = 0.06772\ \text{OC} + 0.08889^{**}\ \text{TP} + 0.41989^{***}\text{Fe-T} + 0.05073\ \text{Clay\%} - 1.7214$$
$$(R^2 = 0.8266^{***})$$

The relative importance of parameters in the predicted model indicates that total iron concentration is the most significantly prominent parameter than all other parameters in explaining the variation in distribution of total cobalt.

The identified model for distribution of total nickel in the sediments of the study area during pre-monsoon is as follows:

$$\text{Ni} = 0.69516^{*}\ \text{Fe-T} - 0.01929\ \text{OC} - 0.51160^{*}\ \text{TP} + 1.95725^{***}\ \text{Clay\%} - 9.0817$$
$$(R^2 = 0.7180^{***})$$

Of the four independent parameters the most significant one, which influenced the distribution of nickel during the pre-monsoon season was found to be the clay percentage. The total phosphorus and total iron also have contributions to some extent.

The model for the distribution of nickel during monsoon was

$$\text{Ni} = 0.46088^{*}\ \text{OC} + 0.21695\ \text{TP} + 1.63667^{**}\ \text{Fe-T} + 0.53266\ \text{Clay\%} - 8.9337$$
$$(R^2 = 0.7618^{***})$$

None of the four parameters was found highly significant. The significant parameters, which explain the variation of nickel during monsoon, are the total iron and organic carbon.

The variation in the distribution of nickel during post-monsoon follows the regression model given below.

$$\text{Ni} = 0.12258\ \text{OC} + 0.34491^{*}\ \text{TP} + 1.53395^{***}\ \text{Fe T} + 0.48345^{*}\ \text{Clay\%} + 1.6889$$
$$(R^2 = 0.7703^{***})$$

The distribution of nickel is found to depend on total iron during this period. The total phosphorus and clay percentage also contribute to the variability of nickel.

The multiple regression model for the variation in distribution of copper during the pre-monsoon period of study was as follows:

$$\text{Cu} = 0.41197^{**}\ \text{OC} + 0.06802\ \text{TP} + 0.20575\ \text{Fe-T} + 0.67244^{***}\ \text{Clay\%} - 7.1813$$
$$(R^2 = 0.8617^{***})$$

This model explains 86% variability and was found statistically significant. The most significant parameter was clay percentage followed by organic carbon.

The distribution of copper depended mainly on organic carbon during monsoon followed by total phosphorus as evident from the regression model.

$$\text{Cu} = 0.45636^{***}\ \text{OC} + 0.20137^{**}\ \text{TP} + 0.39446\ \text{Fe-T} + 0.45022^{*}\ \text{Clay\%} - 7.7713$$
$$(R^2 = 0.8755^{***})$$

During the post-monsoon total iron plays the most important role in the variation of copper in the sediments. Other prominent parameter that influences the distribution of copper was organic carbon.

$$\text{Cu} = 0.18564^{*}\text{OC} + 0.31993^{***}\,\text{TP} + 0.54059^{***}\,\text{Fe-T} + 0.28170^{*}\,\text{Clay\%} - 4.49813$$
$$(R^2 = 0.7813^{***})$$

The multiple regression analysis proved the strong correlation between organic carbon and copper during all the seasons. The positive correlation between Cu and organic carbon during all the seasons showed the stable complex formation of Cu with organic matter (Fernandes, 1997; Jones and Turki, 1997; Zhou et. al.,1998; Ramos et. al., 1999; Xiangdong Li et. al., 2001).

The regression model shown below indicate that none of the four parameters was significant in the distribution of zinc during pre-monsoon. The model also indicates that there may be some other factors, which influence the zinc variability.

$$\text{Zn} = 0.42167\ \text{OC} + 2.52371\ \text{TP} + 0.11778\ \text{Fe-T} + 5.54295\ \text{Clay\%} - 46.5243$$
$$(R^2 = 0.5951^{***})$$

During the monsoon total phosphorus has major role in the variability of zinc. The model explains 86% variability and is statistically significant.

$$\text{Zn} = 1.944406^{*}\ \text{OC} + 3.81826^{***}\ \text{TP} + 3.41811\ \text{Fe-T} + 0.66445\ \text{Clay\%} - 49.1578$$
$$(R^2 = 0.8643^{***})$$

The regression model for distribution of zinc during post-monsoon is as follows:

$$\text{Zn} = 0.40848\ \text{OC} + 4.10442^{***}\ \text{TP} + 4.24449^{***}\ \text{Fe-T} + 0.31496\ \text{Clay\%} - 19.4604$$
$$(R^2 = 0.7102^{***})$$

As the model indicates the total phosphorus and total iron are highly significant in explaining the variation of zinc during post-monsoon. The model explains 71% variability.

The regression model for distribution of cadmium during pre-monsoon was as follows:

$$\text{Cd} = 0.15859^{*}\ \text{OC} + 0.18760^{**}\ \text{TP} - 0.14635\ \text{Fe-T} + 0.09562\ \text{Clay\%} + 7.4745$$
$$(R^2 = 0.8182^{***})$$

The model is statistically significant and it explains 82% of the variability of cadmium. The most important parameter, which influences the distribution of cadmium, was total phosphorus.

The regression model for the distribution of total cadmium during monsoon in the sediments of Chitrapuzha River is as follows:

$$\mathrm{Cd} = 0.16086^{***}\,\mathrm{OC} + 0.18653\,^{***}\mathrm{TP} - 0.00756\,\mathrm{Fe\text{-}T} + 0.04192\,\mathrm{Clay\%} + 7.8911$$
$$(R^2 = 0.9138^{***})$$

The relative importance of the sediment parameters in the identified model indicated that organic carbon content and total phosphorus are the most important parameters in explaining the variability of cadmium during monsoon.

The identified regression model of cadmium for the distribution during post-monsoon

$$\mathrm{Cd} = 0.07399\,\mathrm{OC} + 0.17011^{***}\,\mathrm{TP} + 0.01780\,\mathrm{Fe\text{-}T} + 0.03616\,\mathrm{Clay\%} + 4.5375$$
$$(R^2 = 0.6292^{***})$$

The total phosphorus was found to be the most important parameter in the distribution of cadmium. The model is significant and accounts for 63% of variability of cadmium during post-monsoon.

The regression model for the distribution of lead during pre-monsoon season indicated that the identified sediment parameters are not sufficient to account for the distribution of lead. The model explains only 32% of variability of lead.

$$\mathrm{Pb} = 0.17285\,\mathrm{Fe\text{-}T} - 0.16190\,\mathrm{OC} - 0.05489\,\mathrm{TP} + 0.43835\,\mathrm{Clay\%} + 9.8985$$
$$(R^2 = 0.3245^{*})$$

The combinations of four identified parameters failed to explain the distribution of lead during monsoon, though the model is statistically significant and explain for 46% of variability.

$$\mathrm{Pb} = 0.09470\,\mathrm{OC} + 0.03908\,\mathrm{TP} + 0.21222\,\mathrm{Fe\text{-}T} + 0.26535\,\mathrm{Clay\%} + 2.4717$$
$$(R^2 = 0.4608^{**})$$

As the model indicates the most important parameter, which influences the distribution of lead during post-monsoon season was total iron though other parameters also have significant roles.

$\mathrm{Pb} = 0.52025^{***}\ \mathrm{Fe\text{-}T} - 0.18337^{*}\ \mathrm{OC} + 0.14387^{*}\ \mathrm{TP} + 0.21186^{*}\ \mathrm{Clay\%} + 7.3896$
$(R^2 = 0.6026^{***})$

The identified model explains 60% of variation in distribution of lead.

Multiple regression analysis on total metals in the sediments of Chitrapuzha River indicated that although the four selected parameters significantly affect the distribution pattern, there exist some other factors also that influence metal speciation in surficial sediments. Dissolved organic matter in porewaters, Eh and total sulphide in the sediments may also have influence in the distribution of heavy metals in the sediments of Chitrapuzha River. Delaune et. al. (1981) and Calmano et. al. (1992) also have come to similar conclusions and have demonstrated the importance of dissolved oxygen, pH, salinity and sediment redox conditions in the remobilization of heavy metals in marine and fresh water sediments.

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Chapter 5

HEAVY METAL PARTITIONING IN SURFICIAL SEDIMENTS

5.1 INTRODUCTION

Sediments are complex mixtures of a number of solid phases that may nclude clays, silicates, organic matter, metal oxides such as FeOOH, MnO_2, Al_2O_3, carbonates, sulphides, and a number of minerals. Depending upon the environment, the sediment particle size distribution may range from very small colloidal particles of less than 0.1µm in diameter to large sand and gravel particles several millimeters in diameter. The distribution of trace metals in sediments is an mportant area of research in environmental studies. Sediments not only reflect the current quality of water, but also provide vital information on the transportation and fate of pollutants (Santschi et. al., 1984; Finney and Huh, 1989; Lam et. al., 1997). While the total metal content in sediments provides a convenient means of expressing a measure of pollution, numerous reports have highlighted that such measures are deficient in predicting toxicity of these pollutants (Di Toro et. al., 1990; Arjonilla et. al., 1994). The importance of studies of metal distribution among various geochemical phases of sediment in determining the potential bio-availability and remobilization of trace metals, has been emphasized also by Forstner et. al.(1990), Izquierdo et. al.(1997) and Xiangdong Li et. al.(2001). Thus, t is necessary to identify and quantify the metal forms in order to assess the environmental impacts of contaminated sediments. Several methods for the estimation of different species of metals are described in scientific literature (Kersten and Forstner, 1991). Techniques available for the characterisation of metal binding in well-defined media to specific well-defined surfaces such as, oxides and organic materials (James and Healy, 1972; Hohl and Stum, 1976; Davis and Leckie, 1978) have only limited applications for the aggregated multi-ligand, multi-component surfaces that occur in natural sediments. Empirical methods suggested for quantifying the various metal associations in sediments include sequential chemical extractions (Engler et. al., 1977; Tessier et. al., 1979) and statistical correlations (Luoma and Bryan, 1981&1982; Luoma and Davis, 1983). Models describing partitioning in sediments have also been developed (Oakley et. al., 1981; Davies-Colley et. al., 1984; Nyffeler et. al., 1984; Tessier et. al., 1985; Hirose, 1990).

The most widely used methods are based on the selective sequential extraction whereby several reagents are used consecutively to extract operationally defined phases from sediment in a set sequence (Lopez-Sanchez et. al., 1993).

partition studies are not only useful for determining the degree of association of metals in sediments and to what extent they may be remobilized into the environment (Forstner et. al., 1990; Izquierdo et. al., 1997) but also for distinguishing those metals with a lithogenic origin from those with an anthropogenic origin.

Several workers have attempted to elucidate and predict the availability of metals from sediment phase both by conventional and sequential extraction techniques (Luoma and Jenne, 1976; Tessier et. al., 1979; Samanidou and Fytianos, 1987; Nair et. al., 1991; Nair and Balchand, 1993; Lam et. al., 1997; Izquierdo et. al., 1997; Jones and Turki, 1997; Roux et. al., 1998; Mortimer and Rae, 2000; Xiangdong Li et. al., 2001). This chapter is devoted to discussion of the spatial and seasonal variation of different fractions of metals associated with surficial sediments of Chitrapuzha River.

The details of site selection, sampling and chemical analysis of the samples are furnished in Chapter 2. For partitioning of heavy metals into various accumulative phases, the sequential extraction scheme proposed by Tessier et. al. (1979) was used with a slight modification. Instead of ($HF+ HClO_4$) combination, a 1:1:3 combination of HNO_3, $HClO_4$ and HCl was used to extract residual fraction. There were five steps in the extraction procedure and the metal phase extracted in each step was defined by the extractant used. Because of this operational definition, the fractions extracted have been referred to (in the text and figures) as fractions 1 to 5 along with the chemical symbol of the element under discussion. The numbers representing the fractions are 1 - Exchangeable 2 - Carbonate bound 3 - Fe-Mn oxide bound (reducible) 4 - Organic/sulphide bound (oxidizable) and 5 - Residual. The sum of the concentrations of the five fractions has been indicated by adding the subscript 'T' to the chemical symbol of the metal. Thus for manganese, the five fractions have been represented as Mn_1, Mn_2, Mn_3, Mn_4 and Mn_5 and the sum of the fractions as Mn_T.

5.2 RESULTS AND DISCUSSION

The overall summary statistics, showing the mean, standard deviation, coefficient of variation and range of values for each of the five fractions of the heavy metals studied are furnished in the Tables 5.1 to 5.9. The relative contribution of each fraction to the total concentration of metals is also furnished.

The data showed wide variation as indicated by the percentage coefficient of variation. The spatial and seasonal mean distribution pattern of the five fractions of the nine heavy metals studied are depicted in absolute and relative terms in the Figures 5.1a to 5.9e.

5.2.1 Chromium

Studies on the behaviour of chromium in estuaries received attention along with the studies on other trace metals. There are a number of references to show the distribution and speciation of chromium in various estuaries and oceans. Lam et. al. (1997) studied the distribution of chromium among the various geochemical phases in the coastal sediments of Hong Kong. Izquierdo et. al. (1997) carried out speciation of chromium in the sediments from the salt marshes on the South Atlantic Coast of Spain. Jones and Turki (1997) studied the speciation of chromium in the sediments of Tees estuary. Turner (2000) studied the role of hydrous iron and manganese oxides in regulating chromium contamination.

The total content of chromium determined in surficial sediments during the present study varied from 8.27 to 285 mg/kg, with an average value of 101 mg/kg (Table 4.26).The overall summary statistics showing the maximum, minimum, mean and standard deviation in the values recorded for different fractions of chromium are presented in Table 5.1 along with percentage values.

Table 5.1 Summary statistics on distribution of different chemical fractions of chromium

Fraction	Concentration (mg/kg)					Percentage				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Cr_1	0.05	2.02	0.79	0.57	72.89	0.20	1.69	0.83	0.48	57.41
Cr_2	0.08	4.54	1.21	0.92	75.55	0.16	4.31	1.40	0.92	65.19
Cr_3	3.69	22.59	11.12	4.52	40.65	0.88	20.54	10.68	5.35	50.08
Cr_4	2.67	54.55	24.01	12.75	53.11	13.06	45.79	25.17	7.49	29.76
Cr_5	12.50	117.04	58.39	32.03	54.85	40.55	74.63	59.70	8.77	14.69

Chromium is mainly associated with residual fraction. Chromium associated with other fractions follow the order: $Cr_4 > Cr_3 > Cr_2 > Cr_1$. Chromium in the Cr_5 phase, which is generally considered as environmentally inert, was 40.55 to 74.63% of the total chromium. Figures 5.1a to 5.1e depict the spatial and seasonal mean distribution pattern of the five fractions of chromium in the absolute concentrations as well as in relative terms.

The values of Cr_1, the exchangeable fraction varied from 0.05 to 2.02 mg/kg and this fraction contributed 0.83% towards Cr_T (Table 5.1). The annual mean concentration during the investigation was 0.79 mg/kg. These values were comparable with the Cr_1 values reported by Nair (1992) from Cochin estuary. Many workers have reported lower values of Cr_1 fractions from different parts of the world. Samanidou and Fytianos (1987) reported 0.52% and 0.23% exchangeable fraction in Axios and Aliakmon rivers respectively. Elsokkary and Muller (1990) reported upto 0.1% in Nile River.

Higher values were recorded in Zones 1 and 3 while Stations in Zone 2, which are predominantly sandy, recorded lower values (Fig. 5.1a). The exchangeable fraction includes the chromium dissolved in interstitial water as well as the chromium loosely bound to adsorbing surfaces, which could be replaced by magnesium ions. In sandy sediments the exchange of metals between the interstitial water and the overlying water is more rapid than in clayey environments. This explains the lower concentration of exchangeable fraction in sediments of Stations 4, 5 and 6 (Zone 2). Cr_1 exhibited significant seasonal variations with generally higher concentrations during pre-monsoon and lower values during monsoon seasons.

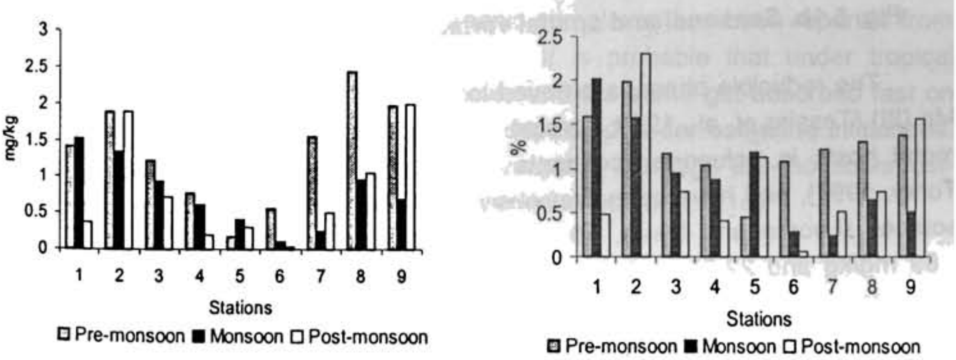


Fig. 5.1a. Seasonal and spatial variations of exchangeable fraction

Cr_2 values ranged from 0.08 to 4.54 mg/kg with annual mean concentration of 1.21 mg/kg. In relative terms this fraction contributed 1.40% to total chromium (Table 5.1). The contribution of carbonate bound form is higher than that of exchangeable fraction but it is insignificant when compared to other fractions of chromium. The range of Cr_2 reported in this study is higher than that reported from many other rivers and estuaries. In Cochin estuary carbonate fraction recorded

0.64% (Nair, 1992). Axios and Aliakmon rivers (Greece) carry 0.52% and 0.69% carbonate bound fraction respectively (Samanidou and Fytianos (1987). The sediments of River Nile contains 0.2 to 1.9% carbonate bound fraction (Elsokkary and Muller 1990). The highest and lowest values were recorded at Stations 8 and 1 respectively. Seasonal variation was significant at all Stations except at Stations 7 and 9, with higher values during pre-monsoon/post-monsoon seasons and lower values during monsoon (Fig. 5.1b). Generally the contribution of Cr_2 fraction towards total chromium was not significant evidencing the lack of affinity of chromium to carbonates.

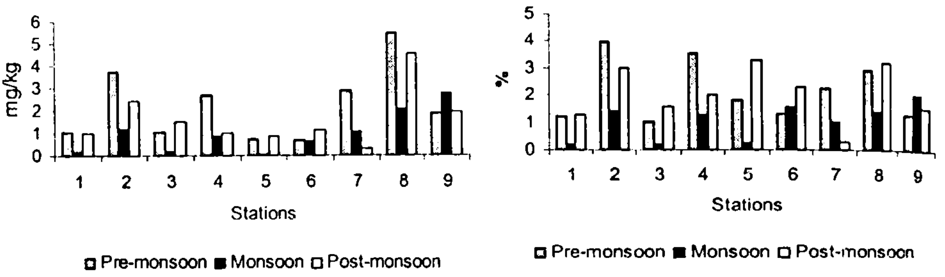


Fig. 5.1b. Seasonal and spatial variations of carbonate bound fraction

The reducible phase is believed to consist of hydrous oxides of Fe (III) and Mn (III) (Tessier et. al., 1979; Kersten and Forstner, 1991). These are major trace metal hosts in estuarine sediments (Calmano and Forstner, 1983; Jones and Turky, 1997), and have been previously identified as important bioavailable metal sources (Luoma and Davis, 1983). The reducible fraction, Cr_3 varied between 3.69 mg/kg and 22.59 mg/kg and this fraction accounts for 10.68% of Cr_T. The percentage of reducible fraction in the sediments of Chitrapuzha River is much higher than that of many other rivers. Reducible fraction accounted for only 8.52% and 3.54% of total chromium in the rivers Axios and Aiiakmon (Samanidou and Fytianos (1987) whereas the same for River Nile was just 0.8% (Elsokkary and Muller, 1990). In absolute terms, highest value was detected at Station 8 but percentage-wise it was at Station 5. Metal concentration in the reducible phase is strongly dependent on particle size (Brook and Moore, 1988). This may be one of the reasons for the higher concentration of chromium in the reducible phase in the Zones 1 and 3. Generally pre-monsoon values were higher and monsoon values lower as in the case of Cr_1 and Cr_2 (Fig.5.1c).

