PHASE TRANSITIONS OF TRACE METALS IN THE AQUATIC ENVIRONMENT OF KUTTANAD, KERALA

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CERTIFICATE

This is to certify that this thesis is an authentic record of the research carried out by Shri. P Unnikrishnan, 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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DECLARATION

I hereby declare that this thesis entitled " PHASE TRASITIONS OF TRACE METALS IN THE AQUATIC ENVIRONMENT OF KUTTANAD, KERALA" is an authentic record of the research work carried out by me under the supervision and guidance of Dr. S. Muraleedharan Nair, Lecturer, Department of Chemical Oceanography, School of Marine Sciences, Cochin University of Science and Technology, in partial fulfilment of the requirements for the Ph.D. degree of Cochin University of Science and Technology and that no part of it has previously formed the basis for the award of any degree, diploma or associateship, fellowship or other similar title or recognition.

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PREFACE

Environmental persistence, fate and interactive effects with living organisms - beneficial or toxic - of trace elements are directly related to the physico-chemical forms in which they occur. Knowledge on the association of trace metals with different environmental compartments in an aquatic system are, therefore, essential for monitoring the trace metal pollution as well as transport, fate and bio-geochemical cycles of trace metals. This thesis is a modest attempt in assessing the trace metal levels and their behaviour in the aquatic environment of Kuttanad, an aquatic system that is severely affected by man's intervention on natural processes, by seriously evaluating the levels of trace metals in dissolved and particulate phases and also in the different chemical fractions of the sediments.

Understanding of the distributions, variations and transfer processes of trace metals in different environmental phases in the backwaters of Kuttanad is vital for the assessment of water pollution problems and study of the ecology of the area which contributes 20% of the rice production in the State of Kerala. Eventhough considerable amount of study has been done on the distribution of trace metals in the Cochin estuary, no data are available on the distribution of trace metals in the backwaters of Kuttanad, which is a continuation of Cochin estuary and forms the southern upstream part of Cochin estuarine System.

The thesis has been divided into 7 Chapters.

Chapter 1 gives a brief description about the estuarine environment with special reference to trace metals. The features of Kuttanad region and an update on scientific information about trace metals in the Cochin estuary are provided in this Chapter along with the aim and scope of the present study.

Chapter 2 gives the description of the study area, sampling procedures for water and sediment, and the various analytical techniques employed for the determination of different parameters. Chapter 3 presents the general hydrographic characteristics viz. temperature, depth, pH, salinity, dissolved oxygen and suspended solids. Concentrations of dissolved major ions like magnesium, calcium, strontium, barium and boron, and data recorded on the sediment characteristics like moisture, texture and organic carbon are also included in this Chapter. The seasonal and spatial variations observed have been critically analysed in relation to the varying estuarine conditions. The inter-relationships between dissolved major ions and environmental variables like chlorinity are also discussed.

Chapter 4 reports the temporal and spatial variations in the distributions of ten dissolved trace metals viz., cadmium, cobalt, copper, chromium, iron, manganese, molybdenum, nickel, lead and zinc. The fluctuations in the concentrations of trace metals during the different seasons of the year are explained against the background of the physico-chemical features and the combined effects of domestic and industrial inputs. Chapter 5 describes the distribution of trace metals associated with particulate phase. Seasonal and spatial variations in the concentrations of particulate trace metals are discussed in this Chapter. The inter relationship with other environmental parameters along with the partitioning of trace metals between water and suspended solids are discussed.

Chapter 6 discusses the cyclic behaviour in the distribution of total sediment associated trace metals viz., cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead and zinc. Sequential chemical extraction experiments for estimating characteristic association of different forms of trace metals and their mobility in sediment are also dealt in this Chapter. The major fractions identified are exchangeable fraction, Fe-Mn oxide bound fraction and the residual fraction, which includes organic bound fraction also. The data on the partitioning studies of sediment associated trace metals provide information on the relative changes of elemental phases and thereby an insight into the diagenetic processes taking place after deposition of the sedimentary components. The above data are also used for the assessment of trace metal mobility in the backwaters of Kuttanad region.

Chapter 7 portrays a flow reactor model of the study area based on the principles of steady state approximation taking into account of the various equilibrium existing between the environmental compartments for the resolution of the complexities that determine the trace metal fluxes.

A list of references is included at the end. The monthly values of various parameters are appended at the end due to their exhaustive nature and is removed from the text, while the corresponding figures depicting the annual mean variations, seasonal variations, zonal variations, summary statistics and the various derived parameters are included in the text itself.

CONTENTS

CHAPTER 1

INTRODUCTION

"Estuaries are a happy land, rich in the nutrients of the continent itself, stirred by the forces of nature like the soup of a French Chef, the home of myriad forms of life from bacteria and protozoan to grasses and mammals: the nursery, resting place and refuge of countless species" – Stanley. A. Cain.

To those of us who enjoy the ocean, an estuary is simply a place where the incoming ocean meets flowing rivers and streams, forming mudflats and marshes. As freshwater meets the ocean, both land and ocean contribute to a beautiful and fragile ecosystem. They are crucial transition zones between land and water that provide an environment for lessons in biology, geology, chemistry, physics, history and social issues. Since colonial times, we have used estuaries and their connecting network of rivers for transporting agricultural goods for manufacturing and trade. Estuaries, in short, are natural treasures – vital ecological and community resources – whose health affects our health and the vibrancy of our communities and economy.