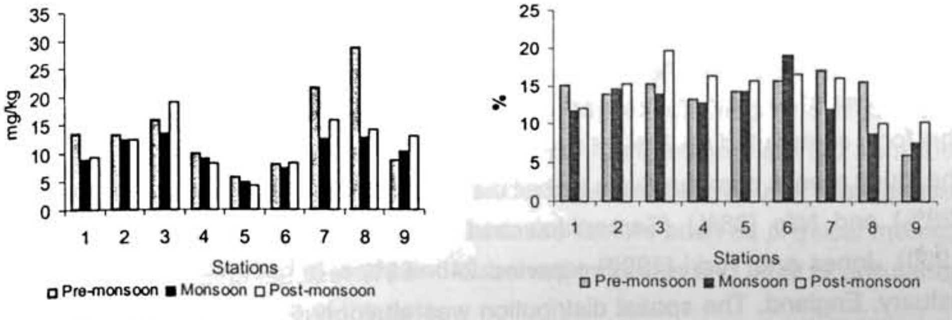


Fig. 5.1c. Seasonal and spatial variations of reducible fraction

The oxidizable fraction, Cr_4 was the second abundant form of chromium determined in Chitrapuzha River. This fraction consists of largely organic and sulphide bound metals (Tessier et. al., 1979; Kersten and Forstner, 1991). The values of Cr_4 ranged from 2.67 to 54.55 mg/kg, which constituted 25.17% of Cr_T. This is comparatively low when compared to the same in other rivers. Axios and Aliakmon rivers carry 32.51 and 66.90% Cr_4 respectively (Samanidou and Fytianos (1987). The sediments of River Nile contains 29.9 to 53.2% oxidizable fraction (Elsokkary and Muller, 1990). The highest values were recorded at the Station 7, which may be attributed to high concentrations of organic content in this region. The ability of chromium to form stable organic complexes has been reported from sewage-amended sites (Lake et. al., 1989). It is probable that under tropical conditions Cr (III) is the predominant species and the same get adsorbed fast on colloidal particles, which may eventually be deposited under estuarine influences. This fraction exhibited significant seasonal variation with high pre-monsoon/post-monsoon values and comparatively low monsoon values (Fig. 5.1d).

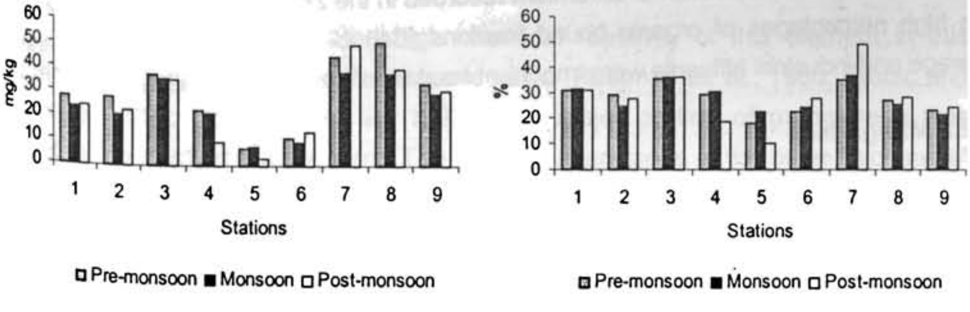


Fig. 5.1d. Seasonal and spatial variations of oxidizable fraction

Because of the geochemical resistance of naturally occurring chromium, it is normally associated with the residual or inert phase (Turner, 2000). Cr_5 was the most abundant fraction of chromium recorded in the sediments of the study area. The values of Cr_5 varied between 12.50 at Station 5 and 117.04 mg/kg at Station 8; this form contributed 59.70% of Cr_T (Table 5.1). The percentage of Cr_5 observed in the study area is comparatively higher than that of the rivers Axios (57%), Aliakmon (28%) and Nile (38%) (Samanidou and Fytianos, 1987; Elsokkary and Muller, 1990). Jones and Turki (1997) reported 24 – 68% residual chromium in the Tees estuary, England. The spatial distribution was analogous to the distribution of total Chromium; related to the grain size distribution of the sediments; the silty-clay sediments in the Zone 3 having the highest Cr_5 value. High concentration of Cr_5 at Stations 8 and 9 may be due to the high percentage of fine particles in the sediments. Lower values were recorded during post-monsoon/monsoon periods and higher values recorded during pre-monsoon (Fig. 5.1e).

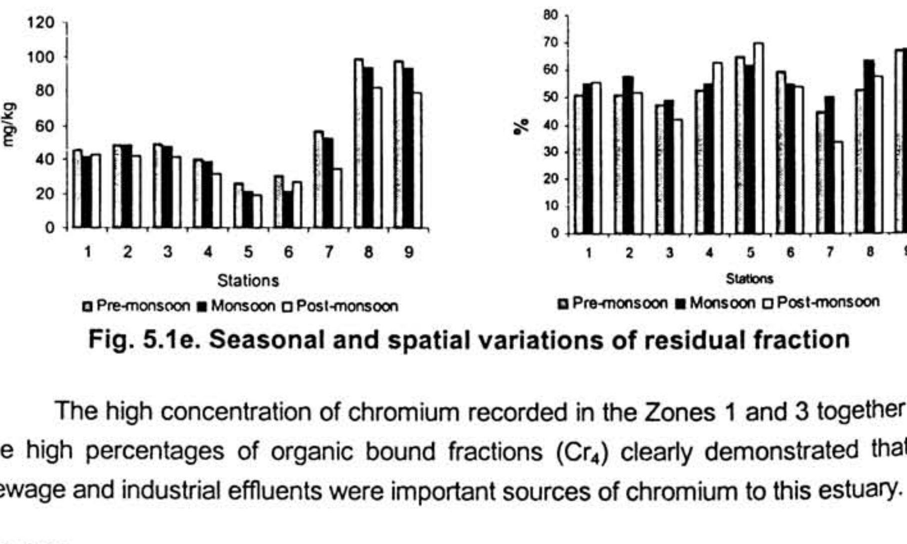


Fig. 5.1e. Seasonal and spatial variations of residual fraction

The high concentration of chromium recorded in the Zones 1 and 3 together with the high percentages of organic bound fractions (Cr_4) clearly demonstrated that the sewage and industrial effluents were important sources of chromium to this estuary.

5.2.2 Manganese

Estuarine reactivity of manganese has been widely studied. Manganese has been reported to exhibit a complex behaviour with removal, addition as well as conservative nature for different estuaries (Burton and Liss, 1976; Wilke and Dayal, 1982; Turner and Millward, 1994). Manganese can occur in sediments as discrete oxide particles, coatings on particles and as manganese (II) adsorbed on organic materials (Graham et. al., 1976; Feely et. al., 1982). In estuaries organic matter accumulation may lead to the dissolution of manganese from sediments (Luoma, 1990). Since manganese can apparently be complexed by dissolved organic materials and can be retained in solution by the control of redox potential through oxidation of the more labile dissolved organics, the amount and kind of organic material present would determine the proportion of manganese exported from the estuary (Wangersky, 1986). It is difficult to understand the behaviour of manganese at the estuarine sediment/water interface because factors such as physical mixing, reactions between suspended loads and dissolved materials and input of pollutants complicate the interpretation of the data.

Manganese is the second most abundant heavy metal In Chitrapuzha River. The concentration of total manganese varied from 14.74 to 868.92 mg/kg with a mean value of 245.18 mg/kg (Table 4.26). In contrast to the behaviour of other metals, a considerable portion of manganese recorded in this river was found to be in the environmentally labile fractions (Table 5.2) leaving an average of only 23.01% as the residual fraction.

Table 5.2 Summary statistics on distribution of different chemical fractions of manganese

	Concentration (mg/kg)					Percentage				
Fraction	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Mn_1	0.06	100.55	15.62	23.81	152.42	0.04	30.51	5.45	6.00	110.08
Mn_2	3.79	203.38	60.63	46.20	76.20	7.69	43.73	23.61	8.68	35.66
Mn_3	2.95	342.20	70.38	67.93	96.52	6.11	58.43	26.09	9.27	35.51
Mn_4	6.98	226.78	56.34	50.53	89.69	6.99	40.49	21.84	7.64	35.00
Mn_5	7.83	178.67	61.10	40.92	66.98	6.87	48.10	23.01	8.82	39.58

This was indicative of the high chemical reactivity of this element in this estuary, which was noted in other estuaries also (Rosental et. al., 1986; Prohic and Kniewald, 1987; Izquierdo et. al., 1997). The major portion of manganese was bound to the easily reducible form. The order of abundance of the other fractions of manganese was $Mn_5 \simeq Mn_2 > Mn_4 > Mn_1$. Chemical partitioning pattern of manganese confirm the anthropogenic sources of manganese in the sediment. The different chemical forms of manganese can affect the solubility and mobility of manganese from sediments. Therefore, manganese in the sediments of Chitrapuzha River has higher mobility and availability. The data revealed significant atial and seasonal variations. Significant interaction between the seasons and tations were also recorded.

Concentration of exchangeable manganese varied over a wide interval, which is vident from the high percentage coefficient of variation. The values ranged from 0.06 100.55 mg/kg, contributing an overall annual mean percentage concentration of .45% (Table 5.2), which is comparable with the concentration of exchangeable anganese in Cochin estuary, Yellow River and Axios River (Hong and Forstner, 983; Samanidou and Fytianos, 1987; Nair, 1992). The distribution of Mn_1 was almost niform in the Zones 1 and 2 but higher values were recorded in Zone 3, the industrial one. The more or less equitable distribution of Mn_1 fraction among the sediments of one 1 and 2, which differed considerably in their texture could be explained on the asis of the estuarine reactivity of manganese (Fig. 5.2a).

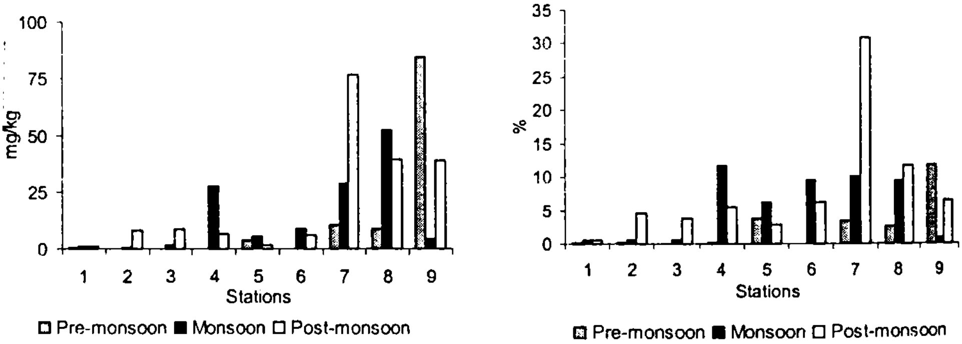


Fig. 5.2a. Seasonal and spatial variations of exchangeable fraction

Though the hydrogenous precipitation of the oxides of iron and manganese and the co-precipitation of trace metals are regarded as a means of removal of trace metals from river water in the early stages of estuarine mixing, many workers (Gibbs, 1986; Windom et. al., 1989; Nolting et. al., 1990; Guieu et. al., 1998) observed variations in the rate of removal of various metals. Although the removal of iron was quite rapid and complete, the removal of manganese was not so. Fukai and Huynh-Ngoc (1968) demonstrated that the manganese precipitation required conditions of higher pH than those normally encountered in estuaries. High concentrations of dissolved manganese in riverine sections, especially during periods of high runoff, also have been reported (Delfino and Otto, 1986). The increased amounts of soluble manganese present in the riverine parts of the estuary compensated for the decreased number of sites involved in cation exchange in the sandy sediments. On the other hand the limited solubility of manganese under saline conditions restricted the availability of manganese ions, which might be involved in exchange reactions in the silty clay sediments of Zone 1. Exchangeable manganese did not exhibit significant seasonal variations.

The Mn_2 fraction in the sediments ranged from 3.79 to 203.38 mg/kg contributing an overall annual mean percentage of 23.61% to total manganese (Table 5.2). The carbonate bound fraction Mn_2 was the second abundant fraction of manganese in the study area during the period. Many workers have reported almost same level of carbonate bound manganese from different rivers. Samanidou and Fytianos (1987) reported 19.64% and 23.15% in Axios and Aliakmon rivers respectively.

Higher values were recorded in Zones 1 and 3. In Zone 1, Mn_2 recorded a gradual decrease towards the bar-mouth in all seasons. This fraction did not show any significant seasonal variation during the study period (Fig. 5.2b).

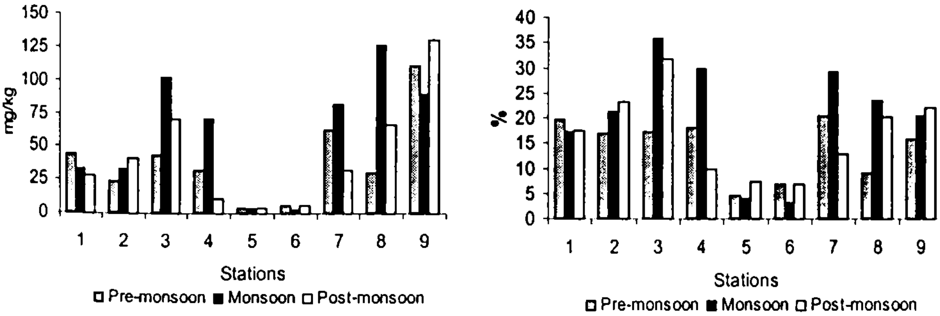


Fig. 5.2b. Seasonal and spatial variations of carbonate bound fraction

At Stations 1, 5, and 6 pre-monsoon values recorded higher values while Stations 3, 4, 7 and 8 recorded high monsoon values. The enhanced values of Mn_2 during monsoon at some Stations may be due to the influence of terrestrial soil particles that contained manganese bound to phosphates and settled preferentially in these sedimentary environments. Once settled, these phosphates release manganese under diagenetic influences, thus showing the monsoonal peak and decreasing trend afterwards.

The oxides/hydroxides of manganese are considered to be important geochemical component in the sorption of trace metals in sediments (Tessier et. al., 1985; Young and Harvey, 1992; Ismail et. al., 1994). The Mn_3 fraction was the most abundant among the various fractions of manganese, which varied from 2.95 to 342.20 mg/kg with an annual mean concentration 70.38 mg/kg (Table 5.2). In percentage terms, it accounted for 26% of total manganese. Concentration of reducible manganese recorded in Chitrapuzha River is higher than the value (8.91%) recorded for Cochin estuary (Nair, 1992). As observed for Mn_2, Zone 3 recorded higher values during all seasons. The highest value of 342.20 mg/kg (58.43%) was recorded at Station 8 during post-monsoon. The high values of Mn_3 in Zone 3 may be attributed to industrial effluents, which might cause rapid precipitation of manganese oxides or to the addition of sand sized particles coated with manganese oxides. Metal concentration in the reducible phase depends also on particle size with significantly higher concentration of manganese in fine sediments (Brook and Moore, 1988). Comparatively higher percentage of clay content in Zones 1 and 3 may provide an explanation for the higher concentration Mn_3 in these Zones. Unlike Mn_1 and Mn_2, Mn_3 exhibited more distinct seasonal variations (Fig. 5.2c).

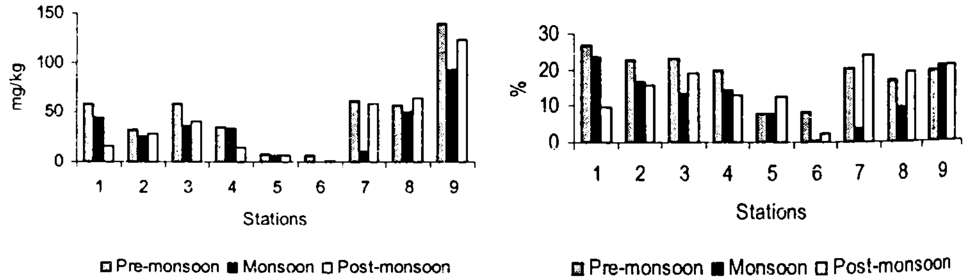


Fig. 5.2c. Seasonal and spatial variations of reducible fraction

Higher values were recorded during pre-monsoon/post-monsoon periods and lower values during monsoon except at Stations 1 and 4. The higher content of Mn_3 during pre-monsoon and post-monsoon seasons may be due to high saline conditions, which might cause the dissolved manganese to precipitate and flocculate. The lowest value of 0.37 mg/kg was recorded at Station 6 during monsoon.

Manganese in the oxidizable phase should be present predominantly as diagenetic or detrital sulphides and chemically bound to organic materials. The Mn_4 fraction ranged from 6.98 to 226.78 mg/kg and the annual mean recorded was 56.34 mg/kg (Table 5.2). This fraction contributed 21.84% to total manganese. Unlike other trace metals studied, the organic bound Mn_4 fraction was found less abundant in Chitrapuzha River. Higher values were recorded in Zone 3 and also at Station 3 in the Zone 1. The sediments of Stations in the Zone 2 recorded the lowest content of Mn_4 during all seasons. Mn_4 fraction did not exhibit any distinct seasonal variation during the investigation (Fig. 5.2d).

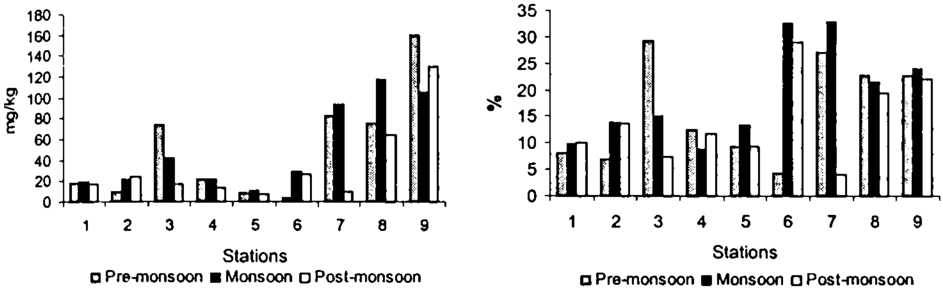


Fig. 5.2d. Seasonal and spatial variations of oxidizable fraction

The residual Mn_5 fraction in surficial sediments varied from 7.83 to 178.67mg/kg, contributing 23% to Mn_T. In absolute terms, higher values were recorded at Stations in Zone 3 and lower values were recorded in Zone 2. Mn_5 fraction exhibited distinct seasonal variation with higher values during pre-monsoon/post-monsoon seasons and lower values during monsoon season except at Stations 3 and 8 where monsoon season recorded higher values than post-monsoon (Fig. 5.2e).

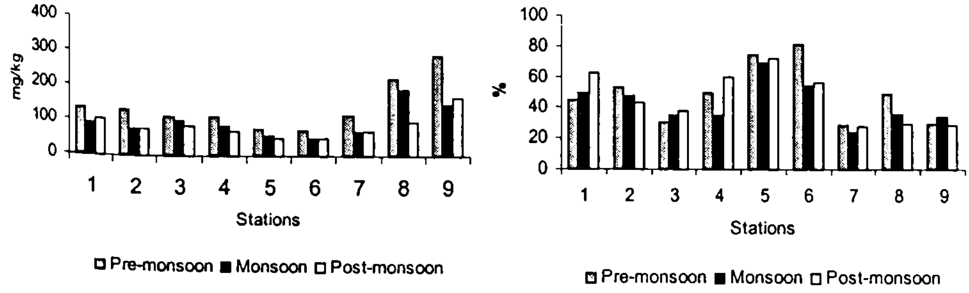


Fig. 5.2e. Seasonal and spatial variations of residual fraction

The high pre-monsoon/post-monsoon values may be attributed to heterogenous oxidative precipitation of manganese on to pre-existing particles (Turner et. al., 1993). The decrease in the percentage contribution of Mn_5 fraction may be attributed to the precipitation of authigenic fractions (as indicated by the enhanced percentages of Mn_2 and Mn_3 fractions), which enriched the total manganese load in sediments bringing down the percentage contribution of Mn_5.

5.2.3 Iron

Iron is the most abundant heavy metal in the surficial sediments of Chitrapuzha River. The concentration of total iron ranged from 1.26 to 57.67 mg/g (Table 4.26). Iron is mainly associated with residual phase (63%) leaving only 37% to labile fractions (Table 5.3). The major portion of iron (63%) was bound to the residual fraction (Fe_5) of the sediments at all Stations. Iron associated with other fractions was in the order $Fe_4 > Fe_3 >> Fe_2 > Fe_1$. Figures 5.3a to 5.3e depict the spatial and seasonal mean distribution pattern of the five fractions of iron in absolute concentrations as well as in relative terms. Though the relative contribution from Fe_1 and Fe_2 were quite small, their seasonal distributions were significant.

Table 5.3 Summary statistics on distribution of different chemical fractions of iron

Fraction	Concentration (mg/kg)					Percentage				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Fe_1	0.14	43.65	5.17	9.23	178.55	0.01	0.53	0.05	0.08	165.56
Fe_2	1.06	547.58	121.85	166.27	136.45	0.01	2.49	0.54	0.73	134.62
Fe_3	84.10	8465.78	3140.54	2245.25	71.49	0.31	43.65	13.72	8.76	63.83
Fe_4	32.16	17045.38	5456.53	3965.39	72.67	0.71	44.15	22.69	12.80	56.40
Fe_5	1689.18	31597.89	14949.87	7335.01	49.06	27.41	98.67	63.01	18.62	29.54

The Fe_1 fraction ranged from 0.14 to 43.65 mg/kg with an overall mean concentration of 5.17 mg/kg. In percentage terms this accounts only for 0.05% of total iron present in sediments (Table 5.3), which is in agreement with the values reported for Cochin estuary (Nair, 1992). Nair (1992) recorded Fe_1 values in the range of 0.01 to 0.23% with a mean value of 0.06%. Concentration of Fe_1 varied over a wide range, which is evident from the high percentage of coefficient of variation. Maximum value was recorded in the sediments of Station 7 and minimum at the Station 9. There were more or less equitable distribution of Fe_1 among all the Stations except at Stations 6 and 7. Fe_1 phase includes the iron dissolved in interstitial water as well as the iron loosely bound to adsorbing surface, which could be replaced by magnesium ions. Presence of high organic matter, which mobilize iron under mildly reducing conditions explain the higher amounts of Fe_1 in the sediments of Stations 6 and 7. This fraction did not exhibit any distinguishable seasonal variation as evident from the Fig. 5.3a.

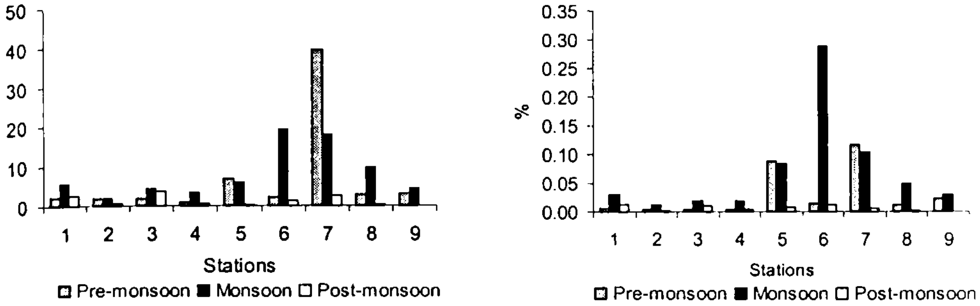


Fig. 5.3a. Seasonal and spatial variations of exchangeable fraction

The Fe_2 fraction ranged from 1.06 to 547.58 mg/kg contributing 0.01 to 2.49% of total iron (Table 5.3). Highest value was recorded at Station 2 and the lowest at Station 5. Very low concentration of this fraction at Stations 8 and 9 was the notable feature in the distribution of this fraction. Very high amounts of Fe_2, both in absolute and relative terms recorded during the monsoon periods suggested that this fraction was associated with the suspended load derived from terrestrial sources under the influence of storm water and erosion. Fe_2 fraction recorded high monsoon values in Cochin estuary also (Nair, 1992). In highly acidic soils of the tropics, the fixation of phosphate as iron phosphates became a well-established phenomenon (Le Mare, 1981). On this basis, it can be concluded that abnormally high values of Fe_2 during the monsoon might be due to trapping of eroded soils rich in iron phosphates (Fig. 5.3b).

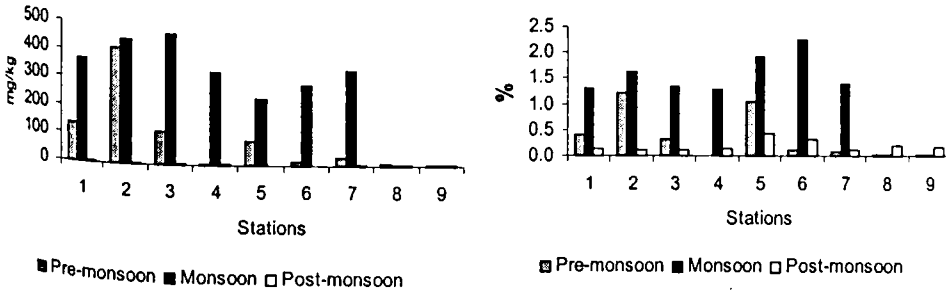


Fig. 5.3b. Seasonal and spatial variations of carbonate bound fraction

The Fe_3 values ranges from 84.10 to 8465.78 mg/kg with an overall annual mean concentration of 3140.54 mg/kg. In relative terms this fraction contributes 13.72% of total iron (Table 5.3). Highest value was recorded at Station 1 and lowest value recorded at Station 9. Fe_3 values exhibited an upstream decrease in Zones 2 and 3 and a down stream decrease towards bar-mouth (Fig. 5.3c).

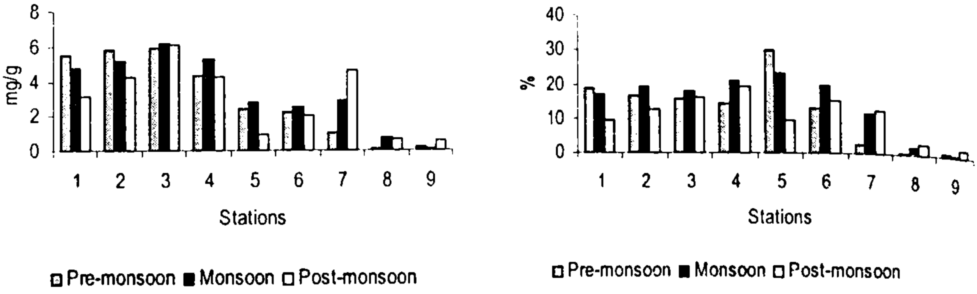


Fig. 5.3c. Seasonal and spatial variations of reducible fraction

Nair (1992) observed lower concentration of hydroxylamine hydrochloride extractable iron in the salt-water intrusion zone in the Cochin estuary and it was attributed to iron desorption at intermediate salinities. Values reported by Samanidou and Fytianos (1987) for Axios River (18.81%) and Aliakmon River (26.82%) are much higher than Fe_3 value recorded for Chitrapuzha River. No significant seasonal trend could be seen in the distribution of Fe_3 (Fig. 5.3c).

The extractant used for the extraction of Fe_3 was acidified hydroxylamine hydrochloride (pH = 2.0), which could dissolve the oxides of iron and manganese that were relatively stable under oxidising conditions (Engler et. al., 1977). Brannon et. al. (1977) noted that the extractant dissolved approximately 85% of manganese oxides while dissolving only 5% of the total iron present in Mobile bay sediments. Tessier et. al. (1979) also observed that manganese oxides were more easily leached down than iron oxides. The iron oxides occur in estuarine sediments in a continuum of states ranging from a highly amorphous oxyhydroxide, which form upon precipitation to increasingly crystalline solids which form as the initial precipitate ages. The chemistry of Fe_3 fraction is controlled by the presence of manganese oxides and organic matter. The influence of organic matter buried into the sediments might account for the high Fe_3 values recorded at Stations 2 and 3, which received effluents from the intensely populated metropolis of Cochin.

The values of Fe_4 fraction were found to be in the range of 32.16 to 17045.38 mg/kg contributing 22.69% of total iron. Overall annual mean concentration of organically bound iron was 5456.53 mg/kg. Highest value was recorded at Station 7 and the lowest at Station 8. Season wise, higher values were recorded during pre-monsoon/post-monsoon seasons except at Station 5 where monsoon season recorded higher values (Fig. 5.3d)

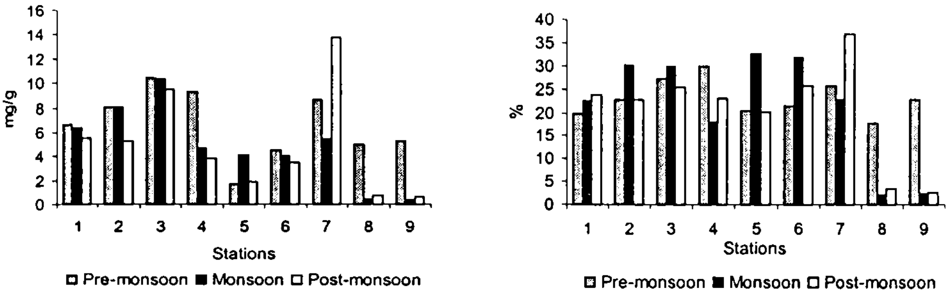


Fig. 5.3d. Seasonal and spatial variations of oxidizable fraction

Fe_4 showed a decreasing trend in Zone 1 towards the bar-mouth, which may be due to the decline in organic content from Station 3 to 1. One characteristic feature noted in the distribution of Fe_4 was the sharp decline in concentration at Stations 8 and 9 during monsoon and post-monsoon periods.

The Fe_5 fraction corresponds to the metal with a natural origin and will not be remobilized into the aquatic medium in the conditions given in nature (Samanidou and Fytianos, 1987; Izquierdo et. al., 1997). Major part of total iron was found in the Fe_5 fraction (Table 5.3). This fraction varied from 1.69 to 31.60 mg/g contributing 63.01% towards Fe_T. Overall annual mean concentration was 14.95 mg/kg. Nair (1992) reported higher percentage of residual fraction in Cochin estuary. Its distribution pattern was analogous to that of total iron in the sediments and was largely influenced by textural properties (Fig. 5.3e).

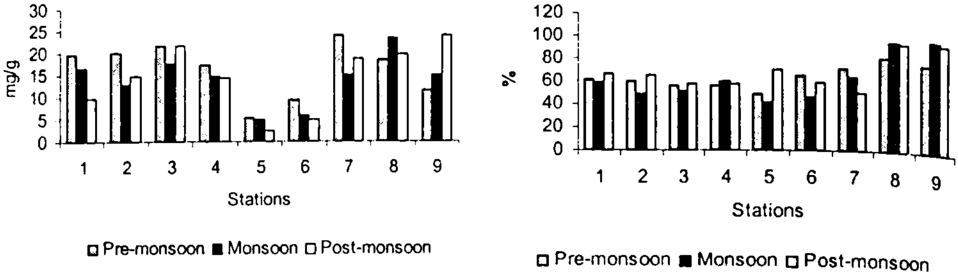


Fig. 5.3e. Seasonal and spatial variations of residual fraction

In absolute terms, sediments of Zones 1 and 3 had higher content of Fe_5 than Zone 2, which was predominantly sandy. Fe_5 exhibited significant seasonal variation with generally higher pre-monsoon/post-monsoon values and lower monsoon values.

5.2.4 Cobalt

Results from the present investigations indicated the relatively low levels of cobalt in Chitrapuzha River. The range of values for total cobalt was 1.25 to 33.33 mg/kg with a mean of 16.39 mg/kg (Table 4.26). The chemical partitioning revealed that 28.73 to 65.66 % of the total cobalt was present in the Co_5 fraction which was considered to be environmentally inert (Table 5.4).

Table 5.4 Summary statistics on distribution of different chemical fractions of cobalt

Fraction	Concentration (mg/kg)					Percentage				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Co_1	0.08	3.72	0.84	0.67	80.26	0.60	23.05	5.64	3.76	66.58
Co_2	0.10	3.24	1.03	0.71	68.79	0.88	17.11	6.85	3.75	54.83
Co_3	0.11	4.65	2.18	0.97	44.58	4.82	30.54	14.62	4.42	30.21
Co_4	0.48	8.67	3.42	1.74	50.66	14.45	32.83	22.16	4.31	19.47
Co_5	1.22	13.58	7.95	3.59	45.13	28.73	65.66	50.75	6.72	13.24

Cobalt associated with other fractions follow the order: $Co_4 > Co_3 > Co_2 > Co_1$. The seasonal and spatial variations of different fractions are plotted in Figures 5.4a to 5.4e.

The Co_1 values ranged from a minimum of 0.08 to a maximum of 3.72 mg/kg contributing 5.64% to total cobalt. Nair (1992) recorded lower concentration (2.40%) of exchangeable fraction in Cochin estuary. The values were comparatively higher in Zone 3, the industrial Zone and lower in Zone 2. Higher values were recorded during pre-monsoon/post-monsoon periods except at Stations 1, 3, 4 and 5 where higher values were recorded during monsoon season (Fig. 5.4a).

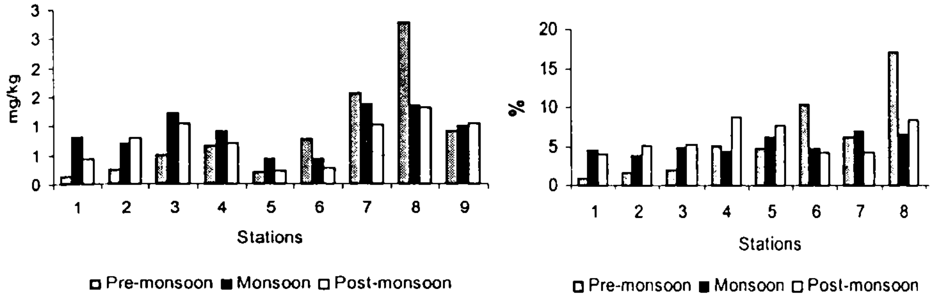


Fig. 5.4a. Seasonal and spatial variations of exchangeable fraction

The carbonate bound Co_2 values ranged from 0.10 to 3.24 mg/kg with mean value of 1.03 mg/kg. In percentage terms this contributes 6.85%. Concentration of carbonate bound cobalt recorded in Cochin estuary was only 2.35% (Nair, 1992). Maximum value was recorded at Station 8 and minimum value at Station 9. As observed in the case of Co_1, Co_2 recorded higher concentrations in Zone 3 and lower concentrations in Zone 2 (Fig. 5.4b).

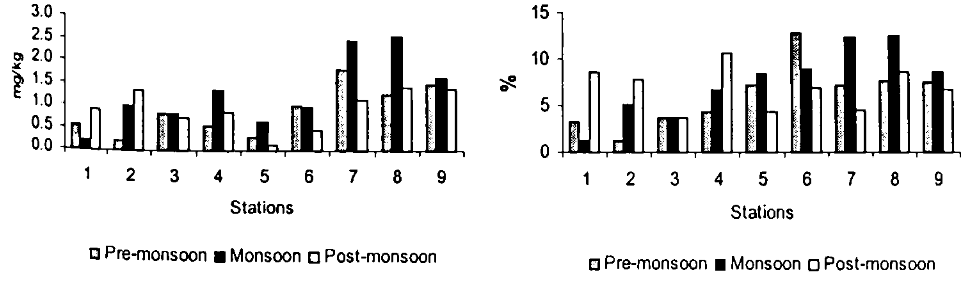


Fig. 5.4b. Seasonal and spatial variations of carbonate bound fraction

In Zone 3 higher values were recorded during monsoon season but no significant seasonal change was noted in Zones 1 and 2. Comparatively high values of Co_2, both in absolute and relative terms during monsoon period suggested that this fraction was associated with the suspended load derived from terrestrial sources under the influence of storm water and erosion.

The reducible fraction Co_3 varied from 0.11 to 4.65 mg/kg contributing 14.62% to total cobalt. Values were higher in Zones 1 and 3 than in Zone 2, which was rich in sand. In relative terms distribution was almost uniform through out the study area but seasonal differences were significant (Fig. 5.4c).

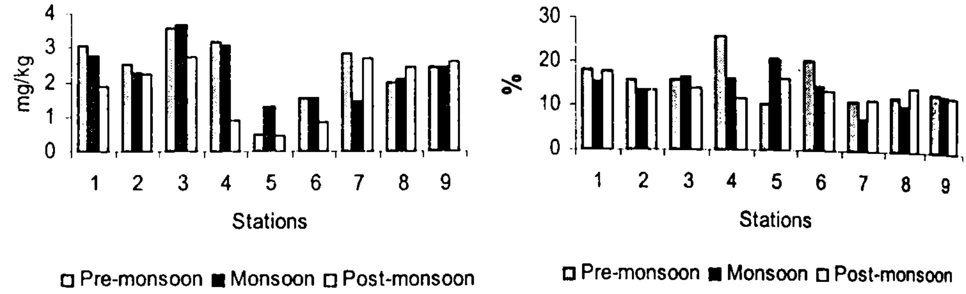


Fig. 5.4c. Seasonal and spatial variations of reducible fraction

Pre-monsoon/post-monsoon values were higher than monsoon values except at Stations 3 and 5. The spatial distribution pattern of reducible cobalt has some similarity to the distribution of reducible manganese. Smith (1990) reported that there was a general tendency for total cobalt to increase with manganese, particularly with the easily reducible fraction, in the acidic grassland soils of England. In aquatic systems manganese is probably removed from water column by oxyhydroxide precipitation and cobalt by co-precipitation. Their behaviour in the sediment is very sensitive to redox conditions (Amdurer et. al., 1983). When mixed down into suboxic sediments (depending on the concentration of organic material in the sediments, temperature, bioturbation etc., this may be just below the sediment surface) manganese oxide is reduced releasing manganese and cobalt to the pore water.

The Co_4 fraction ranged from 0.48 to 8.67 mg/kg and the annual mean recorded was 3.42 mg/kg. This fraction contributed 22.16% to the total cobalt, which is comparable to concentration of Co_4 in Cochin estuary Nair (1992). The highest (8.67 mg/kg) and lowest (0.48 mg/kg) values were recorded at Stations 7 and 5 respectively. The concentration of Co_4 was low in Zone 2 when compared to Zones 1 and 3 (Fig.5.4d).

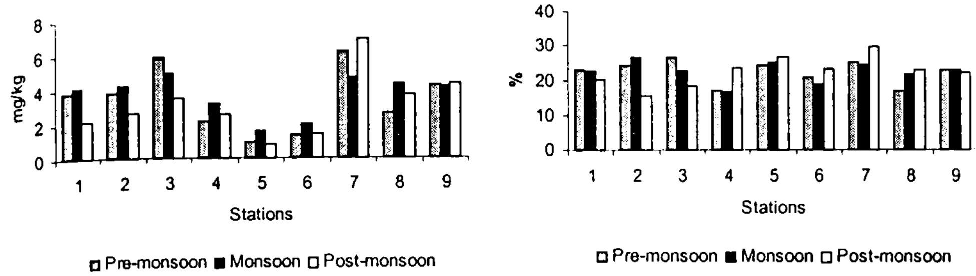


Fig. 5.4d. Seasonal and spatial variations of oxidizable fraction

The enhanced values in the sediments of Zones 1 and 3 might be due to high organic content in these sediments. The distribution of this fraction did not record any significant seasonal variation during the study. The minimum variability in the percentage values suggested that the sediments attained certain equilibrium between the precipitation and remobilization of this fraction of cobalt.