Estuaries are one among the highly productive ecosystems, accounting for one-half of the living matter of the world's ocean. Unfortunately, these ecosystems usually bear the brunt of human waste and contamination because they were and are the first areas of human settlement. Organic effluents such as domestic sewage is s serious problem - the discharge of small quantities of sewage into estuarine systems can actually increase the productivity of the ecosystem, but excessive quantities will deplete oxygen - causing severe threats to aquatic life. Industrial wastes, with its large load of heavy metals, can be toxic even at low concentrations. Estuaries receive all materials coming from the river catchments This material, fine sediments, contaminants, and other pollutants may accumulate in the estuary and remain there for long periods before being definitely washed to the open sea - thus affecting the sustainability of an ecosystem which is immensely valuable from an ecological, social and economic perspectives.

Estuarine and coastal zones are the sites of major discharges of urban and industrial pollutants. While there are common basic biogeochemical processes, differences in time scales of mixing and transport, in biological productivity or in sedimentary regimes, lead to major differences in pollutant routes, cycling and fate in coastal zones. Data from riverine systems of differing geology, climatology and physio-graphy as well as differing anthropogenic influences are needed to better assess natural variability and to provide a basis for differentiating natural from unnatural values.

An estuary will typically contain waters in a mixing series from river water, which globally has an estimated average dissolved salt content of 120 mg/l (Livingstone, 1963), to sea water with a salinity approaching that of the open ocean, which is typically about 35 ‰. Such an environment is an important transition zone in the series of aquatic environment in which aqueous solutions and solid phases interact during the major sedimentary cycle. The particular problems of estuarine chemistry over and above those inherent in the chemistry of any natural water system arise because of the marked gradients in ionic strength and in concentrations of individual chemical species, and the generally high concentration of suspended matter and its variable composition. The shallowness of most estuaries, with associated possibilities of sediment resuspension, together with the frequently high levels of biological activity, can introduce additional complexity.

In river waters, there are wide variations in both the total concentration of dissolved salts and the composition of the dissolved material with respect to both the major and minor constituents. Coastal sea water, by comparison, can be regarded as of approximately uniform composition, although considerable variations occur for some of the minor constituents. Within each estuary, there will be at least one individually characteristic mixing series between dilute and saline end members.

The main factors leading to variations in the composition of river waters have been discussed by Livingstone (1963) and Gibbs (1970). Some rivers receive a major part of their dissolved salts in precipitation over the drainage area. Dissolved silicon and potassium enter largely from rock weathering (Gibbs, 1970). Variation in the composition of precipitation and in subsequent evaporation leads to regional and seasonal variations, but rivers are generally characterised by low concentrations of total dissolved salts. Where rock weathering is the dominant influence on composition, regional variations are determined primarily by the geological character of the drainage area. Temporal variations arise mainly through differences in the proportions of ground water flow and surface runoff (Livingstone, 1963). The general trend is for the latter to cause dilution of the river water, with striking effects in some cases.

The basic influence on estuarine chemical processes is related to the compositional gradient associated with it. The shallowness of most estuaries makes complexity due to the sediment resuspension and biological activity. The high river discharge creates virtually a fresh water surface layer near the head of the estuary. This flows seaward over a saline lower layer. Estuarine mixing mainly involves three processes; the precipitation of dissolved material, the uptake of dissolved material into solid phase and the release of material into solution. The relative composition of river water differs from that of sea water and their mixing yields in principle estuarine water in which the proportions of the major ions and trace elements differ from those in the oceans and rivers. The extent of mixing in an estuary depends upon a large number of factors such as the seasonally variable river flow, the tidal cycle, the wind character, the topography and the relative temperatures of river water and the sea water.

KUTTANAD

Kuttanad is an amazing labyrinth of shimmering waterways composed of lakes, canals, rivers and rivulets. Kuttanad is called the rice bowl of Kerala, because for her wealth of paddy crops are at the very heart of the backwaters. The scenic country side of Kuttanad also has a rich crop of bananas, casava and yams, which accompany the rice bowl as "side dishes" This is perhaps the only land in the world where farming is done below sea level. Inland waterways, which flow above land level, are an amazing feature of this unique land.

Location

Kuttanad is a low-lying area, located in the State of Kerala, in the south-west coast of Indian peninsula. The area is located in central Kerala and is south of Kochi, "the Queen of Arabian Sea" Originally it was a part of the shallow coastal area of the Arabian Sea. As a result of geological uplift, a shallow bay was formed into which the rivers draining from the mountains to the east discharge. The coast has been formed by the silt deposits carried by these rivers. The bay has become an extensive brackish water lagoon and backwater system extending from Alappuzha (Alleppey) in the south to Kochi (Cochin) in the north, and connected to the sea by the Cochin channel. The Kuttanad covers parts of the districts of Alleppey, Kottayam, and Pathanamthitta, which comprise a total of 54 villages in 10 talukes (sub-districts) with a total population of 1.4 million. The area of Kuttanad extends over 1,100 km^2 (110,000 ha) and supports a population of over 1.4 million. The area has a monsoon climate with a wet season from mid of May to November and a dry season from December to April.

Background

The Vembanad Lake is situated at southern part of Cochin backwater system. Bunding of shallow parts of the lagoon started at least a century ago. Bunds were not intended to prevent flooding by the rivers, but to enable paddy cultivation between the end of the wet season (November) and the time when water in the southern part of the lagoon became too saline for agriculture (March), known as punja cultivation. This type of cultivation is characterized by the dewatering of land left to flood at the end of the wet season.

The area separated from the shallow parts of the lagoon by the construction of bunds is called "padasekharams" which means a group of paddy fields. The total area of paddy fields thus reclaimed is about 55,000 ha, and some of the paddy fields thus reclaimed are located 2.5 m below mean sea level (MSL). A landscape of innumerable waterways was developed as a result of such reclamations of land.

A spillway was constructed at Thottappally in 1955 to divert floodwaters of the Pamba, Manimala and Achenkoil Rivers straight to the sea. The intention was to limit flood levels to below the bund levels, which would enable cropping in the wet season in the "padasekharams" But its capacity was insufficient to keep flood levels below the low bund crests, partly because the channel leading to the spillway was not constructed as wide as planned. As a consequence, cropping in the wet season was limited and flood damage occurred regularly. In 1975, a salinity barrier was constructed at Thanneermukkam to retain fresh water and reduce saltwater intrusion in the dry season. South of the barrier, where water in the lagoon is fresh, is known as Vembanad Lake. While the barrier has improved crop production, the side effects, particularly on fisheries and the aquatic environment, have been significant and have led conflicts between the farming and fisheries communities.

The four rivers draining into the Kuttanad area are the Pamba River, Manimala River, Meenachil River and Achencovil River. The Pamba River is the third longest river (176km) in Kerala. It is formed by the confluence of the Pamba Aar, the Kakki Aar, the Arudai Aar, the Kakkad Aar and Kall Aar. The drainage area of the river is 2235 sq.km. and annual yield is 4641 Mm^3.The Manimala River rises at an altitude of 1156 m, above MSL in Tatamala and gains shape only from Elamkadu Estate. It drains an area of 847 sq.km. and the length of the river is just 90 km. with an annual yield 1829 Mm^3 The Meenachil River is formed by joining of several streams originating from the Western Ghats. Although the length of the river is only 78 km, the drainage area is considerably larger (1272 sq.km) with an annual yield 2349 Mm^3 Several small streams originating from the Pasikida Mettu, Ramakkul Teri and Rishi Malai at altitudes ranging between +700 m and +160 m above MSL join together to form Achenkoil River. The length of the river is 128 km. The total drainage area is 1484 sq.km. with an annual yield 2873 Mm^3

Economic activities

Agriculture is the major economic activity in the area, employing about 40 % of the population directly. Paddy is virtually the only crop grown in the "padasekharams" and the poor drainage conditions makes most of the land in the "padasekharams" unsuitable for other crops. Coconut is grown on the bunds and on higher areas. The main paddy crop in the Kuttanad is still the punja crop grown in the early part of the dry season, November-March.

Estuarine fisheries are another activity in the Kuttanad area employing about 21,000 full and part-time fishermen (KWBS, 1989). Estuarine fisheries are of significant commercial importance. A survey revealed an annual production of 7,200 M.T. of fish valued at Rs.96 million in the lagoon and 70 % of the 3,000 M.T. of marine prawns landed annually at Cochin consist of species which spend part of their life cycle in the estuarine environment of the Cochin backwater (KWBS, 1989).

Secondary (predominantly coconut-based household and cottage industries) and tertiary (trade, commerce) activities are more developed in the western plains and some eastern areas. The coir production, through retting of coconut husk, is a traditional occupation and a major economic activity in the area. More than 70 % of coir produced in India comes from Kerala, which annually produces about 120,000 M.T. of the fibre. A major portion of the fibre used for coir industry is produced in Alleppey district. This industry employs approximately 3,83,000 people, about 84% of whom are women (KWBS, 1989). Coconut husk is transported from plantations to coastal area for retting. The process involves immersion of husk in shallow backwaters for 6 to 9 months. After that, decayed material is removed from the fibre by pounding. Bacteria act on the organic matter during the process and release putrefied and toxic materials into the environment. Hydrogen sulphide, methane and phenol compounds are released into water which kill fauna and flora. Several stretches of backwaters have become unusable due to this activity. pH value of water in retting area often becomes significantly lower than that in a non-retting zone. The concentration of phosphates, nitrates and hydrogen sulphide is higher (KWBS, 1989). The presence of sulphide imparts a greyish black colour to water, restricting light penetration and inhibiting photosynthesis. It damages the fragile ecosystem. The husks have to be submerged in water for a period of 4 to 12 months to obtain the fibre for further processing in the "coir" industry. About 250 ha of water area is used for this activity in the Kuttanad (KWBS, 1989). The retting process is promoted by flushing with oxygen-rich water. Thus, most sites are located in areas subject to tidal flushing. The areas used for retting become anoxic for part of the year.

The industries in and around the area are agro-based, consisting of various types of rubber processing units in the east and coconut processing plants in the west.

Topography

There are three identifiable topographic features: the dry (or garden) lands, wet lands and water areas. The dry lands vary in elevation from 0.50 – 2.50 m above mean sea level (MSL) and are about 31,000 ha in area. Most of the population lives on these lands, which mainly occur in the peripheral areas of the Kuttanad. The wetlands include low lying areas slightly above MSL (11,000 ha) and areas below MSL reclaimed from the lagoon (55,000 ha). Lakes, rivers and channels make up the remaining 13,000 ha.

Rainfall, weather and climate

The total annual rainfall of the state of Kerala, varies widely ie., from about 4500 mm in the northern part of Kerala to about 2000 mm in the south. The southwest monsoon, the principal rainy season of Kerala, accounts for about 73 % of the total annual rainfall. Further the rainfall during southwest monsoon decreases from the northern districts (85 %) to the southern districts (54 %). The northeast monsoon (7 – 25 %) and the hot weather pre-monsoon thunder showers during March- May (10 – 20 %) respectively accounts for the rest of the rainfall. The average rainfall in the Kuttanad area is about 3,000 mm/year.

From the stand point of weather and climate, the calendar year in Kerala can be divided into the following four seasons (Abdulla Bava, 1996).