The residual fraction Co_5 varied from 1.22 to 13.58 mg/kg contributing 50.75% towards Co_T. Its distribution pattern paralleled that of total cobalt (Fig. 5.4e) though there were seasonal differences. This suggested that major portion of total cobalt was always found in this fraction. This observation was further supported by its relative distribution values, which exhibited minimum variation. The Co_5 fraction showed significant seasonal variations with generally higher pre-monsoon/post-monsoon values in Zones 1 and 3 but in Zone 2 monsoon season recorded higher values (Fig. 5.4e).

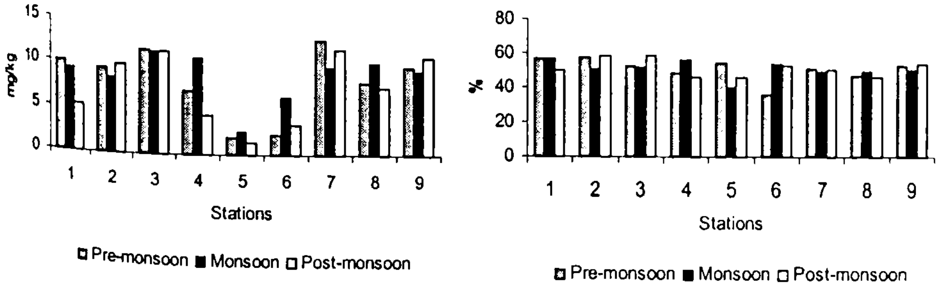


Fig. 5.4e. Seasonal and spatial variations of residual fraction

5.2.5 Nickel

A number of workers have investigated the geochemical behaviour and distribution of nickel in estuaries. Lam et. al. (1997) investigated the speciation of nickel in the coastal sediments of Tolo harbour, Hong Kong. He studied the role of different parameters that influence the distribution of metals in various phases. Nickel was found to distribute more into exchangeable and carbonate bound phases as sulphide content of sediments decreased, while the reducible metal oxide phase become important with increased total sulphide content. Jones and Turki (1997) reported that nickel was hosted mainly by residual phase in Tees estuary. Izquierdo et. al. (1997) also observed that residual phase was the most important host for nickel in the salt marshes on the Southern Atlantic Coast of Spain.

The concentration of total nickel varied from 5.30 to 116.73 mg/kg with a mean value of 62.60 mg/kg (Table 4.26). Seasonal and spatial distributions of the various fractions of nickel determined in the surficial sediments of Chitrapuzha River are presented in Figures 5.5a to 5.5e. Major portion of nickel was bound to the residual fraction (41.46%) in the sediments at all Stations in the study area. Nickel associated with other fractions was in the order $Ni_4 > Ni_2 > Ni_3 > Ni_1$ (Table 5.5). The data revealed significant spatial and seasonal variations. Significant interactions between the seasons and Stations were also recorded.

Table 5.5 Summary statistics on distribution of different chemical fractions of nickel

Fraction	Concentration (mg/kg)					Percentage				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Ni_1	0.99	18.22	6.43	4.64	72.18	1.32	27.16	10.67	6.15	57.68
Ni_2	1.04	18.78	9.16	4.76	51.93	1.87	27.39	14.62	5.30	36.22
Ni_3	1.21	14.34	7.17	3.68	51.35	2.41	19.26	11.26	3.40	30.17
Ni_4	1.17	35.42	14.65	8.48	57.85	6.47	35.60	21.96	6.19	142.13
Ni_5	4.12	54.48	27.21	13.86	50.93	24.03	57.80	41.46	8.22	19.83

The Ni_1 values ranged from 0.99 to 18.22 mg/kg, contributing 10.67 % of total nickel (Table 5.5). Highest value of 18.22 mg/kg was recorded at Station 8 and the lowest (0.99 mg/kg) at Station 5. Comparatively higher values were recorded in Zone 3 and the values exhibited a gradual decrease towards the bar-mouth (Fig. 5.5a).

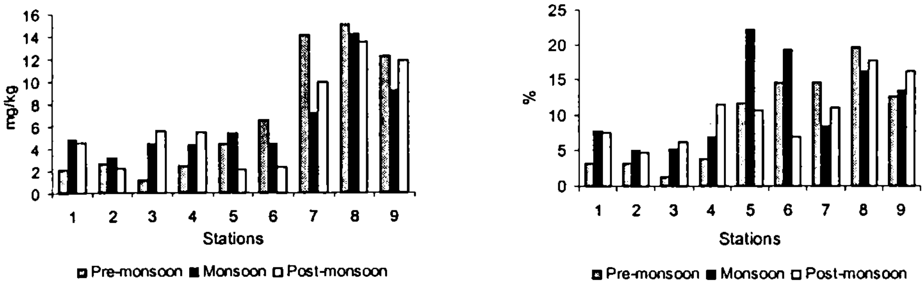


Fig. 5.5a. Seasonal and spatial variations of exchangeable fraction

The higher percentage of Ni_1 recorded in the riverine Stations (Zone 3) indicated the higher solubility and mobility of nickel in slightly acidic riverine waters in comparison to more saline alkaline waters of the lower estuary. The effluents discharged from industries may also contribute to the higher concentration of Ni_1 fraction in the Zone 3. Seasonally higher values were recorded during pre-monsoon/post-monsoon periods except at Stations 2 and 5 in absolute terms (Fig. 5.5a). Percentage of exchangeable nickel in Chitrapuzha River is much higher than that observed for Cochin estuary (1.45%) by Nair (1992) indicating high nickel pollution due to industrial activities on the banks of the river.

The Ni_2 values varied from 1.04 to 18.78 mg/kg contributing 14.62% of Ni_T (Table 5.5). Highest (18.78 mg/kg) and lowest (1.04 mg/kg) values were recorded at Stations 8 and 5 respectively as observed for Ni_1. Comparatively higher values were recorded in Zones 1 and 3 and lower values in Zone 2 (Fig. 5.5b).

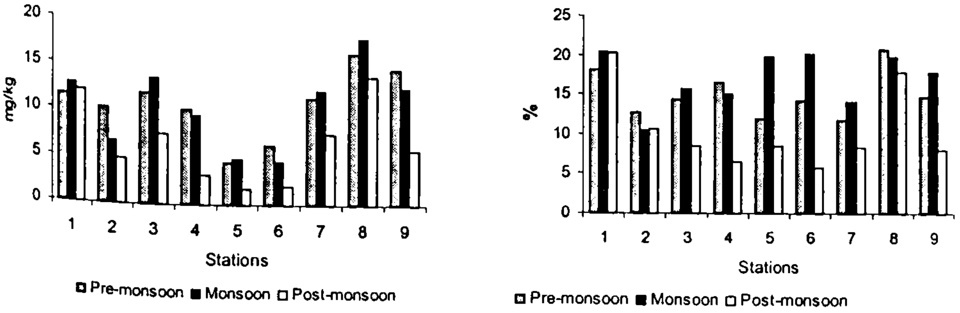


Fig. 5.5b. Seasonal and spatial variations of carbonate bound fraction

No significant trend was observed in the seasonal variations of Ni_2. The istribution pattern suggested the influence of land drainage especially from ıdustrial area on the supply of this form of nickel to the estuary, most probably ssociated with soil phosphates. When compared to carbonate bound nickel in ;ochin estuary (1.40%) the level is much higher in Chitrapuzha River

The reducible fraction Ni_3 ranged from 1.21 to 14.34 mg/kg with an overall ınnual mean concentration of 7.17 mg/kg (Table 5.5). In relative terms this ıccounts for 11.26% of total Ni (Ni_T). The concentrations of Ni_3 in the Zones 1 and } were significantly higher than that of Zone 2. The highest and lowest values vere noted again at Stations 8 and 5 respectively. Pre-monsoon and post-nonsoon values were generally higher than monsoon values in absolute and 'elative terms. The very low percentage of this fraction indicated the low mobility of nickel in these environments (Fig. 5.5c).

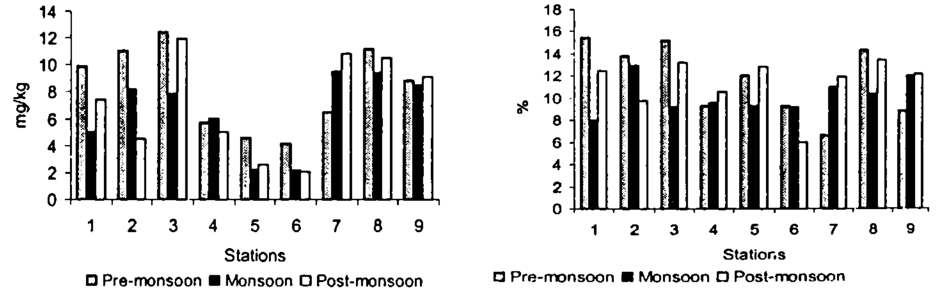


Fig. 5.5c. Seasonal and spatial variations of reducible fraction

Ni_4 values ranged from 1.17 to 35.42 mg/kg with a mean concentration of 14.65mg/kg (Table 5.5). In percentage terms this contributes 21.96% to the total nickel. The highest and lowest absolute values were recorded at Stations 7 and 6 respectively. In percentage terms Station 9 recorded the highest value. The pre-monsoon and post-monsoon values were generally higher than monsoon values in absolute as well as in relative terms (Fig. 5.5d). Sediments of the Zone 2 had the least concentration of Ni_4, which may be due to the higher percentage of sand in this Zone.

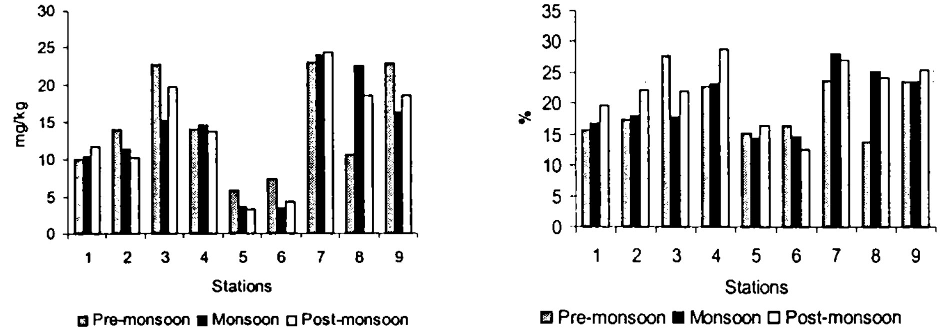


Fig. 5.5d. Seasonal and spatial variations of oxidizable fraction

The residual fraction Ni_5 ranged from 4.12 to 54.48 mg/kg contributing 24.03 to 57.80% of total nickel. This fraction contributed average 42% of total nickel. The silty-clay sediments of Zones 1 and 3 recorded relatively higher values than the sandy sediments of Zone 2. The highest and lowest values in absolute terms were recorded at Stations 2 and 5 respectively. The distribution pattern of Ni_5 was analogous to that of total Ni suggesting that a definite portion of total nickel was always found in this fraction. The percentage-wise distribution did not exhibit much variation. Seasonally pre-monsoon and post-monsoon values were higher than that of monsoon values as in the case of total nickel (Fig. 5.5e).

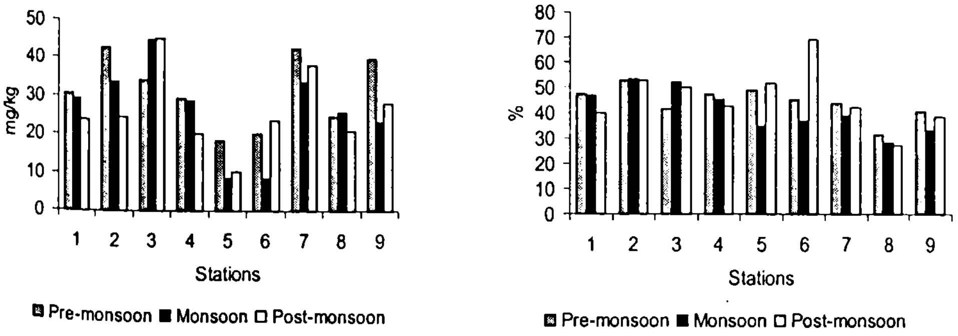


Fig. 5.5e. Seasonal and spatial variations of residual fraction

A comparison of residual nickel shows that residual nickel in Chitrapuzha River is lower than that of many other rivers. While Nair (1992) recorded 84.23%

sidual nickel in Cochin estuary, Jones and Turki (1997) reported 64-78% residual ckel in the sediments of Tees estuary. Izquierdo et. al. (1997) reported 70.3% nd 70.6% residual nickel in San Carlos and San Juan esteros, Spain respectively.

2.6 Copper

Several reports are available on the geochemical behaviour and distribution f the copper in the sediments of rivers estuaries. Adediran and Kramer (1987) bserved variations in copper adsorption on clay, iron and manganese oxides and rganic fractions along a salinity gradient. Luoma (1986) from both theoretical odeling and laboratory studies showed that copper was not partitioned xclusively to a single component of estuarine sediment and that copper istribution among components might change from sediment to sediment. All vailable approaches suggest that copper competitively partitions among a variety f components in oxidised estuarine sediments and that partitioning is driven by the ighly variable chemical characteristics of those sediments.

Total copper in the sediments of Chitrapuzha River determined during the resent study varied from 2.92 to 68.24 mg/kg with a mean value of 28.47mg/kg Table 4.26). Residual and oxidizable phases are of similar importance as metal osts. The most abundant fraction of copper was Cu_5 at all the Stations except at Stations 7 and 9 where the organic bound fraction, Cu_4 was the most abundant Table 5.6). The second most abundant form, Cu_4 constituted annual mean concentration of about 42% of total copper. The other fractions follow the order $Cu_2 > Cu_3 \simeq Cu_1$. The dominance of the residual fraction of Cu in the sediments of the estuary is probably due to the low levels of total copper in sediments. Most of the copper may come from the parent material of geological origin and may exist in the residual form in the sediments. High copper level in the residual and organic phases may be due low mobility of copper in the sediments (Xiangdong Li et. al., 2001). The Station-wise seasonal mean variations of the five fractions of copper determined by chemical extraction are depicted in Figures 5.6a to 5.6e.

Table 5.6 Summary statistics on distribution of different chemical fractions of copper

Fraction	Concentration (mg/kg)					Percentage				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Cu_1	0.02	1.29	0.40	0.34	85.27	0.08	13.76	2.01	2.39	118.48
Cu_2	0.06	4.73	1.06	1.06	100.48	0.18	19.73	4.49	3.91	87.12
Cu_3	0.04	1.75	0.51	0.45	87.51	0.31	8.26	2.22	1.43	64.59
Cu_4	0.84	35.89	12.71	9.47	74.52	18.71	69.98	42.06	10.87	25.84
Cu_5	0.48	37.34	14.13	8.39	59.41	16.26	69.22	49.21	11.58	23.54

The exchangeable fraction Cu_1 ranged from 0.02 to 1.29 mg/kg with a mean concentration of 0.40 mg/kg. In percentage terms this range contributes only 2%. Relatively higher values were recorded in Zones 1 and 3 and lower in Zone 2. Cu_1 exhibited significant seasonal variations with higher values during post-monsoon and lower values during pre-monsoon (Fig. 5.6a). Percentage of exchangeable copper in the study area is in agreement with the value observed by Nair (1992) for Cochin estuary while relatively low percentage was reported from many other rivers.

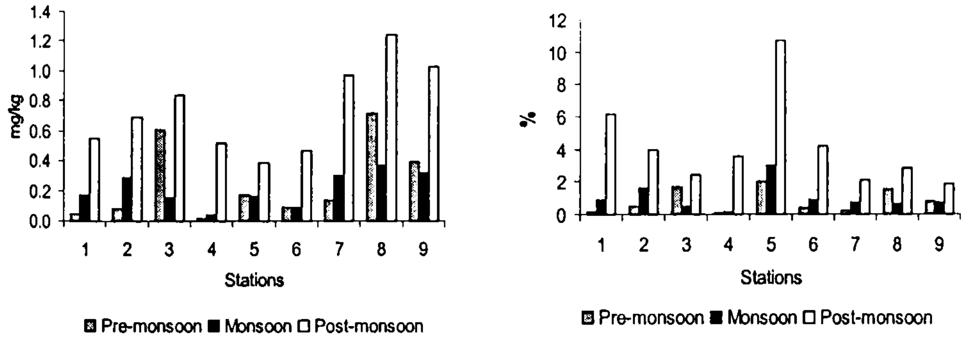


Fig. 5.6a. Seasonal and spatial variations of exchangeable fraction

The Cu_2 fraction varied from 0.06 to 4.73 mg/kg with annual mean concentration of 1.06 mg/kg. In percentage terms this fraction contributes 4.49% to Cu_T. The highest value was recorded at Station 8, which receives industrial effluents and the lowest value at Station 3 in the saline Zone 1. Generally higher values were recorded during monsoon and post-monsoon periods, which indicated the terrestrial input of this form of copper probably associated with phosphates and agricultural soils eroded during monsoon rains (Fig.5.6b). This finding is consistent with observations made by Nair (1992) in respect of Cochin estuary.

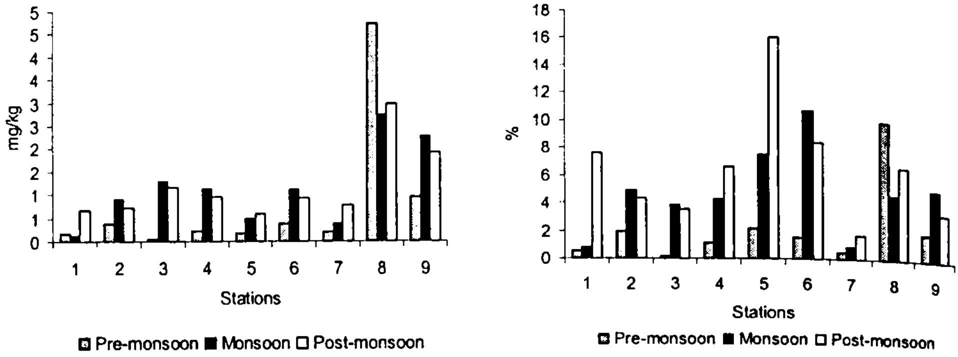


Fig. 5.6b. Seasonal and spatial variations of carbonate bound fraction

As observed for Cu_1, Cu_3 was distributed in comparatively low amounts, the values ranging from 0.04 to 1.75 mg/kg with annual mean concentration of 0.51mg/kg. In percentage terms this contributed 2.22 % of total copper. Higher values were recorded in Zone 3, the industrial Zone and lower values in the sand rich sediments of Zone 2. The low values recorded for this fraction was a feature different from what has been recorded in other estuaries. Many workers detected significant portion of copper in this phase. Turner (2000) reported high concentration of reducible fraction in Fal, Hayle, Helford and Tavy estuaries, U.K; but only low content was observed in Poole and Dee estuaries, U.K. Samanidou and Fuytianos (1987) reported 3.08% and 4.97% Cu_3 from Axios and Aliakmon rivers respectively. Brannon et. al. (1977) detected only very little copper extracted by hydroxylamine hydrochloride or dithionite reagents, in Mobile Bay sediments. Also they found no correlation between copper and manganese or iron extracted in these fractions. No significant seasonal trend could be seen in the seasonal distribution of reducible copper in the study area (Fig. 5.6c).