1. Winter (January – February)
2. Hot weather period (March – May)

3. Southwest monsoon (June – September)
4. Northeast monsoon (October –December)

Two seasons are apparent: the wet season from June to November and the dry season from December to May. The wet season starts with southwest monsoon, which lasts until September, and continues with the northeast monsoon until November. Conditions are generally less severe in the northeast than in the southwest monsoon. Some rain usually falls in the dry season. Although significant rainfall can occur in March and April, the amounts are very variable. For the purpose of discussion, the calendar year is divided into three:

The monsoon season (June to September)
The post-monsoon season (October to January) and
The pre-monsoon season (February to May)

Thanneermukkam barrier

The Thanneermukkam barrier across the estuary was commissioned in 1975. The barrier was designed to prevent salinity intrusion into the southern part of the Cochin estuarine system (Kuttanad backwaters) in the dry season and also to retain the fresh water from the rivers flowing into the estuary. The structure has been relatively successful in keeping the water in the Kuttanad fresh and enabling cropping in the dry season to be increased. However, the barrier has had various adverse effects. Some were foreseen at the time of its conception, such as the reduction in fisheries and an increase in aquatic weed growth. Others were unforeseen, such as the effect of the elimination of tidal flushing on pollution levels. The situation has been aggravated in recent years by the introduction of high yielding paddy varieties, which require heavy doses of fertilizers and pesticides. About 20,000 M.T of fertilizers and 500 M.T of pesticides are used annually in the Kuttanad and some enters the waterways and lake when water is pumped out of the paddy fields (KWBS, 1989). Since the construction of the barrier, the southern part of the Cochin backwater has been transformed into an area where salinities are too low for the prawns and fish that constitute the major resources for the estuarine fishery. Moreover, the migration routes of marine fish and prawns are interrupted by the barrier, its gates being closed during the pre-monsoon period when maximum upstream migration takes place (Kurup et al., 1990). The area south of the barrier is lost as a nursery ground for post larval prawns, which need salinities of about 15-20 ‰ for optimal growth (Kurup et al., 1990). The edible crab, which once supported a good fishery in this part of the backwater, is no longer found south of the barrier. During the closure of the barrier in the dry season, the upstream area is no longer flushed by the tides and water is polluted by pesticides from the agricultural lands and by organic waste dumped into the Kuttanad waters. Pollution is a contributory factor to the reduction in numbers of the giant freshwater prawn.

In total, 45 % of the rural population and 35 % of the population of the town of Allepey have no proper sanitation facilities (KWBS, 1989). In certain areas where salinity is not a constraint for using the water for drinking purposes, levels of contamination were found to be in general ten times higher than the allowable level according to the Indian Standards for production of drinking water by simple disinfections (KWBS, 1989). Sabarimala, one of the largest pilgrim centers in South India, is near the Pamba River. About 10 million people reach here annually from various parts of India after the monsoon season. These pilgrims use the Pamba River for their sanitation purposes. This also has a major role in polluting the Pamba River and consequently the Kuttanad area.

Trace metals in estuary

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. Trace metals, because of their relatively long half-life and biological significance, constitute one such class among non-degradable contaminants causing great concern.

The term "trace metal" or "trace element" is used in current literature to designate those elements, which occur in small concentrations in natural systems. For all practical purposes, the terms such as "trace metals", "trace inorganics", "heavy metals" "micro elements" and "micro nutrients" are treated as synonymous with the term trace elements (Forstner and Wittmann, 1983). Metals such as Fe, Zn, Cu, Mo, Cr, Co and Mn are essential for life but can be toxic when present at elevated levels.

Sources of metal pollution

The various anthropogenic activities by which trace metals are introduced into the aquatic systems include smelting, mining, shipping, industrial effluent discharge, urbanization, application of fertilizers, algicides, fungicides, automobile exhaust etc. Secondly, the natural processes that contribute metals to the aquatic environment include weathering of rocks, leaching of ore deposits, natural fires in the forests, terrestrial and marine volcanism etc. The above sources directly regulate the net flux of trace metals that interplay with natural/artificial systems and pose relevant questions of their cycling, transport and ultimate removal. Studies designed at quantifying these phenomena have led to the formulation of conceptual ideas of metal speciation.

In general, it is possible to distinguish between seven different sources from which metal pollution of the environment originates: (1) geological weathering (2) industrial processing of ores and metals (3) the use of metals and metal components (4) burning of fossil fuels, production of cement and bricks (5) leaching of metals from garbage and solid waste dumps (6) animal and human excretions which contain heavy metals and (7) non-point sources.

Upon attempting to locate the source of metal input of receiving water bodies, a distinction is often made between diffused non-point and point sources. Essentially, rural areas and agricultural land are regarded as non-point source, since the metal supply originates from vast regional areas.

Geological weathering is the source of baseline or background levels. It is to be expected that in areas characterized by metal-bearing formations, these metals will also occur at elevated levels in the water and bottom sediments of the particular area. Obviously, mineralized zones, when economically viable, are exploited to retrieve and process the ore. This inturn, leads to disposal of tailings, discharge of effluents and possibly smelting operations which result in atmospheric pollution. In consequence, the general problem arises of how to distinguish between natural geological weathering and metal enrichment attributable to human activities. During the processing of ores, metal bearing dust particles are formed, which may only be partially filtered out by air purification system. Appreciable quantities of metals go to waste during chemical metal refinement processes (e.g. galvanizing and pickling). Use of metals and metal compounds in industries poses another problem. For e.g., chromium salts used in processes in tanneries cause chromium pollution in the environment. Chlor-alkali industry is a major source of Hg pollution in the aquatic system. Similarly, copper compounds used as plant protection agents, zinc in water pipes and tetraethyl lead as anti-knock agent in gasoline are anthropogenic sources of Cu, Zn and Pb in the environment. Fossil fuel mobilization is particularly high for arsenic, zinc, cadmium, copper (coal), nickel and vanadium (oil). Strong emissions of zinc, lead, selenium and arsenic result from cement production (Goldberg, 1971).