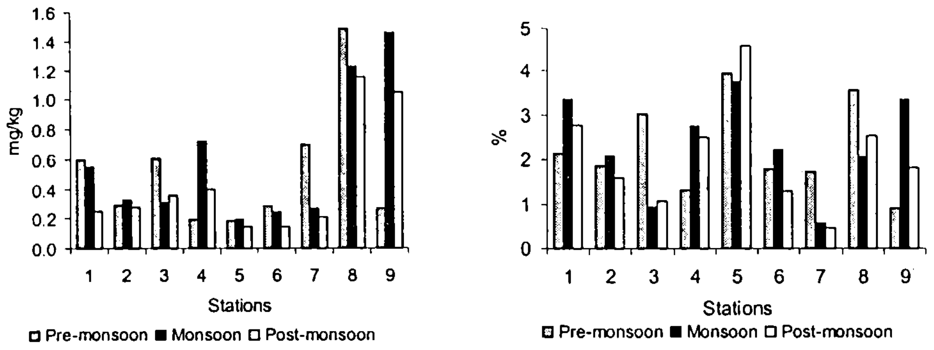


Fig. 5.6c. Seasonal and spatial variations of reducible fraction

The oxidizable form, which is the dominant fraction of copper host in the sediments studied, consisted largely organic and sulphide bound metals (Tessier et. al., 1979; Kersten and Forstner, 1991). It varied from 0.84 to 35.89 mg/kg with annual mean concentration of 12.71 mg/kg. This fraction contributed 42% of total copper in the study area (Table 5.6). The highest and lowest values detected were at Stations 7 and 5 respectively. Station 7 is in a region where organic carbon content was very high and Station 5 is in a region, which is very poor in organic content. Spatially, high concentrations were noted in Zone 3 and lower values in Zone 2. A gradual decline was observed in concentration of Cu_4 towards bar-mouth in the Zone 1, which may be due to tidal flushing and with the impact of waves, which removes the finer particles of the sediments from the bar-mouth. It exhibited significant seasonal trend in percentage-wise distributions with generally higher values during pre-monsoon and lower values during monsoon (Fig.5.6d). The enhancement of Cu_4 values during the pre-monsoon period indicated coagulation of organic matter rich in trace metals and their deposition during the more quiescent periods.

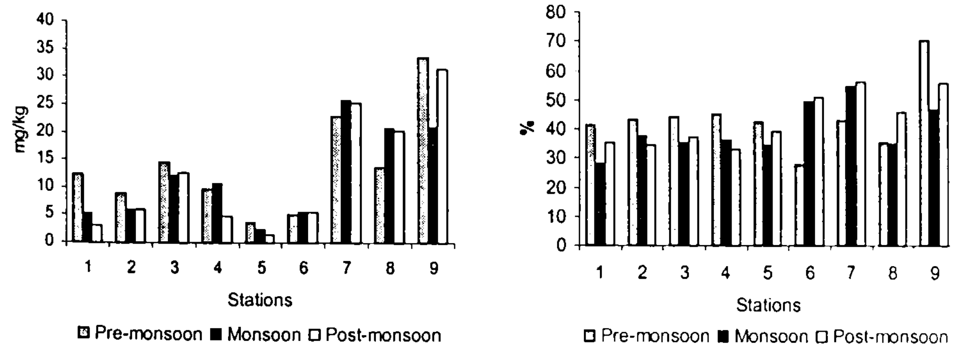


Fig. 5.6d. Seasonal and spatial variations of oxdizable fraction

Copper could easily form complexes with organic matter due to the high stability constant of organic-Cu compounds (Xiangdong Li et. al., 2001). Fernandes (1997), Zhou et. al., (1998), and Ramos et. al. (1999) reported significantly high concentrations of copper associated with organic matter in sediment. Jones and Turki (1997) reported that oxidizable fraction of copper accounted for 60 to 81% of total copper in the surficial sediments of Tees estuary, North-east England. Relationships observed between copper and organic micro pollutant in contaminated sediments (Witt and Trost, 1999) suggest that the sorptive behaviour of copper is largely governed by that of the complexing ligands and that copper complexes partition into the sediment organic matter in an 'organic compound-like' fashion. The preferential association of copper with organic matter (over hydrous oxides) in industrialized estuaries is evident from solid-state speciation studies.

The residual fraction Cu_5 varied from 0.48 to 37.34 mg/kg with a mean concentration of 14.13 mg/kg (Table 5.6). In relative terms this fraction accounted for 49.21% of Cu_T. The highest and lowest values were noted at Station 8 in the industrial Zone and Station 5 in the sandy sediments of Zone 2 respectively. Cu_5 concentration was found high in the Zone 3 and low in the Zone 2. The spatial pattern of Cu_5 followed the same pattern followed by other metals and was thus controlled by the geochemical and hydrological processes. The copper associated with this fraction cannot be remobilized under the conditions normally encountered in nature. Seasonally pre-monsoon/post-monsoon values were generally higher, but at Stations 3, 4 and 8 monsoon values recorded higher values (Fig.5.6e). Percentage of residual copper in Chitrapuzha River is much lower than the concentration of Cu_5 reported from Cochin estuary (74.21%) by Nair (1992) but it is comparable with that reported by Samanidou and Fytianos (1987) from Axios River (49.69%). Izquierdo et. al. (1997) reported 58.7% copper in the sediments of Bay of Cadiz, Spain.

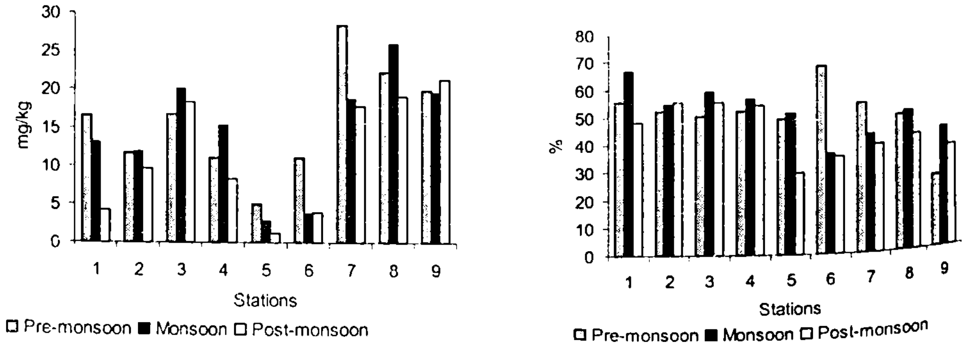


Fig. 5.6e. Seasonal and spatial variations of residual fraction

5.2.7 Zinc

In Chitrapuzha River zinc ranks third in abundance. Total zinc varied from 7.13 to 1029.18 mg/kg with an average concentration of 177.24 mg/kg (Table 4.26). High reactivity of zinc was indicated by the high variability recorded for all fractions of zinc determined (Table 5.7). Seasonal and spatial distributions of various fractions of zinc determined in the surficial sediments of Chitrapuzha River are presented in Figures 5.7a to 5.7e. Zn_5 was the dominant fraction but it contributed only 38.17% in the study area. Zinc associated with other fractions followed the order $Zn_4 > Zn_3 > Zn_2 > Zn_1$. Chemical partitioning pattern of zinc confirmed the anthropogenic sources of zinc in the sediment. It also indicated the higher mobility and availability of zinc in the sediments of Chitrapuzha River. The data revealed significant spatial and seasonal variations. Significant interaction between the seasons and stations were also recorded.

Table 5.7 Summary statistics on distribution of different chemical fractions of zinc

Fraction	Concentration (mg/kg)					Percentage				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Zn_1	0.04	16.65	3.80	4.59	120.74	0.03	7.97	2.39	1.89	79.13
Zn_2	0.81	48.86	18.65	14.32	76.79	0.57	45.54	13.52	7.85	58.08
Zn_3	0.08	232.34	32.84	34.10	103.84	1.11	47.48	20.86	8.31	39.83
Zn_4	1.36	158.88	46.22	45.46	98.35	5.87	39.14	25.05	6.95	27.74
Zn_5	2.35	256.78	63.01	56.68	89.95	13.81	54.04	38.17	9.75	25.53

Zn_1 ranged from 0.04 to 16.65 mg/kg contributing 2.39% to the total zinc. Values varied over a wide range as the percentage coefficient of variation indicated (Table 5.7). The highest and the lowest values were noted at Stations 9 and 7 respectively. Zones 1and 3 recorded higher values and Zone 2 noted lower values during the study. Relatively lower values of Zn_1 in Zone 2 might be due to sandy nature of sediments. Zn_1 exhibited significant seasonal variations with generally higher pre-monsoon/post-monsoon values and low monsoon values (Fig. 5.7a). Concentration of exchangeable zinc in the surficial sediments of Chitrapuzha River is slightly higher than that recorded by Nair (1992) for Cochin estuary (1.75%).

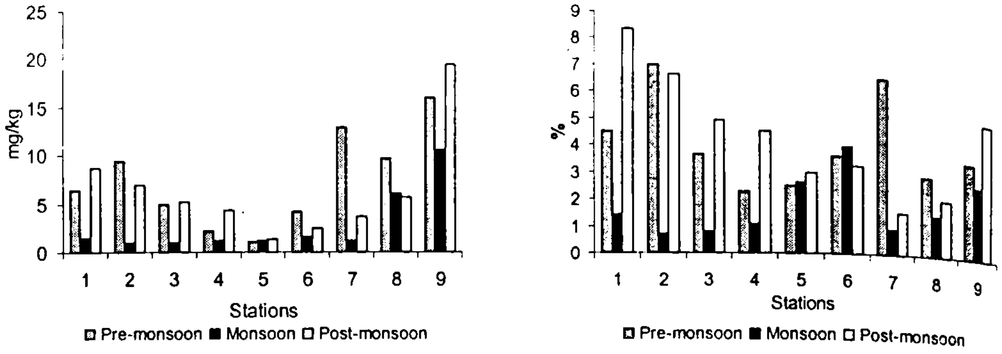


Fig. 5.7a. Seasonal and spatial variations of exchangeable fraction

The carbonate bound fraction Zn_2 varied from 0.81 to 48.86 mg/kg with a mean concentration of 18.65 mg/kg (Table 5.7). In percentage terms it accounted for 13.52% of Zn_T. The highest and lowest values were recorded at Stations 9 and 7 respectively. As observed for Zn_1, Zn_2 also exhibited significant seasonal variations with high pre-monsoon/post-monsoon values and low monsoon values except at Stations 4 and 5 where monsoon values recorded high values (Fig. 5.7b). Concentration of carbonate bound zinc in Chitrapuzha River is higher than that reported for Cochin estuary (6.43%), Axios River (8.36%) and Aliakmon River (3.8%) (Nair, 1992; Samanidou and Fytianos, 1987).

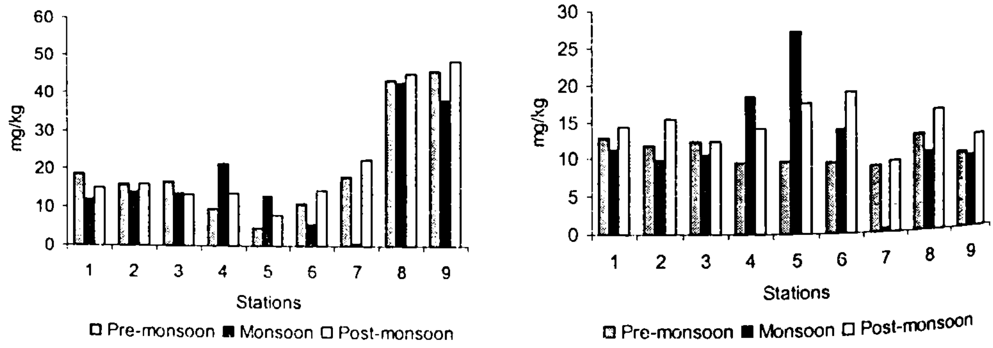


Fig. 5.7b. Seasonal and spatial variations of carbonate bound fraction

The association zinc with oxides of iron and manganese of soils and sediments has been widely recognized (Comber et. al., 1995; Fernandes, 1997; Ma and Rao; 1997; Ramos et. al., 1999; Xiangdong Li et. al., 2001). Zinc adsorption on to these oxides has higher stability constants than on to carbonates. The reducible fraction Zn_3, the third most abundant form of zinc ranged from 0.08 to 232.34 mg/kg with a mean concentration of 32.84 mg/kg (Table 5.7). In relative terms this fraction contributed 20.86%. Percentage of easily reducible zinc in Chitrapuzha River can be compared with that of other rivers/estuaries. Samanidou and Fytianos (1987) reported 13.37% from Aliakmon River and 28.41% from Axios River. Nair (1992) observed only 9.37% Zn_3 in the sediments of Cochin estuary whereas Pardo et. al. (1990) observed higher concentration (33.75%) in Pisuerga River (Spain). The highest and lowest values were recorded at Stations 8 and 5 respectively. The values of Zn_3 in the industrial Zone (Zone 3) were higher when compared to the values in Zones 1 and 2. The distribution of Zn_3 did not exhibit a distinct seasonal variation during the study (Fig. 5.7c). The distribution pattern of Zn_3 clearly demonstrated the influence of iron-manganese oxide precipitation in scavenging the metal under the influence estuarine mixing.

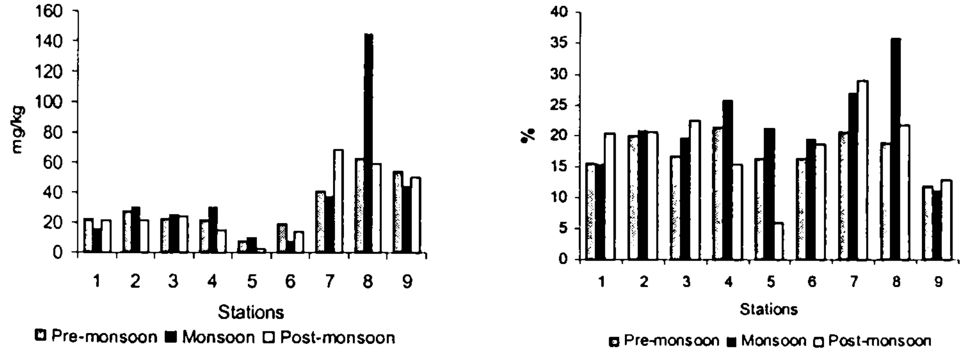


Fig. 5.7c. Seasonal and spatial variations of reducible fraction

The oxidizable fraction Zn_4 varied from 1.36 to 158.88 mg/kg with a mean concentration of 46.22 mg/kg (Table 5.7). In relative terms this accounted for 25% of Zn_T. The highest and lowest values recorded for zinc in this fraction were at Stations 9 and 5 respectively during the post-monsoon season. Distribution of Zn_4 was analogous to that of Zn_3 in Zones 1 and 2. Higher content of organic matter and fine grains in the sediments of this region may be a reason for higher concentration of Zn_4 in Zone 3. Seasonal trend in the distribution of Zn_4 was not quite distinct (Fig. 5.7d).

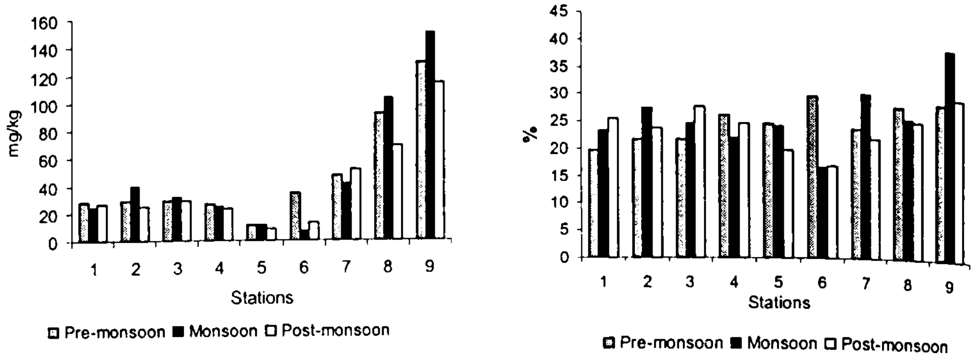


Fig. 5.7d. Seasonal and spatial variations of oxidizable fraction

There are a number of references to indicate the influence of organic matter and sulphides on the concentration of Zn_4 in an estuary. Nair (1992) reported that Zn_4 contributed 24.28% of total zinc in the Cochin estuary. The high content of organic zinc in river waters would get flocculated and sedimented at the early stages of mixing, thus contributing an appreciable percentage of this fraction during the monsoon and post-monsoon periods. However, the higher content of Zn_4 recorded during pre-monsoon had to be attributed to the autochthonus production of organic materials under the influence of enhanced productivity during these periods, and also to the coagulation and sedimentation of these products in a comparatively quiescent aquatic environment.

The residual fraction Zn_5 composed of detrital silicate minerals, resistant sulphides, and refractory organics (Tessier et. al., 1979; Salamons and Forstner, 1980) is an important carrier of metals. Metals bound within the silicate mineral lattices probably account for the bulk of the metals in this phase, and concentrations are largely governed by catchment geology (Carrel et. al., 1995). The distribution of particle size and organic matter in the study area agree with the seasonal and spatial distribution of Zn_5. The most abundant fraction of zinc, Zn_5 ranged from 2.35 to 256.78 mg/kg with a mean concentration of 63 mg/kg (Table 5.7). In percentage terms it accounted for 38.17% of total zinc. It showed homogenous distribution in the study area. The highest and lowest values were recorded at Stations 9 and 5 respectively. The spatial and seasonal distribution of Zn_5 (Fig. 5.7e) was analogous to that of total zinc especially in the Zones 2 and 3 since major portion of total zinc is associated with this fraction.

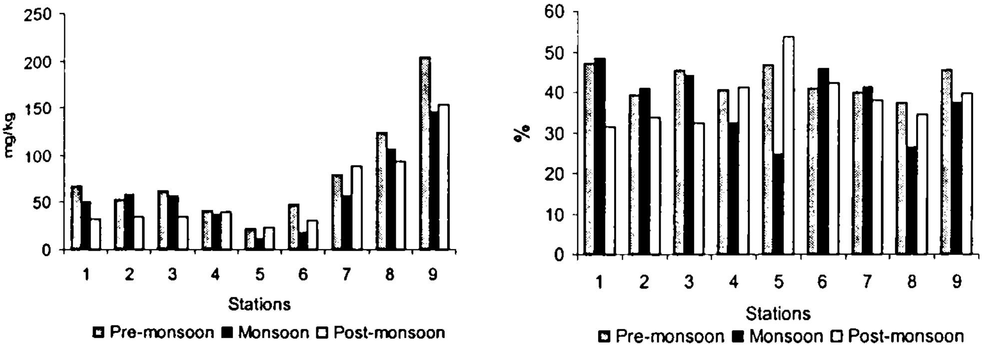


Fig. 5.7e. Seasonal and spatial variations of residual fraction

5.2.8 Cadmium

The present investigations indicated the relatively low levels of cadmium in Chitrapuzha River. Kudo et. al. (1996) studied the distribution of cadmium and phosphate in the southwest Pacific Ocean and showed that a correlation analysis between cadmium and phosphate should be done to understand the biogeochemical cycles in the ocean. Hinojosa et. al. (2001) reported distribution of dissolved cadmium for the upper 1000-m water column in the Gulf of California. They established the strong correlation between cadmium and phosphate in the Gulf of California. Brook and Moore (1988) reported the relationship between particle size and chemical control of cadmium in the bed sediments from the Clark Fork River, Montana. Speciation of cadmium in sediments was carried out by many workers such as Nair (1992), Jones and Turky (1997), Izquerdo et. al. (1997) and Mortimer and Rae (2000).

Cadmium was the least abundant of the trace metals estimated in the surficial sediments of Chitrapuzha River. The total cadmium in the sediments varied from 2.29 to 34.47 mg/kg with a mean concentration of 12.87 mg/kg (Table 4.26). Distribution of cadmium among different phases was similar to that of zinc. As in the case of zinc, residual and organic phases were the most important hosts of cadmium. Residual cadmium accounted for only 34.33% leaving 65.67% in labile phase. Cadmium associated with various phases follow the order: $Cd_5 > Cd_4 > Cd_3 > Cd_2 > Cd_1$. The seasonal and spatial variations are depicted in the Figures 5.8a to 5.8e.