It is of special interest to note that soil cultivation has been estimated to be responsible for 95-99 % of soil erosion (McElroy et al., 1975). The sediment resulting from soil erosion is today recognized as being the largest single pollutant affecting water quality. Robinson (1973) correctly pointed out that "...sediment is our greatest pollutant"

Concentrations of trace metals in coastal estuaries can be elevated due to high inputs from natural as well as anthropogenic sources. Thus, understanding the transport and distribution of trace metals in estuaries is a goal of environmental chemists. An assessment of the distribution of trace metals amongst various physical and chemical phases provides information which enhance our knowledge of the processes responsible for the behaviour of the metal in the estuaries, as well as the potential impact of the metal on the biota.

Estuarine behavior of trace metals

An estuary is a mixing zone of riverine and oceanic waters with widely varying compositions where end members interact both physically and chemically. The trace element chemistry in the estuarine environment has been an area of considerable research in the past decades. The importance of estuaries lies in the fact that they act as a mediator (filter) in the transfer of trace elements from continents to oceans. Estuaries, thus can be either a source or a sink for different trace metals. Therefore, it is imperative to study the composition of water and particles in the estuaries along with temporal fluctuations to identify different biogeochemical processes and pathways in metal cycling. It has been suggested that exchange reactions play a major role in the behaviour and transport of trace metals in estuaries (Bourg, 1983; Forstner et al., 1990).

Once introduced into the aquatic system, trace metals undergo chemical, physical and biological reactions such as sorption at solid-water interfaces, diffusive fluxes across the sediment-water interface, uptake by planktonic organisms, sedimentation etc. As a result of these reactions, a large fraction of the trace metals introduced into the aquatic environment is normally found associated with the bottom sediments. Typically, sedimentary metal concentrations are three to four orders of magnitude higher than those in the dissolved phase.

Uptake of trace metals by sediments and suspended particulates

The uptake of trace metals by sediments and suspended particulate matter may generally be due to the following:

1. physico-chemical adsorption,
2. biological uptake,
3. physical accumulation of metal enriched particulate matter by sedimentation or entrainment.

The degree of physico-chemical adsorption will be influenced by the nature of the surface of the sediment or particulate matter. Electrophoretic measurements suggest that the surfaces of particulate matter are coated with a thin film of natural organics and this film will exert a significant influence over the adsorption of trace metals by natural particulate matter. Natural organic matter has a very important influence on the distribution of trace metals in aquatic systems. It may complex with the trace metal keeping it in solution.

The metal-organic complex may be sorbed by particulate matter or the organic matter may be adsorbed to particulate matter, where it may then be able to complex with trace metal ions in the solution phase.

In addition to physico-chemical uptake, trace metals may be actively taken up by bacteria and algae. This results in sediment enrichment, when the metal enriched biomass is incorporated. Sedimentation of enriched particulate matter is the other potentially important mechanism by which sediments may concentrate trace metals.

During estuarine mixing the trace metals in the dissolved and particulate forms can behave either conservatively or non-conservatively depending on various physico-chemical factors such as pH, Eh, suspended solids, ionic strength and the extent of solid-solution exchange. Another important factor, which can influence the behavior of trace metals in estuaries, is the hydrogenous precipitation of Fe and Mn oxides in the low salinity region. The freshly formed colloidal particles are excellent scavengers of substitution or surface adsorption processes.

The chemical behaviour of a trace metal during its transport within the estuary is determined to a large extent by its chemical form in which it is transported by the river as given below.

- in solution as inorganic ion and both inorganic and organic complexes
- adsorbed onto surfaces
- in solid organic particles
- in coatings on detrital particles after coprecipitation with and sorption onto mainly iron and manganese oxides
- in lattice positions of detrital crystalline material and
- precipitated as pure phases, possibly on detrital particles.

This scheme allows the distinction of trace metal as fractions that are readily available (dissolved and adsorbed), fractions that become available after chemical changes (organically bound and in oxide coatings) and forms that are practically unavailable for release (in crystal structures of suspended particles).

There are somewhat conflicting reports on the behaviour of trace metals during estuarine mixing and these conflicting reports of different workers may be accounted for reasons such as decomposition of pre-existing solids (which release the incorporated metals), differences in rate of mixing, nature of solids supplied by the end members and dependency of solids association of trace metals on the grain size distribution. Muller and Forstner (1975), Jouanneau et al., (1983), Duinker (1983) and George (1989) have reported non-conservative behaviour of particulate associated metals in various estuaries, while Windom et al., (1988), have reported the conservative behavior of particulate associated as well as dissolved metals. Bourg (1983) suggested that the uptake or release of trace elements by pre-existing solids in estuaries be probably related to ion exchange processes, at least for some elements. Some of the reports on the trace metal distribution in the Indian estuaries include that of Paul and Pillai (1983a), in the Cochin Estuary, Satyanarayana et al., (1985a & b) in Vishakhapatnam Harbour, and Zingde et al. (1988) in the Mindhola River Estuary.

Physical speciation studies are generally performed by filtration steps to determine the quantity of metals associated with operationally defined size fractions. Such physical separations are typically used to yield data on metals in the particulate vs. dissolved phase.

To assess the impact of (contaminated) sediments on the environment, information on total concentrations of metals in sediment, alone, are not sufficient. Only a part of the metals present may take part in short-time geochemical processes or may be bio-available. For this reason, a series of different extraction procedures have been devised to gain a more or less 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 sediment into exchangeable, reducible and resistant fractions in the sediments.

Some of the earlier investigations carried out to assess the trace metal content of sediments of Cochin Estuary were Murty and Veerayya (1981), Venugopal et al. (1982), Paul and Pillai (1983a), Ouseph (1987), Nair et al. (1990) and Jayasree and Nair (1995). Of these, Murty and Veerayya (1981) studied the distribution pattern of Fe, Mn, Ti, Ni, Co and Cu in the sediments of Cochin Estuary and in the Vembanad Lake. This was the only study, which reported trace metal distribution from the southern upstream part of the Cochin Estuary. This study was conducted during the period November-December 1969, before the construction of the salinity barrier at Thanneermukkam.

Scope of the present study

The impacts of developmental projects on the environment are a matter of serious concern. Kuttanad area is a typical example of such thoughtless developmental interventions. Kuttanad is a low-lying, shallow bay formed as a result of geological uplift. It has become an extensive brackish-water lagoon extending over 1100 kms through the Vembanad lake and Cochin Estuary to the Arabian Sea. Four major rivers drain into it. It supports about 1.4 million people. The major economic activity is agriculture involving 40% of the population. About 1.5% of the people are engaged in aquaculture. However, human interventions, like salinity barrier at Thanneermukkam, extensive use of chemical fertilizers and pesticides, etc., have invited ecological disasters. The declining productivity has forced farmers and fisher folk to change their traditional professions. In this context a thorough study on the various environmental parameters of this area is of utmost concern for any environmentalist for an accurate assessment of the impact of human interventions on an otherwise pristine environment. The trace metal distribution in the Kuttanad backwaters is considerably influenced by the tropical features of the location and by human activities including agricultural activities and construction of salinity barrier. Though a number of studies on the trace metal distributions in water, particulates and sediments are available from Cochin Estuary, they are mainly concentrated on the northern part of the Cochin estuarine system. No systematic attempt has so far been made to assess the distribution of trace metals in the various environmental compartments of the southern upstream part of the Cochin estuarine system, except some scanty data reported by Murty and Veerayya (1981) and that too, before the construction of the salinity barrier at Thanneermukkam in 1975. Though total metal concentrations in sediments are useful for the assessment of metal pollution in the aquatic system, they are seldom sufficient to satisfactorily describe the various environmental processes in the aquatic system. Therefore, during the last decade, the major objectives of research on metal-polluted waters have changed from the initial surveys of sources and pathways to more detailed investigations of the mechanisms controlling the mobility and bioavailability of different metal species. Partitioning study on trace metals in sediments was conducted as it is a general experience that the environmental behavior and toxicity of an element can only be understood in terms of its physico-chemical form in which it occurs. Information on the partitioning of trace metals in sediments from Cochin Estuary and from other estuaries of Indian coast are relatively scarce. Nair et al. (1991) and Babukkutty (1991) have attempted to assess the partitioning behaviour of trace metals in sediments from the northern part of Cochin estuarine system. The objectives of the study are highlighted as:

to establish the background levels of various toxic metals (viz., cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead and zinc) in different compartments of the aquatic system for assessing the extent of environmental pollution.

to describe the spatial and temporal variations of metals in the aquatic environment of Kuttanad.

❖ to assess the influence of various environmental processes on the estuarine metal reactivity.

to understand the processes of transport and transformations of metals in different compartments of the aquatic system during metal transfer through the estuary.

❖ to compare the behaviour of various metals viz., cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead and zinc.

❖ to study the diagenetic processes occurring within the sediment and the sediment-water inter-face.

to study the partitioning of trace metals in sediments and assess the potential mobility of these trace metals in the aquatic environment of Kuttanad.

to identify the possibility to quantify the lateral addition of trace metals and the geochemical reactivity with the help of a coceptual model.