Table 5.8 Summary statistics on distribution of different chemical fractions of cadmium

Fraction	Concentration (mg/kg)					Percentage				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Cd_1	0.04	1.57	0.52	0.43	82.13	0.40	10.33	4.03	2.36	58.71
Cd_2	0.10	8.52	1.65	1.79	108.57	1.20	37.47	11.28	6.60	58.54
Cd_3	0.46	9.57	3.22	2.15	66.65	7.87	41.55	24.10	7.29	30.23
Cd_4	0.66	8.07	3.31	1.85	55.81	7.32	44.57	26.32	6.44	24.48
Cd_5	1.41	13.67	4.43	2.70	60.98	19.90	46.34	34.33	5.80	16.88

The values of Cd_1 ranged from 0.04 to 1.57 mg/kg, which accounted for 4% of total cadmium (Table 5.8). Concentration of exchangeable cadmium was low when compared to the values reported by Pardo et. al. (1990) from Pisuerga River (4.85%), Nair (1992) from Cochin estuary (5.76%) and Jones and Turki (1997) from Tees estuary (10%). The highest and lowest values of Cd_1 recorded at Stations 8 and 3 respectively. Stations in Zones 1 and 3 recorded comparatively higher values than the Stations in Zone 2. The distribution of Cd_1 exhibited significant seasonal variations with generally higher values during monsoon and post-monsoon seasons and lower values during pre-monsoon season (Fig 5.8a).

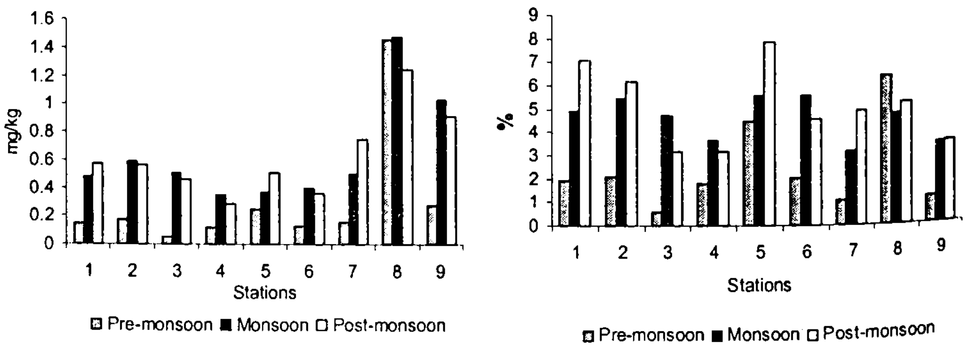


Fig. 5.8a. Seasonal and spatial variations of exchangeable fraction

At Station 8, Cd_1 showed higher values during all seasons, which may be due to discharge of effluents from industries in this region. Elsokkary and Muller

(1990) observed that in polluted sediments of the Nile River, a significant portion of cadmium existed in the exchangeable form whereas in unpolluted sediments, the values were much lower. The industrial effluents received in the Zone 3 may be a reason for the higher values of exchangeable fraction in that Zone.

The carbonate bound fraction Cd_2 varied from 0.10 to 8.52 mg/kg with a mean value of 1.65 mg/kg (Table 5.8). In percentage terms it accounts for 11.28% of Cd_T. Zone 3 recorded comparatively high concentration of Cd_2 but Zones 1 and 2 noted only low values. The pre-monsoon and post-monsoon values were higher than the monsoon values except at Stations 8 and 9 where seasonal variations may be disturbed by discharge of industrial effluents containing phosphates (Fig. 5.8b). Cd_2 fraction is expected to be associated with the phosphates and carbonates in the sediments. High concentration of Cd_2 in Zone 3 may be attributed to high concentration of phosphate in the sediments of this region. Multiple regression analysis also has proved the role of phosphate in the distribution of cadmium in the surficial sediments.

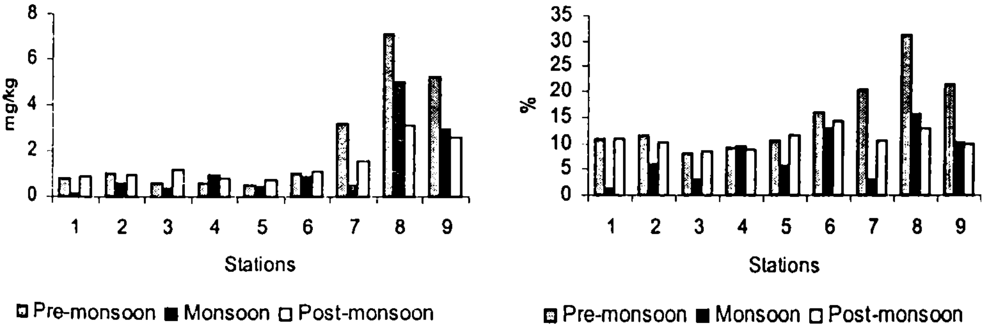


Fig. 5.8b. Seasonal and spatial variations of carbonate bound fraction

The reducible fraction Cd_3 in the sediments of Chitrapuzha River ranged from 0.46 to 9.57 mg/kg with a mean concentration of 3.22 mg/kg (Table 5.8). This fraction accounted for 24.10% of total cadmium. The concentration of the Cd_3 fraction is higher than the value reported from Cochin estuary (8.13%) by Nair (1992) but lower than the value reported from Pisuerga River (46.76%) by Pardo et. al. (1990) and from Tees estuary (9 – 40%) by Jones and Turki (1997). Higher and lower values were recorded at Stations 9 and 6 respectively. Zone 3 recorded higher values and Zone 2 recorded lower values during all seasons. In relative terms all Stations recorded almost uniform distribution (Fig. 5.8c). Higher values were recorded during monsoon except at Station 3 where post-monsoon recorded higher values.

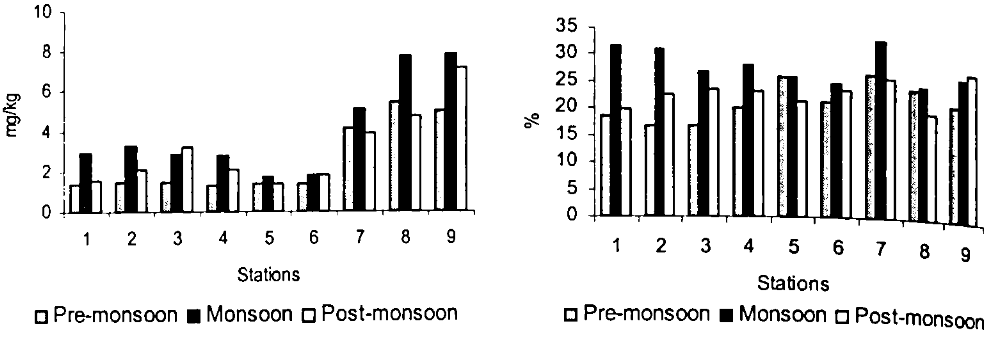


Fig. 5.8c. Seasonal and spatial variations of reducible fraction

The oxidizable fraction, Cd_4 was the second prominent fraction, which ranged from 0.66 to 8.07 mg/kg with a mean value of 3.31 mg/kg (Table 5.8). In relative terms this accounted for 26.32% of total cadmium. In absolute terms Cd_4 recorded higher values in Zone 3 and lower values in Zone 2. The spatial distribution of Cd_4 was in agreement with distribution pattern of organic content and sediment texture (Fig. 5.8d). The highest and lowest values were recorded at Stations 9 and 5 respectively. In absolute terms the seasonal variation was not distinct but in percentage terms seasonal distribution exhibited an increasing trend during pre-monsoon and post-monsoon (Fig.5.8d). A gradual decline in values towards the bar-mouth is evident from the graph, which may be due to the decrease in the percentage of fine grains and consequent reduction in organic content in sediments of this region.

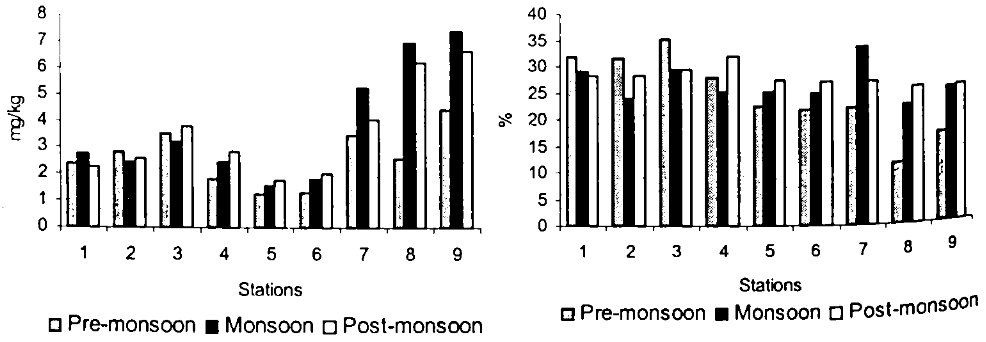


Fig. 5.8d. Seasonal and spatial variations of oxidizable fraction

The residual fraction, Cd_5 varied from 1.41 to 13.67 mg/kg with a mean value of 4.43 mg/kg (Table 5.8). In percentage terms, this fraction contributed 34.33% of total cadmium. The comparatively lower percentages of this fraction indicated that cadmium was highly reactive. The highest and lowest values were recorded at Stations 9 and 5 respectively. The spatial distribution of Cd_5 was analogous to that of total cadmium, which indicated that major portion of cadmium was associated with residual fraction. Generally, the pre-monsoon values were higher and monsoon values lower in percentage terms (Fig. 5.8e). Residual cadmium in Chitrapuzha River is lower than the concentration (43.73%) reported by Nair (1992) from Cochin estuary and (57.5%) reported by Izquierdo et. al. (1997) from Bay of Cadiz, Spain.

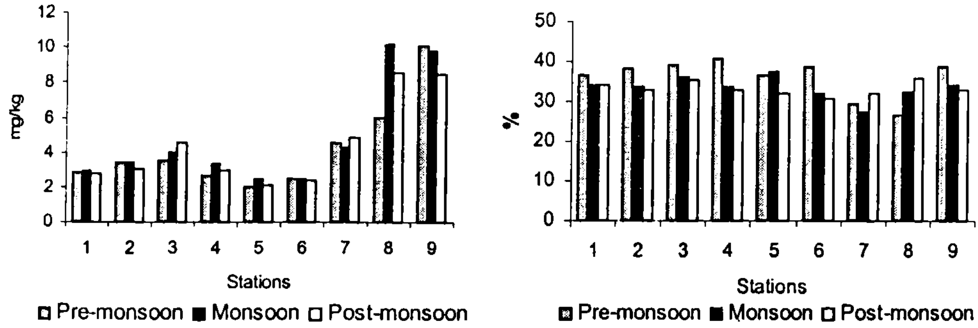


Fig. 5.8e. Seasonal and spatial variations of residual fraction

5.2.9 Lead

There are many studies reported on lead from aquatic systems, which deal with distribution of lead in different compartments of aquatic system. Jones and Turki (1997) assessed the concentration of both total lead and chemical forms of lead in the sediments of Tees estuary. Izquerdo et. ai. (1997) carried out speciation of lead in the sediments of Odiel and Bay of Cadiz salt marshes (Spain). Mortimer and Rae (2000) studied the lead speciation in estuarine oxic to suboxic salt marsh sediments of Severn estuary. Sharma et. al., (1999) estimated the concentration of lead in the Upper Laguna Madre (U.S.A) and the results normalized to grain size, aluminium and iron to understand the processes controlling metal concentration in the area. Nair et. al., (1991) has carried out lead speciation on the surficial sediments of Cochin estuary. An attempt was also made to identify anthropogenic sources of lead.

The total lead content in the study area varied from 0.93 to 41.91 mg/kg with a mean value of 22.40 mg/kg (Table 4.26). The most abundant fraction of lead was Pb_5, which constituted 67.86% leaving 32.14% in the labile form (Table 5.9). The second most abundant form was Pb_4, which constituted annual mean concentration of about 21.81% of total lead. The other fractions follow the order $Pb_3 > Pb_2 > Pb_1$. High percentage of lead in the residual phase may indicate that lead in the sediments is less mobile than other metals. The dominance of the residual fraction of lead in the sediments of the estuary is probably due to the low levels of total lead in sediments. Most of the lead may come from the parent material of geological origin and may exist in the residual form in the sediments. The Station-wise seasonal mean variations of the five fractions of lead determined by chemical extraction are depicted in Figures 5.9a to 5.9e.

Table 5.9 Summary statistics on distribution of different chemical fractions of lead

Fraction	Concentration (mg/kg)					Percentage				
	Min	Max	Mean	SD	%CV	Min	Max	Mean	SD	%CV
Pb_1	0.02	0.70	0.31	0.16	51.53	0.83	7.69	1.75	1.27	72.67
Pb_2	0.05	2.89	0.73	0.57	77.74	1.83	10.05	3.13	1.63	52.11
Pb_3	0.10	6.39	1.33	1.23	92.08	2.84	18.97	6.68	4.45	66.71
Pb_4	0.13	10.48	7.83	2.30	46.05	11.38	30.01	21.81	4.00	18.32
Pb_5	0.57	31.01	15.77	7.20	45.66	56.78	73.74	67.86	3.57	5.27

The values of Pb_1 varied from 0.02 to 0.70 mg/kg which contributed only 1.75% of the total lead (Table 5.9). In absolute terms the highest and lowest values of lead in this fraction were at Stations 9 and 5 respectively. Stations in the Zones 1 and 3 recorded higher values than at Stations in the Zone 2. The high values in Zones 1 and 3 may be attributed to the silty-clay nature of sediments, which had high adsorption sites to hold lead ions amidst the competition from calcium and magnesium ions in saline waters. The distribution of Pb_1 exhibited significant seasonal variation with generally high pre-monsoon/post-monsoon values and low monsoon values (Fig. 5.9a). The enhancements of Pb_1 values during pre-monsoon and post-monsoon seasons were resulted from the coagulation and settling of fine particles, which had more exchange sites.

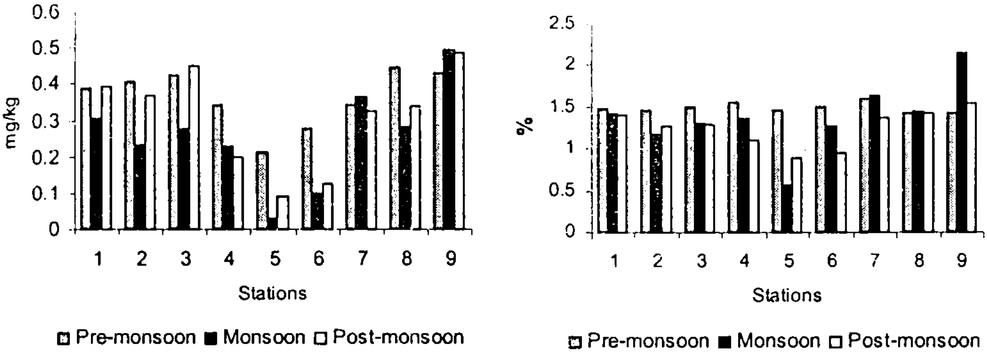


Fig. 5.9a. Seasonal and spatial variations of exchangeable fraction

The Pb_2 values varied from 0.05 to 2.89 mg/kg with a mean concentration of 0.73 mg/kg (Table 5.9). In percentage terms this accounted for 3.13% of total lead. The highest and lowest values recorded were at Stations 7 and 5 respectively. The concentration of Pb_2 was higher in Zones 1 and 3 and lower in Zone 2 as observed for Pb_1. Seasonally pre-monsoon and post-monsoon values recorded higher values than monsoon values (Fig. 5.9b). Precipitation of lead carbonates or occlusion of lead in to hydrogenous carbonate minerals under saline influence was indicated by the pronounced enhancement in Pb_2 fraction during pre-monsoon and post-monsoon seasons. The decrease in concentration of Pb_2 in Zone 1 towards the bar-mouth indicated remobilization of Pb_2 under the influence of increased salinities, either due to competition from calcium and magnesium ions exchange sites or due to formation of chloride complexes of lead.

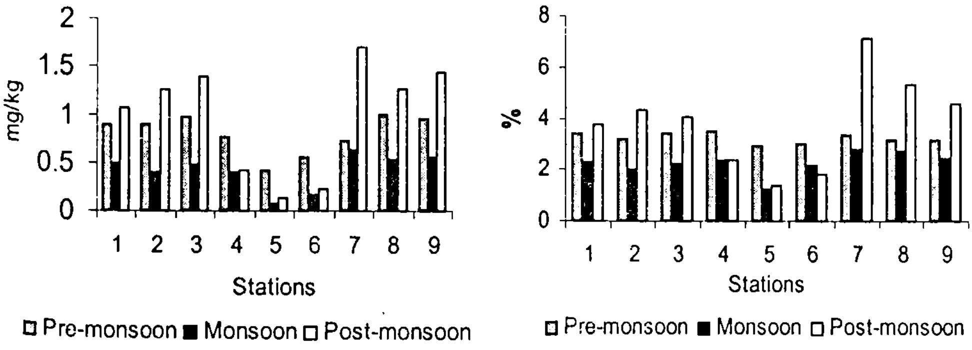


Fig. 5.9b. Seasonal and spatial variations of carbonate bound fraction

Lead in the reducible phase, Pb_3 was considered to be associated with the freshly precipitated oxides and hydroxides of iron and manganese. This fraction varied from 0.10 to 6.39 mg/kg with a mean concentration of 1.33 mg/kg (Table 5.9). In relative terms it contributed 6.68% to total lead. The highest and lowest values of Pb_3 were recorded at Stations 9 and 5 respectively. The decrease in values of Pb_3 in the Zone 2 may be due to the sandy nature of sediments. Higher values were recorded during pre-monsoon/post-monsoon periods and lower values during monsoon season (Fig. 5.9c). A comparison shows that reducible lead in Chitrapuzha River is lower than that of many other rivers: Pardo et. al. (1990) reported 33.67% from Pisuerga River, Samanidou and Fytianose (1987) reported 25.50% from Axios River, and Nair (1992) recorded 5.68% reducible lead in Cochin estuary.

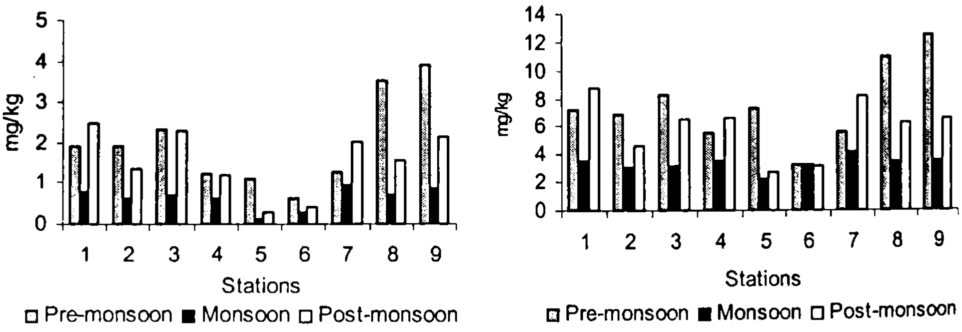


Fig. 5.9c. Seasonal and spatial variations of reducible fraction

Pb_4 ranged from 0.13 to 10.48 mg/kg with a mean concentration of 7.83 mg/kg (Table 5.9). In percentage terms it accounted for 21.81% of total lead. The highest and lowest values recorded at Stations 8 and 5 respectively. As observed for Pb_3, Pb_4 recorded higher values in Zones 1 and 3 and comparatively lower values in Zone 2. This fraction exhibited significant seasonal variations with high pre-monsoon/post-monsoon values and lower monsoon values (Fig. 5.9d). Concentration of oxidizable lead in the sediments of Chitrapuzha River is higher than that reported by Nair (1992) from Cochin estuary (10.37%).