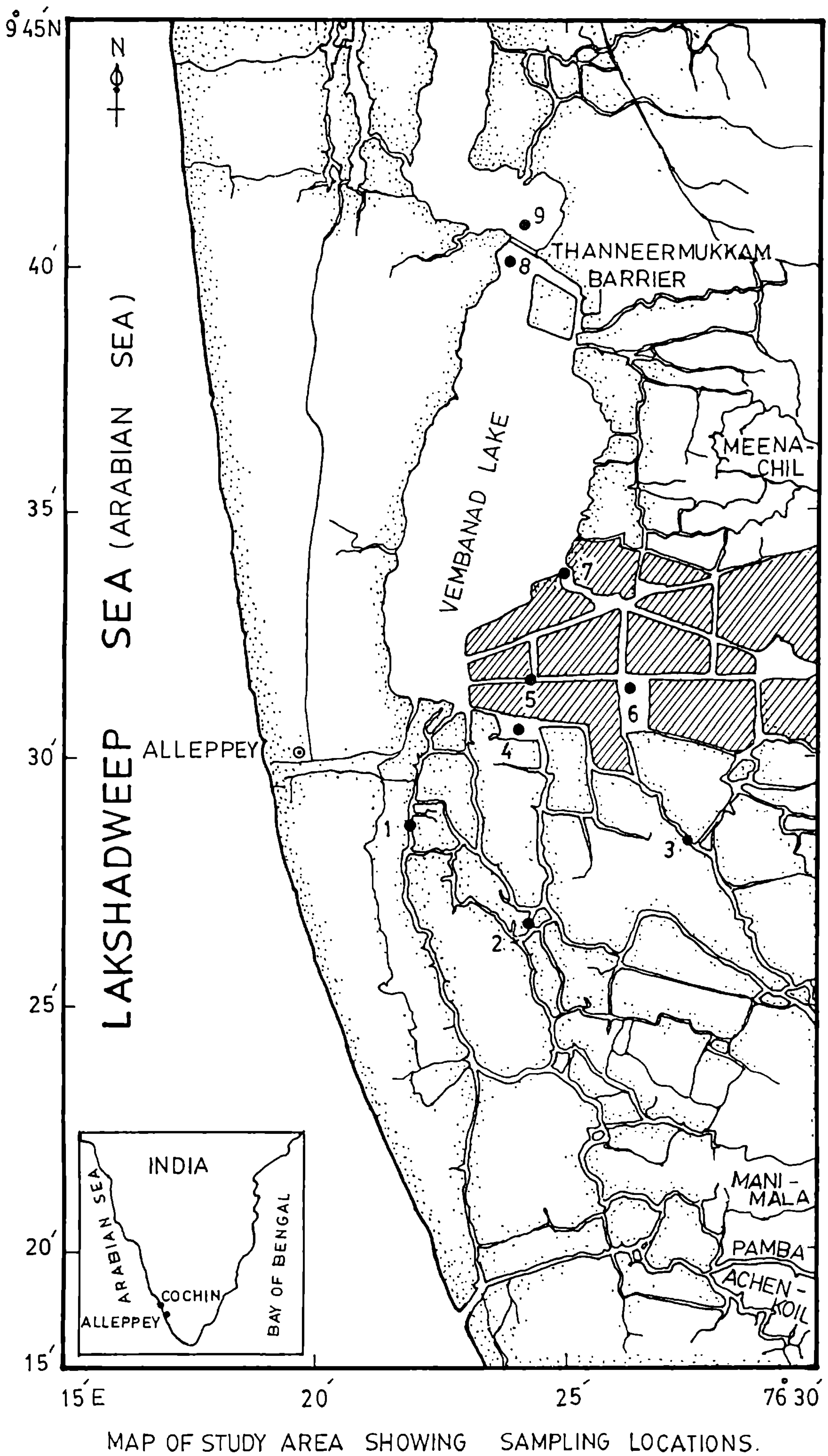
CHAPTER 2

MATERIALS AND METHODS

A brief description of the study area, collection procedure, sampling techniques and various analytical methods employed are given in this Chapter.

2.1 THE STUDY AREA

Cochin backwater system (Figure 2.1), situated in the state of Kerala, between 9° 28' -10° 10' N and 76° 13' 76° 31' E, is the largest estuarine system in the south-west coast of India and it runs almost parallel to the southern part of the west coast of India. It has all the characteristics of a tropical positive estuary (Pritchard, 1967; Qasim and Gopinathan, 1969; Madhupratap et al., 1977). Lying between Azhikode in the north and Alleppey in the south, this estuary extends over an estimated length of 60 kms and an area of 21,050 hectares. The Cochin backwater system is connected to the Arabian sea through a permanent opening, the Cochin barmouth, which is about 450 m wide and 8 to 13 m deep. Here, the depth is maintained by dredging as this opening is used for navigational activities. The barmouth is also responsible for the tidal flux of the Cochin backwater system and is the only source of sea water intrusion into the estuary. Tides are of semi diurnal type, showing substantial range and time. The average tidal range near the mouth of the estuary is 0.9 m. Before the commissioning of the salinity barrier, tidal effects were extended upto some 80 kms south of Cochin barmouth, and the deltaic region of the lower Kuttanad (southern part of the Cochin backwater system) used to become brackish gradually



MAP OF STUDY AREA SHOWING SAMPLING LOCATIONS.

Figure 2.1.

from December onwards, attaining a salinity of about 5×10^{-3} in the interior waters (Josanto, 1971).

The northern part of Cochin backwater system includes the Cochin estuary and the barmouth. The Cochin shipyard and the Cochin port are situated in this part of the backwater system and the hydrography in this part is mainly controlled by the rivers, Muvattupuzha and Periyar and also by the tidal influx through the barmouth. The southern and upstream part of the backwater system includes the Vembanad Lake and the adjoining backwaters of Kuttanad. In this part, the hydrography is mainty controlled by the discharges from four rivers namely Pamba, Manimala, Meenachil and Achancovil and the "Thanneermukkam" salinity barrier. Saline water intrusion from Arabian sea acting through the Cochin barmouth into the southern part of the estuarine system is regulated by the "Thanneermukkam salinity barrier, a 1402 m long salt-water barrier, commissioned in 1975. The purpose with which the salinity barrier was constructed was to prevent the incursion of saline water into the southern part of the estuary during the period December to March, thereby facilitating the farmers to cultivate two crops of paddy per year. This upstream part of Cochin backwater system is surrounded by a vast area of low-lying highly fertile agricultural lands. Nutrient rich alluvial sediments transported by the above four rivers from the western mountain ranges settle over the low fields, especially during floods. This makes the soil and water highly fertile and therefore, agriculture and fisheries are the main activities in this area. Many of the paddy fields in this area are below sea level, a unique feature of this area. Damage of paddy crops was a common phenomenon in the early days due to the intrusion of saline water from the Arabian sea through the Cochin barmouth. In early years, cultivation was done in the low lying area by creating mud barriers around the agricultural lands and then pumping out water from the low lying area into the estuary. After cultivation, water is allowed to enter the paddy fields and the whole area gets flushed with water. Generally, the gate of the regulator will be closed from January to May in the summer season and after that the gate will remain open allowing the discharge of flood water into Cochin estuary during monsoon season.

The study area and the location of the sampling sites are depicted in Figure 2.1. Considering the various geographical and hydrodynamical features, 9 representative stations were identified in the upstream part of the Cochin backwater system for the periodic collection of samples. The stations are

1. Pallathuruthy
2. Nedumudi
3. Kavalam
4. Vattakkayal
5. C-Block
6. 24,000
7 Chithira
8. Thanneermukkam Bund, South
9. Thanneermukkam Bund, North