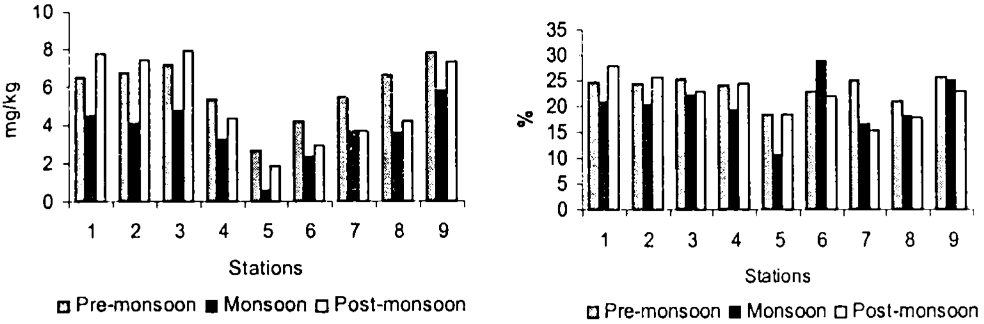


Fig. 5.9d. Seasonal and spatial variations of oxidizable fraction

The lead associated with residual fraction cannot be remobilized under the conditions normally encountered in nature. Pb_5 was the most abundant fraction in lead speciation determined in the sediments, which varied from 0.57 to 31.01mg/kg with a mean concentration of 15.77 mg/kg (Table 5.9). In percentage terms it contributed 67.86% of total lead. The highest and lowest values were noted at Stations 8 and 5 respectively. The spatial distribution of Pb_5 was analogous to that of total lead, which indicated that a prominent portion of total lead was associated with Pb_5. In absolute terms, Pb_5 exhibited significant seasonal variations (Fig. 5.9e). While higher values were noted during pre-monsoon and post-monsoon seasons, monsoon recorded comparatively lower values. The seasonal variation was not distinct in percentage values. Percentage of residual lead in Chitrapuzha River is lower than the concentration of Cu_5 reported from Cochin estuary (76.78%) by Nair (1992) but it is higher than that reported by Samanidou and Fytianos (1987) from Axios River (28.20%) and Aliakmon River (23.62%).

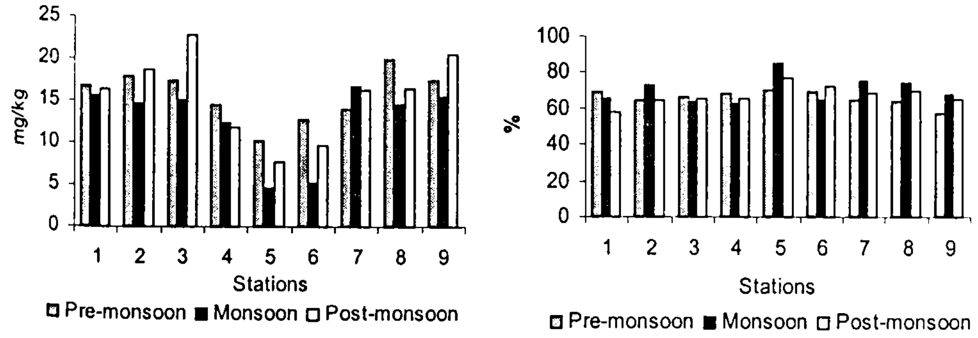
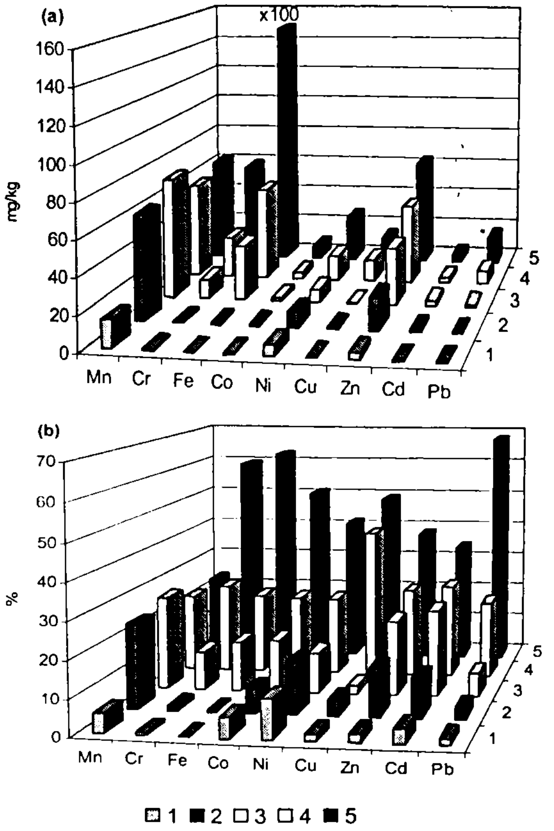


Fig. 5.9e. Seasonal and spatial variations of residual fraction

5.3 COMPARATIVE STUDY ON DISTRIBUTION OF METALS IN DIFFERENT PHASES

The spatial and seasonal distribution patterns of the five fractions of each of the nine heavy metals have been traced in relation to sedimentological and geochemical processes that are active in a tropical tidal river. It was established that the estuarine processes had the potential to significantly alter the chemical speciation of metals in the sediments. In this section a comparative study is attempted on the distribution of metals among different sediment phases.

The overall average concentration of different fractions of heavy metals studied and their average percentage distribution are presented in Figures. 5.10a and 5.10b. Residual phase was found the prominent metal host for all metals. Lead recorded highest percentage (67.86%) among the metals in residual phases.



1 - Exchangeable; 2 - Carbonate bound; 3 - Easily reducible; 4 - Organic bound; 5 - Residual

Fig. 5.10 Chemical partitioning of heavy metals in the sediments of Chitrapuzha River

a) Concentration (mg/kg) ; b) percentage

Oxidizable phase was the second most important host for all metals. Copper behaved in a very different manner. Oxidizable phase was as important as residual in the case of copper. This fraction accounts for 42.06% of total copper. Distribution of manganese among different phases was noticeable. All the phases except exchangeable were of similar importance as manganese hosts. A high variability was observed, in both the absolute and relative amounts of various fractions of the metals. This is expected since the chemistry of metals differed greatly; so too their extractability from sediments by various extractants.

5.3.1 Exchangeable Phase

The metals present in the exchangeable fraction are usually thought to be the most loosely bound form and readily mobile (Tessier et. al., 1979; Tessier and Cambell., 1987). Numerous studies performed on sediments or on their major constituents (clays, hydrated oxides of iron and manganese, humic acids) have demonstrated the adsorption of metals; changes in water ionic composition are likely to affect sorption–desorption processes. Magnesium chloride (pH 7) is admirably suited for the simultaneous determination of all exchangeable cations. Since it has no effect on carbonates, oxides, silicates, sulphides or organic matter in the sediments, the metals extracted could be regarded as the best estimate of exchangeable heavy metals present in sediments.

A number of sediment forming materials with large surface area such as clay minerals, amorphous iron and manganese oxides as well as organic substances are capable of adsorbing heavy metals either by cation exchange or as a result of intermolecular attraction. In sediments these substrates for ion adsorption occur in the form of associations and the properties of such aggregates are quite different from that of constituent particles. Thus it is impossible to establish a general order of affinities, applicable to individual heavy metals, based solely on ionic charge and ionic radii. Under estuarine conditions, the changing salinities and pH variations further complicate the issue (Bourg, 1983; Bilinski et. al. 1991).

The Station-wise annual mean data for the exchangeable fraction of metals is presented in Table 5.10. While manganese, iron, cobalt and nickel recorded their lowest annual mean concentrations in Zone 1, the other metals recorded in Zone 2. Highest values for all the metals were in the Zone 3. The order of abundance of the exchangeable fraction of the metals, in absolute quantities was, manganese > nickel > iron > zinc > cobalt > chromium > cadmium > copper > lead. In percentage terms, the order of abundance was nickel > cobalt > manganese > cadmium > zinc > copper > lead > chromium > iron (Tables 5.1 to 5.9).

Table 5.10 Annual mean concentration of the exchangeable fraction of heavy metals

Station	Cr_1	Mn_1	Fe_1	Co_1	Ni_1	Cu_1	Zn_1	Cd_1	Pb_1
mg/kg									
1	1.11	0.77	3.44	0.46	2.67	0.26	2.79	0.40	0.36
2	0.92	3.00	1.39	0.57	3.79	0.35	3.65	0.44	0.34
3	0.70	3.47	3.32	0.91	3.72	0.53	2.57	0.34	0.38
4	0.33	11.45	1.70	0.75	4.09	0.19	1.36	0.25	0.26
5	0.30	3.55	4.45	0.29	3.97	0.24	0.91	0.38	0.12
6	0.24	4.81	7.57	0.49	4.42	0.22	2.42	0.30	0.17
7	0.77	38.34	19.88	1.31	8.91	0.47	5.61	0.46	0.34
8	1.16	33.21	4.29	1.80	15.31	0.77	6.80	1.39	0.35
9	1.54	42.03	2.54	0.98	11.04	0.58	8.12	0.74	0.47
Percentage									
1	1.17	0.57	0.02	3.12	4.89	2.41	2.22	4.65	1.48
2	1.01	1.92	0.03	3.46	6.20	2.03	2.49	4.56	1.29
3	0.65	1.49	0.02	4.05	4.12	1.54	1.92	2.86	1.52
4	0.54	6.15	0.04	6.05	7.89	1.27	1.53	2.88	1.52
5	1.03	5.90	0.06	6.19	16.12	5.23	2.49	5.99	2.29
6	0.74	8.12	0.11	6.42	15.47	1.83	4.10	4.05	2.55
7	0.56	12.76	0.08	5.77	8.80	1.04	2.89	3.05	1.56
8	0.71	6.20	0.04	10.65	18.75	1.64	2.18	5.49	1.54
9	1.05	5.95	0.03	5.06	13.79	1.14	1.73	2.71	2.03

The lowest annual mean concentration of exchangeable fractions was recorded for lead (0.31mg/kg) and the highest (15.62 mg/kg) was for manganese (Fig. 5.10a). When only 1.75% of total lead was found in exchangeable phase, 5.45% of total manganese was present in this phase. The higher percentage of nickel, cobalt and manganese in the exchangeable fraction may be due to their affinity towards clay minerals and other adsorbing phases of sediments. The distribution of lead (1.75%), iron (0.05%), and chromium (0.83%) in the exchangeable fraction was very low and geochemically insignificant (Tables 5.1 to 5.9 and Fig. 5.10b). For manganese, iron, cobalt, nickel and lead the percentage exchangeable fraction showed decreasing trend from riverine to near marine regions (Table 5.10). The decrease in percentages of exchangeable fraction was due to the increase in salinity towards marine regions.

5.3.2 Carbonate Bound Phase

Several workers (Chester and Huges, 1967; Gupta and Chen, 1975) have shown that significant amounts of heavy metal could be associated with sediment carbonates. This fraction would be highly susceptible to changes in pH. Sodium acetate buffered at pH 5.0, was generally used for selectively extracting the carbonate fraction from the sediments. With this reagent, dissolution of the sediment carbonate was essentially complete and the attack on silicates and sulphide minerals was minimum. The organic fraction is not affected by this reagent. The Station-wise annual mean data for the carbonate bound fraction of metals is presented in Table 5.11.

Table 5.11 Annual mean concentration of the carbonate bound fraction of heavy metals

Station	Cr_2	Mn_2	Fe_2	Co_2	Ni_2	Cu_2	Zn_2	Cd_2	Pb_2
(mg/kg)									
1	0.75	38.70	169.41	0.56	7.29	0.33	11.75	0.59	0.81
2	1.23	46.13	282.60	0.84	12.15	0.67	14.29	0.85	0.85
3	0.74	84.72	194.57	0.79	10.92	0.83	13.48	0.69	0.94
4	0.88	50.83	110.05	0.91	7.58	0.78	13.81	0.78	0.52
5	0.56	8.86	107.72	0.36	3.68	0.42	7.42	0.57	0.21
6	0.80	14.48	100.17	0.81	5.84	0.81	9.28	1.00	0.32
7	0.85	71.48	121.17	1.78	8.40	0.45	12.61	1.74	1.01
8	2.91	87.31	6.23	1.72	15.73	3.48	42.40	5.05	0.92
9	2.19	143.12	4.74	1.47	10.84	1.72	42.83	3.56	0.97
Percentage									
1	0.78	22.52	0.58	4.32	12.00	2.99	10.64	7.62	3.09
2	1.38	30.35	0.96	4.76	19.64	3.74	12.42	9.33	3.33
3	0.67	33.81	0.56	3.75	12.92	2.53	10.38	6.56	3.10
4	1.60	28.39	0.43	7.28	12.96	4.00	16.10	9.30	2.61
5	2.09	14.77	0.99	6.67	14.72	8.61	23.16	9.33	2.73
6	2.14	25.09	0.79	9.55	18.58	6.89	18.03	14.31	3.04
7	0.66	24.62	0.49	8.04	8.61	1.02	6.95	11.27	4.06
8	1.81	16.84	0.03	9.63	18.97	7.10	14.09	19.98	3.36
9	1.50	22.68	0.03	7.63	13.20	3.55	9.93	13.82	2.87

Generally, metals bound carbonates recorded their lowest annual mean concentrations in Zone 2 and highest values in Zone 3 as observed for exchangeable fraction. The ord of abundance of the carbonate bound fraction of the metals, in percentage terms was, manganese > nickel > zinc > cadmium > cobalt > Copper > lead > chromium > iron (Tables 5.1 to 5.9). Lowest annual mean concentration was recorded for Pb_2 (0.73mg/kg) and the highest (121.85mg/kg) was for Fe_2. In relative terms Fe_2 (0.54%) and Mn_2 (23.61%) occupied the lowest and highest positions. (A distinct spatial variation, related to the salinity gradient as discussed in the case of exchangeable fraction was not observed for carbonate bound fractions. While chromium, zinc, cadmium and lead recorded higher values during pre-monsoon and post-monsoon seasons, iron and cobalt indicated monsoonal increase. Carbonate phase plays important role in scavenging manganese, nickel, zinc and cadmium, which accounted for 23.61%, 14.62%, 13.52% and 11.28% respectively.

5.3.3 Easily Reducible Phase

The easily reducible fraction is generally referred to as the oxides/ hydroxides of iron and manganese, which constitute significant sinks of heavy metals in aquatic systems, particularly under oxidizing conditions. The oxides /hydroxides of manganese and iron play and important role in scavenging heavy metals (Tessier et. al., 1979; Turner 2000) from pollution sources and from other naturally occurring geochemical phases in sediments. The processes involved are those of adsorption and co-precipitation (Adediran and Kramer, 1987). Under reducing conditions or acid conditions the sorbed metals are readily mobilized and this phenomenon is the basis of estimation of heavy metals in the easily reducible phase. The oxides/hydroxides of manganese and iron are major heavy metal hosts in estuarine sediments (Calmano and Forstner, 1983; Jones and Turki, 1997) and have been identified as important bioavailable metal sources (Louma and Davis, 1983). During early diagenesis microbially mediated redox reactions quickly result in the reduction of some of these insoluble Fe (III) and Mn (IV) oxides, and the release of soluble Fe(II) and Mn (II) species to the pore water. Dissolution will also release metals associated with the oxide phase to the pore water, possibly to the overlying water column (Petersen et. al., 1995), and to benthic biota. Leaching of sediments with a reducing agent such as hydroxylamine hydrochloride in presence of acetic acid, which keeps the liberated ions in solution, removes heavy metals associated with iron and manganese oxides.

Brannon et. al., 1977) noted that while the extractant dissolved approximately 85% of the manganese oxide, only 5% of the iron present was dissolved. Tessier et. al. (1979) also observed that manganese oxides were more easily leached than iron oxides. The Station-wise annual mean concentrations as well as percentage contributions of this fraction with respect to total metals, are presented in Table 5.12.

Table 5.12 Annual mean concentration of the easily reducible fraction of heavy metals

Station	Cr_3	Mn_3	Fe_3	Co_3	Ni_3	Cu_3	Zn_3	Cd_3	Pb_3
(mg/kg)									
1	10.60	50.71	4474.16	2.57	7.95	0.47	17.45	1.96	1.45
2	10.85	41.82	5022.82	2.34	8.19	0.30	26.00	2.26	1.29
3	16.20	58.48	6027.40	3.32	9.85	0.42	23.88	2.52	1.76
4	9.04	40.99	4617.53	2.38	5.60	0.44	21.98	2.06	1.00
5	4.92	11.25	2027.76	0.73	2.69	0.17	6.75	1.48	0.49
6	6.35	16.07	2232.24	1.31	2.79	0.22	13.58	1.69	0.44
7	15.19	76.67	2820.37	2.31	8.96	0.39	48.45	4.37	1.39
8	16.44	184.51	492.41	2.16	10.98	1.28	88.51	5.96	1.90
9	10.53	152.94	281.98	2.46	7.51	0.92	48.96	6.67	2.28
Percentage									
1	9.63	30.48	17.37	16.83	12.58	2.76	17.14	23.31	6.11
2	10.13	27.74	17.65	14.25	13.18	1.85	21.77	23.33	5.94
3	12.38	23.77	16.60	15.45	11.61	1.68	18.74	22.22	6.75
4	12.53	23.00	18.85	17.70	10.29	2.19	25.07	23.78	5.52
5	13.08	17.86	23.72	15.68	10.48	4.08	16.14	24.37	7.79
6	13.73	24.94	17.44	16.17	9.97	1.76	24.68	23.16	3.64
7	9.94	25.75	8.85	10.01	10.06	0.93	27.50	28.42	6.31
8	8.77	37.90	1.83	12.42	13.39	2.71	25.36	22.88	8.75
9	5.89	23.41	1.21	13.09	9.81	2.01	11.36	25.44	9.29

No significant variation was observed in the distribution of metals in this phase. The order of abundance of easily reducible metals in percentage terms was manganese > cadmium > zinc > cobalt > iron > nickel > chromium > lead > copper (Tables 5.1 to 5.9). Cu_3 recorded lowest annual mean concentration in absolute (0.51 mg/kg) and relative (2.22%) terms. In absolute terms, Fe_3 recorded highest value (3140.54 mg/kg) but on relative basis Mn_3 occupied highest position (26.09%). The easily reducible fraction plays a greater role in scavenging manganese, cadmium, zinc and cobalt, accounting for 26.09%, 24.10%, 20.86% and 14.62%

respectively (Table 5.1to 5.9 and Figure 5.10 b). No general trend could be observed in the seasonal distribution of reducible metals. While chromium, cobalt, nickel and lead exhibited higher values during pre-monsoon/post-monsoon periods, cadmium recorded monsoonal increase. Manganese, iron, copper and zinc did not exhibit any significant seasonal variations.

5.3.4 Oxidizable Phase

Hydrogen peroxide in nitric acid medium was used to oxidise organic and sulphide matter in the sediment samples. The heavy metals solubilised after the oxidation of organic matter constituted the organic phase. Ability of heavy metals to form organic complexes has been reported by several investigators. (Lake et. al., 1989; Pardo et. al., 1990; Nolting et. al., 1999; Moore, 1991; Gerringa et. al., 1998; Xiangdong Li et. al., 2001). These complexes get flocculated and sedimented during estuarine mixing and thus contributing an appreciable percentage to total metals. Data on the Station-wise variation of organic and sulphide bound heavy metals in the sediments of Chitrapuzha River are presented in the Table 5.13.

Table 5.13 Annual mean concentration of the oxidizable fraction of heavy metals

Station	Cr_4	Mn_4	Fe_4	Co_4	Ni_4	Cu_4	Zn_4	Cd_4	Pb_4
(mg/kg)									
1	24.07	35.00	6189.75	3.35	11.91	6.95	22.26	2.47	6.03
2	21.15	34.02	7097.10	3.57	10.74	7.01	30.94	2.62	5.30
3	35.00	51.51	10025.23	4.80	19.15	13.05	30.08	3.50	6.23
4	17.54	34.71	5917.18	2.62	14.00	8.43	19.39	2.37	4.61
5	6.73	21.40	2554.66	1.12	4.17	2.44	8.01	1.52	1.70
6	9.66	14.57	3992.89	1.59	4.95	5.43	15.49	1.74	2.97
7	45.05	70.02	9222.17	5.99	27.87	24.55	46.45	4.25	5.48
8	32.01	98.15	2043.29	3.56	17.06	18.01	99.39	5.24	5.74
9	24.88	147.43	2066.55	4.22	22.01	28.46	143.93	6.11	6.89
Percentage									
1	25.50	18.37	24.97	21.41	21.05	34.99	21.98	29.68	22.52
2	23.17	18.13	25.36	22.02	17.23	38.42	25.80	27.85	20.54
3	32.32	22.61	27.58	22.46	22.35	39.03	23.63	31.33	21.54
4	27.74	18.41	23.03	18.97	25.60	38.05	20.59	28.27	22.90
5	20.14	28.76	29.87	25.18	18.04	38.48	20.64	24.90	22.09
6	25.49	19.25	28.59	20.71	17.19	42.63	21.29	24.59	24.18
7	35.61	25.53	27.93	26.23	29.25	51.13	27.89	27.57	20.48
8	19.53	20.32	7.66	20.13	20.38	38.43	29.81	19.96	20.85
9	17.02	25.16	9.24	22.31	26.59	57.39	33.82	22.76	21.14

Lowest overall annual mean concentration was recorded for Cd_4 (3.31mg/kg) and the highest (5456.53mg/kg) was for Fe_4 (Table 5.1 to 5.9). Spatial and seasonal distribution of metals in oxidizable phase was generally consistent with that of organic matter and clay content in the sediments. In relative terms Pb_4 (21.81%) and Cu_4 (42.06%) occupied the lowest and highest positions. For all metals except iron, the highest concentration in this fraction was detected in the Zone 3, the industrial region (Figs. 5.1 to 5.9). This is attributed mainly to the high organic matter in this Zone. Organic fraction constituted major portion for all metals studied, especially for copper. It was the second most important metal host for all the metals except manganese. The oxidizable fraction constituted 42% of total copper in the study area. The order of abundance of oxidizable fraction in terms of percentage in the sediments of Chitrapuzha River was copper > cadmium > chromium > zinc > iron > cobalt > nickel > manganese > lead.

5.3.5 Residual Phase

The residual fraction is generally composed of primary and secondary weathered minerals which are for most part a very stable portion of the elemental constituents (Brannon et. al., 1977). Since metals bound to this fraction were expected to be stable and biologically inactive, strong acid digestion was required to dissolve the metals out of the residual phase. A solution of perchloric acid, nitric acid and hydrochloric acid in the ratio 1:1:3 was used to bring about digestion. The Station-wise annual mean concentrations as well as percentage contributions of residual fraction with respect to total metals are presented in Table 5.14. All metals recorded lowest concentration at Station 5. Metals except cobalt and nickel recorded their highest mean concentration either at Station 8 or 9. The residual fraction represented an essentially non-labile component, and the results confirmed that this form was an important sink for heavy metals in sediments. Generally heavy metal concentrations observed in this fraction were higher than any other fractions except for manganese (Table 5.1 to 5.9). For chromium, iron, cobalt and lead more than 50% of total metal was detected in this fraction. Cadmium and manganese seemed to be the most loosely bound metals in the study area since the percentages of residual fraction of these metals detected was the lowest. Nickel, copper and zinc showed lower percentage values in Zone 3, indicating anthropogenic input of these metals (Table 5.14).

Table 5.14 Annual mean concentration of the residual fraction of heavy metals

Station	Cr_5	Mn_5	Fe_5	Co_5	Ni_5	Cu_5	Zn_5	Cd_5	Pb_5
(mg/kg)									
1	57.13	62.04	15323.30	8.16	32.25	11.29	50.61	2.93	18.34
2	56.82	53.54	15945.19	9.19	28.98	10.06	46.50	3.30	18.07
3	55.77	58.75	20217.63	11.44	41.84	18.29	58.11	4.02	20.32
4	33.49	50.20	15375.74	7.37	24.66	11.57	32.31	2.97	13.90
5	19.61	29.79	4195.40	1.93	10.65	3.02	13.14	2.18	4.55
6	20.20	29.94	6762.95	3.93	11.54	6.28	22.43	2.40	8.13
7	65.02	46.98	19259.83	11.27	41.17	21.53	58.62	4.52	17.87
8	110.36	130.98	20554.73	8.45	23.59	25.08	96.33	8.20	18.75
9	107.12	140.22	16914.02	9.85	30.16	20.01	189.04	9.37	22.02
Percentage									
1	60.76	28.06	57.06	54.48	49.47	56.84	48.02	35.10	68.24
2	62.58	21.86	56.03	55.51	43.75	53.96	37.51	34.98	70.06
3	51.46	18.31	55.25	54.29	48.83	55.22	45.34	37.04	68.42
4	54.60	24.04	57.68	50.00	43.26	54.49	36.71	35.84	68.07
5	60.65	32.71	45.37	46.28	40.64	43.61	37.58	35.49	65.50
6	54.95	22.61	53.13	47.15	38.79	46.88	31.91	33.90	66.79
7	51.27	12.97	62.66	49.95	43.29	45.88	34.77	29.69	68.54
8	67.83	21.20	90.45	47.17	28.51	50.11	28.56	31.68	67.84
9	73.21	25.33	89.50	51.91	36.60	35.91	43.15	35.27	67.29

Higher percentage of metals in residual fraction was pointed out in many studies on estuarine sediments (Tessier et. al., 1980; Martin et. al., 1987). The abundance of metals associated with this phase followed the order: lead > iron > chromium > cobalt > copper > nickel > zinc > cadmium > manganese (Table 5.1 to 5.9). The order of abundance clearly indicated the high environmental mobility of zinc, cadmium and manganese. Low percentages of zinc, cadmium and manganese in the residual fraction were reported for several other estuaries (Samanidou and Fytianose, 1987; Prohic and Kniewald, 1987; Pardo et. al., 1990; Izquierdo et. al., 1997; Jones and Turki, 1997; Ismail et. al., 1994). The chemical speciation thus showed the existence of a category of heavy metals, which are relatively depleted in the residual phase.

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Chapter 6

SUMMARY

Heavy metal contamination in aquatic system is one of the largest threats to environmental quality and human health. The concentration of pollutants in different environmental compartments are related to each other through the action of inter-compartment mass transfer processes. Such mass transfer processes decide the fate of pollutants, both organic and inorganic. A thorough assessment of the relative concentrations of pollutants in the different environmentally significant compartments of an aquatic system is an essential pre-requisite for any systematic hazard evaluation programme. The present investigation involves such a comprehensive approach, in which the water, particulate and sediment phases of Chitrapuzha tropical tidal river have been collected and analysed in a single study. In a gradually changing environment, the knowledge of chemical speciation of heavy metals in sediments is essential for the full understanding of processes controlling heavy metal distribution in estuaries. The salient features of the study are summarized in the following paragraphs.

Based on specific geographical features, water flow regimes and anthropogenic activities, 9 sampling locations were selected. Samples were collected at monthly intervals between January and December 1999. Stations 1-3, (Zone 1) are saline, Stations 4 - 6 (Zone 2) are of intermediate salinities and Stations, 7-9, (Zone 3) are fresh water Zones. Salinity values ranged from 0.03 x 10^{-3} to 32.30 x 10^{-3} in surface waters and from 0.03 x 10^{-3} to 32.60 x 10^{-3} in bottom waters during the period of study. No deoxygenated conditions were observed at any Station in the lower reaches of Chitrapuzha. Variations in dissolved oxygen ranged between 2.16 to 10.30 ml/l in surface waters and between 2.25 to 7.96 ml/l in bottom waters. The pH variations were in the range of 6.10 to 8.10 (in surface water) and 6.20 to 10.60 (in bottom water). Generally the Stations in Zone 3 recorded high clay content while the Stations in Zone 2 recorded high percentage of sand. Sand, silt and clay were present almost equally in the sediments of Zone 1. Zone 1 and 3 recorded higher values of sediment organic carbon during all seasons whereas Zone 2 (especially Station 5 and 6) recorded minimum values. Lower organic content at Stations 5 and 6 was associated with the prominent coarse sandy sediment fractions. In Zone 1, sediment organic carbon exhibited a decreasing trend towards the bar-mouth. The concentration of total phosphorus varied from 0.29 mg/g to 101.44 mg/g. The total phosphorus in the surficial sediments exhibited an increasing trend from Stations 1 to 9 except at Stations 5 and 6 where the sediments were sandy. The very high concentration of phosphorus at Stations 7 to 9 is attributed to the discharge of effluents containing phosphorus fertilizers from the fertilizer manufacturing company situated near Station 9 and also to the spilling of phosphoric acid while pumping acid from the cargo barges to the fertilizer company.

The concentration of dissolved metals varied over a wide interval; iron was the most abundant and cobalt was the least abundant in the study area. The observed order of abundance was: iron > zinc > manganese > nickel > lead > copper > chromium > cadmium > cobalt in both surface and bottom waters. All the metals recorded higher annual mean concentrations in the industrial Zone (Zone 3) of Chitrapuzha River. The concentration of metals except cadmium in water was high during low salinity period (monsoon) indicating an inverse relationship. No significant correlation was struck between the dissolved metals and the hydrographic parameters pH, dissolved oxygen and suspended solids. The quantification of trace metal enrichment in waters of Chitrapuzha River was attempted by calculating the enrichment ratio. The concentration of dissolved metals from a far upstream site, which is free from industrial pollution (Station R), was considered for the calculation of enrichment ratio. The calculations showed that enrichment of metals was high in the Zone 3. Enrichment of metals in water was found to be high during monsoon, but nickel showed high enrichment during pre-monsoon period. Iron is depleted in the Stations 3, 4 and 5 during pre-monsoon and post-monsoon periods while zinc showed depletion in Zone 1 and 2 during pre and post-monsoon. Enrichment ratios proved that Cadmium was the only metal that is enriched to very high level in the study area.

A large fraction of the heavy metals carried by the Chitrapuzha River is bound to the suspended particulate matter. Results indicate that the distributions of particulate metals along the river are significantly influenced by strong dilution of the river-borne materials by seawater. Investigation revealed the following salient features with respect to the seasonal and spatial distribution of particulate heavy metals. The concentration of these metals varied over a wide interval; iron was the most abundant and cadmium was the least abundant metal in the study area. The observed order of abundance which differs from that of dissolved metals, was iron > manganese > zinc > lead > nickel > chromium > cobalt > copper > cadmium in both surface and bottom particulates. The spatial variations of particulate metals generally followed the trend found in dissolved metals. When chromium, iron, nickel, copper, zinc, cadmium and lead exhibited higher values in Zone 3, manganese and cobalt recorded higher values in the Zone 2. There was an inverse relationship between metal levels in particulate matter and salinity. Unlike dissolved metals, particulate metals were subjected to considerable variations seasonally. While chromium, iron. manganese and nickel recorded higher values during the monsoon season, cadmium and cobalt showed higher values during post-monsoon season. While zinc recorded higher values during pre-monsoon season, copper and lead recorded no significant seasonal variations.

The concentration of total metals in sediment varied over a wide interval. The large variations in trace metal distribution observed were primarily due to the variations in particle size, organic matter content, net deposition rates and sediment mixing. Iron was the most abundant (annual mean 25.56 mg/g) and cadmium (annual mean 12.87 mg/kg) was the least abundant metal in the study area. The observed order of abundance was: iron > manganese > zinc > chromium > nickel > copper > lead > cobalt > cadmium. All the metals showed a decreasing tendency towards the bar-mouth, which may be due to the tidal flushing and the impact of waves that remove the finer fractions of the sediments from the bar-mouth. Mixing of contaminated estuarine sediment with relatively uncontaminated marine material may be another factor causing the above depletion. A similar decrease in concentration of sediment metals was reported in the Cochin estuary previously by Nair (1992). Except iron and lead, all other metals recorded higher concentration in Zone 3. Discharge of effluents containing heavy metals from various industries including fertilizer and petrochemical units may be the major reason for it. Chemical substances such as rock phosphate, phosphoric acid and sulphur falling into water while transferring them from cargo barges to the fertilizer firm may also contribute to high level of metals in the sediments in this Zone.

Other factors that may enhance metal concentration in Chitrapuzha River are the high concentration of organic carbon, phosphorus and fine grains in the sediments. All the metals recorded their minimum values in Zone 2, which was a result of the predominantly sandy nature of the sediment in this Zone. Another striking observation was the similarity in the spatial distribution pattern of the heavy metals cobalt, nickel and lead. At all the Stations, their annual mean variation was found to be analogous. The uniformity in spatial variation of metals in the sediment suggests similarity in estuarine mixing behavior and occurrence of sources of metals.

All the metals exhibited significant seasonal variations. Metals except cadmium generally recorded higher values during pre-monsoon and post-monsoon periods and lower values during monsoon period. Higher concentration of metals during pre-monsoon and post monsoon periods may be attributed to high saline conditions, which might cause the dissolved metals to precipitate and flocculate. The decrease in concentration of sediment total cadmium during pre-monsoon and post-monsoon seasons may be due to the formation of chloride complexes occurring during the mixing of fresh water with seawater. It may also be attributed to the desorption of exchangeable cadmium due to the increase in concentration of major ions during saline intrusion.

Quantification of trace metal enrichment in the sediments of Chitrapuzha River during different seasons was attempted by calculating the enrichment factor. Seasonal enrichment factors of heavy metals were calculated to assess the extent of metal pollution in sediments. It was found that all the trace metals were enriched in Chitrapuzha River to varying extents. The enrichment factors showed no significant seasonal variation except in the case of lead. Enrichment factor for lead exhibited seasonal variation with higher values during pre-monsoon and post-monsoon seasons. The depletion of cobalt at stations 1 to 6 during all the seasons may be attributed to absence of contributing sources. The contamination was found high in Zone 3. Zinc, chromium and cadmium showed strong enrichment when compared to other metals in Chitrapuzha River especially at Stations 8 and 9.

In order to gain understanding about variables, which influence the distribution pattern of total metals during different seasons, a number of sediment parameters were examined. The sediment parameters considered were sediment organic carbon, total phosphorus, total iron and clay content. Multiple regression analysis was performed on the total metal concentrations considering these variables as independent. The regression models were generally found to fit all metals and the combination of four factors explained 46% to 91% of variations in the distribution of total metals in the sediments irrespective of seasons. For lead this combination could explain only 32% of variations during pre-monsoon. The analysis has categorically proved the existence of a patent relationship between total phosphorus and metal distribution. Multiple regression analysis on total metals in the sediments of Chitrapuzha River indicated that besides the four selected parameters, there exist some other factors also that influence the pattern of metal speciation in surficial sediments.

Spatial and seasonal distribution patterns of the five fractions viz. exchangeable, carbonate bound, residual, oxidizable and residual fractions of each of the nine heavy metals in the sediments were studied in relation to sedimentological and geochemical processes that are active in a tropical tidal river. For partitioning of heavy metals into various accumulative phases, the sequential extraction scheme proposed by Tessier et. al. (1979) was used. In terms of pattern of speciation, significant differences among metals and between Stations were identified. It was established that the estuarine processes had the potential to significantly alter the chemical speciation of metals in the sediments. Survey revealed the differences in behaviour of metals in preferential accumulation in sediments. Residual phase was found to be the most prominent host for all metals except manganese. Lead recorded highest percentage (67.86%) among the metals in residual phases. Oxidizable phase was the second most important host for metals. Copper clearly showed its affinity for organic matter in the sediment phase. Oxidizable metal fraction accounted for 42.06% of total copper in the sediments. Distribution of manganese among different phases was noticeable. All the phases except exchangeable were of comparable importance as manganese hosts. A high variability was observed, in both the absolute and relative amounts of various fractions of the metals. This is expected since the chemistry of metals differed greatly; so too their extractability from sediments by various extractants.

In percentage terms, the order of abundance of exchangeable metals was: nickel > cobalt > manganese > cadmium > zinc > copper > lead > chromium > iron. The lowest annual mean concentration of exchangeable fractions was recorded for lead (0.31mg/kg) and the highest (15.62 mg/kg) was for manganese. When only 1.75% of total lead was found in exchangeable phase, 5.45% of total manganese was present in this phase. The higher percentage of nickel, cobalt and manganese in the exchangeable fraction may be due to their affinity towards clay minerals and other adsorbing phases of sediments. The distribution of lead (1.75%), iron (0.05%), and chromium (0.83%) in the exchangeable fraction was very low and was geochemically insignificant. For manganese, iron, cobalt, nickel and lead, the percentage exchangeable fraction showed a decreasing trend from riverine to near marine regions. The decrease in percentages of exchangeable fraction was due to the increase in salinity towards marine regions. Exchangeable metals except manganese and iron exhibited significant seasonal variations. Chromium, cobalt, nickel, zinc and lead recorded comparatively higher values during pre-monsoon and post-monsoon seasons. Cadmium recorded high concentration during monsoon and post monsoon seasons while copper recorded high post-monsoon values.

The order of abundance of the carbonate bound fraction of the metals, in percentage terms was, manganese > nickel > zinc > cadmium > cobalt > copper > lead > chromium > iron. The carbonate phase played an important role in scavenging manganese, nickel, zinc and cadmium, which accounted for 23.61%, 14.62%, 13.52% and 11.28% respectively. All metals except manganese, cobalt and nickel exhibited significant seasonal variations. While chromium, nickel, cadmium and lead recorded higher values during pre-monsoon and post-monsoon seasons iron and copper recorded high values during monsoon season. The order of abundance of easily reducible metals in percentage terms was manganese > cadmium > zinc > cobalt > iron > nickel > chromium > lead > copper. The easily reducible fraction played a greater role in scavenging manganese, cadmium, zinc and cobalt, accounting for 26.09%, 24.10%, 20.86% and 14.62% respectively. No general trend could be observed in the seasonal distribution of reducible metals. While chromium, manganese, cobalt, nickel and lead exhibited higher values during pre-monsoon/post-monsoon periods, cadmium recorded a monsoonal increase. Iron, copper and zinc did not exhibit any significant seasonal variations.

Spatial and seasonal distribution of metals in the oxidizable phase was generally consistent with that of organic matter and clay content in the sediments. In relative terms Pb_4 (21.81%) and Cu_4 (42.06%) occupied the lowest and highest positions respectively. For all metals except iron, the highest concentration in this fraction was detected in the Zone 3, the industrial region. This is attributed mainly to the high organic matter in this Zone. Organic fraction constituted major portion for all metals studied, especially for copper. It was the second most important metal host for all the metals except manganese. The oxidizable fraction constituted 42% of total copper in the study area. The order of abundance of oxidizable fraction in terms of percentage in the sediments of Chitrapuzha River was copper > cadmium > chromium > zinc > iron > cobalt > nickel > manganese > lead. All metals in the oxidizable phase except manganese and cobalt generally exhibited significant seasonal variations with high values during pre-monsoon and post-monsoon seasons.

Generally heavy metal concentrations observed in the residual fraction were higher than that in any other fractions except for manganese. For chromium, iron, cobalt and lead more than 50% of total metal was detected in this fraction. Nickel, copper and zinc showed lower percentage values in Zone 3, indicating anthropogenic input of these metals (Table 5.14). Higher percentage of metals in residual fraction was reported in many studies on estuarine sediments (Tessier et. al., 1980; Martin et. al., 1987). The abundance of metals associated with this phase followed the order: lead > iron > chromium > cobalt > copper > nickel > zinc > cadmium > manganese. The order of abundance clearly indicated the high environmental mobility of zinc, cadmium and manganese. Chemical speciation showed the existence of a category of heavy metals, which are relatively depleted in the residual phase. All metals in the residual phase generally exhibited significant seasonal variations with higher values during pre-monsoon and post-monsoon seasons and lower values during monsoon season.

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