Stations 1 to 8 are south of the salinity barrier and station 9 is north of the salinity barrier. Station 1 is riverine in character and is near to the Alleppey town. It remains as fresh water zone throughout the year. Agriculture (coconut, paddy) and fishing are the main occupation of the people in this area. The station receives sewage and domestic discharges from the urban town, Alleppey. Stations 2 and 3 are also riverine, and coconut and paddy cultivation and fishing are the main activities of the people in these areas. These two stations also remain as fresh water region throughout the year. Stations 4, 5 and 6 are the outlets of the paddy fields. Paddy cultivation, collection of shells and fishing are the important activities in these areas. Station 7 is another outlet of paddy fields at the same time it is in the Vembanad Lake. Station 8 also is in the Vembanad Lake and is just south of the salinity barrier. Station 9 lies north of the salinity barrier and is estuarine. Fishing, agriculture and coconut husk retting for coir industries are the main activities of the people at stations 7, 8 and 9. Based on the salinity characteristics of the surveyed area, stations 1 to 9 can be grouped into three zones. Zone 1 which includes stations 1, 2 and 3, is the riverine zone, where the salinity generally remains less than 2×10^{-3} in the monsoon, pre-monsoon and post-monsoon seasons. This zone remains as fresh water zone throughout the year. Zone 2 comprises stations 4 to 7 which are partially estuarine in character as this ~~zone becomes saline~~ only in the pre-monsoon season. The stations in this zone are more closer to the paddy fields. Station 4 acts as a sink for the discharges of Pamba river and also the drainages from the paddy fields. Stations 8 and 9 are grouped together as zone 3, which becomes saline in the pre-monsoon and post-monsoon seasons. Station 8 and station 9 are the southern and northern parts respectively of the salinity barrier, "the Thanneermukkam bund"

2.2 SAMPLING PROCEDURES

Monthly field collections, spread over a period of 14 months (from October 1995 to November 1996), were carried out in the above nine stations. Monthly cruizes were conducted using a fibre glass boat "King Fisher" of the School of Industrial Fisheries of the Cochin University of Science and Technology. Surface water samples were collected using a clean plastic bucket, and bottom water samples were collected using a pre-cleaned teflon Hytech water sampler and stored in 5L plastic containers, previously cleaned with HNO_3 followed by rinsing several times with de-ionised and Milli-Q waters for avoiding contamination from the containers. Sediment samples were collected using a stainless steel, plastic lined van Veen grab. At each station, 2 to 3 grabs of sediments were sampled and the top 5 cm layer was carefully skimmed from all the grabs using a polythene spoon, homogenised, and stored in ice-box storage in closed polythene containers for transport to laboratory. The samples were stored in deep freezer at –20°C till analyses were performed.

2.3 ANALYTICAL PROCEDURES

All glasswares used for the analyses were cleaned thoroughly with soap solution and then soaked in 6 M HNO_3 for at least 48 hours and washed well with de-ionised water and finally with Milli-Q water. All reagents used were MERCK/BDH GR/Analar grade unless otherwise specified..

2.3.1 General hydrographical parameters

Temperature, pH, dissolved oxygen and salinity

Temperature was measured by using (1/10°C) mercury-in–glass thermometer and pH by using a portable digital pH meter. Salinity was determined argentometrically, by the modified Mohr's method, developed by Knudsen (Grasshoff et al., 1983). Dissolved oxygen was estimated using modified Winkler method (Grasshoff et al., 1983).

Suspended particulate matter (SPM)

Suspended solids were determined gravimetrically by filtering the water samples, immediately after collection, through Whatmann membrane filter papers of pore size 0.45 µm. The Whatmann filter papers used for separating the suspended solids were previously soaked in 5 M HNO_3 for 24 hours and washed thoroughly with Milli-Q water for removing any metal contamination from the filter paper as the suspended solids along with the filter paper were digested later to find particulate metals. The filter paper containing the suspended solids was washed with 5 ml of Milli-Q water (Owens et al., 1997) to remove sea salts and dried at 80°C in an air oven to constant weight. The filter paper together with the suspended solids was weighed and the difference in weights gave the suspended loads in water, which is expressed in mg/l. Each filter paper was then separately stored in acid washed polythene petridishes for particulate trace metal analyses. The filtrate obtained was collected in a plastic container which was previously cleaned by soaking in 5% HNO_3 and then washing several times with de-ionised water followed by rinsing with Milli-Q water.

Dissolved major elements

A portion of the filtrate obtained as above was acidified with sub-boiling distilled HNO_3 to a pH 2 and was used for the analyses of dissolved major elements like calcium, magnesium, strontium, barium and boron. The acidified filtrate was directly aspirated (without any pre-concentration) into the argon plasma of a Jobin-Yvon (France) make Inductively Coupled Plasma Atomic Emission Spectrometer (JY-24 Model ICP-AES), for determining dissolved Ca, Mg, Sr, Ba and B, using addition method. The concentrations of major elements in estuarine waters were found to be comparatively higher, and the use of ICP-AES in the analyses of estuarine waters for major elements, without sample pre-concentration has been reported by many workers (Dehairs et al., 1989; Thompson and Walsh, 1989; Coffey et al., 1997).

2.3.2 Sediment characteristics

Moisture content

Approximately 10 g of homogenised wet sediment sample was taken and the percentage of moisture in the sample was determined. The sample was kept in a hot air oven at 90°C for 48 hours. The difference in weights of the wet and dry samples gave the moisture content.

Organic carbon

The wet sediment samples were washed with minimum quantity of Milli-Q water and dried in the hot air oven maintained at 80° - 90°C and then finely powdered in an agate mortar. Sediment organic carbon was estimated by chromic acid oxidation method (El Wakeel and Riley, 1957; Gaudette et al., 1974).

Textural analysis

To understand the variations in grain sizes of sediments, textural analysis was carried out by sieving and pipette analysis. A known quantity of wet sediment sample was dispersed overnight in 0.025 N solution of sodium hexametaphosphate (Calgon). The coarse fraction (sand) was separated from the dispersed sediments by wet sieving using a 230 mesh (63 µm) ASTM sieve (Carvar, 1971). The filtrate containing the silt and clay fractions was subjected to pipette analysis (Krumbein and Pettijohn, 1938; Lewis, 1984) and the nomenclature of the sediments was found. Representative samples comprising pre-monsoon, monsoon and post-monsoon seasons were subjected to the textural analyses.

2.3.3 Analyses of trace metals

The schematic representation of the analyses of trace metals in different phases of the aquatic system is given in Figure 2.2.

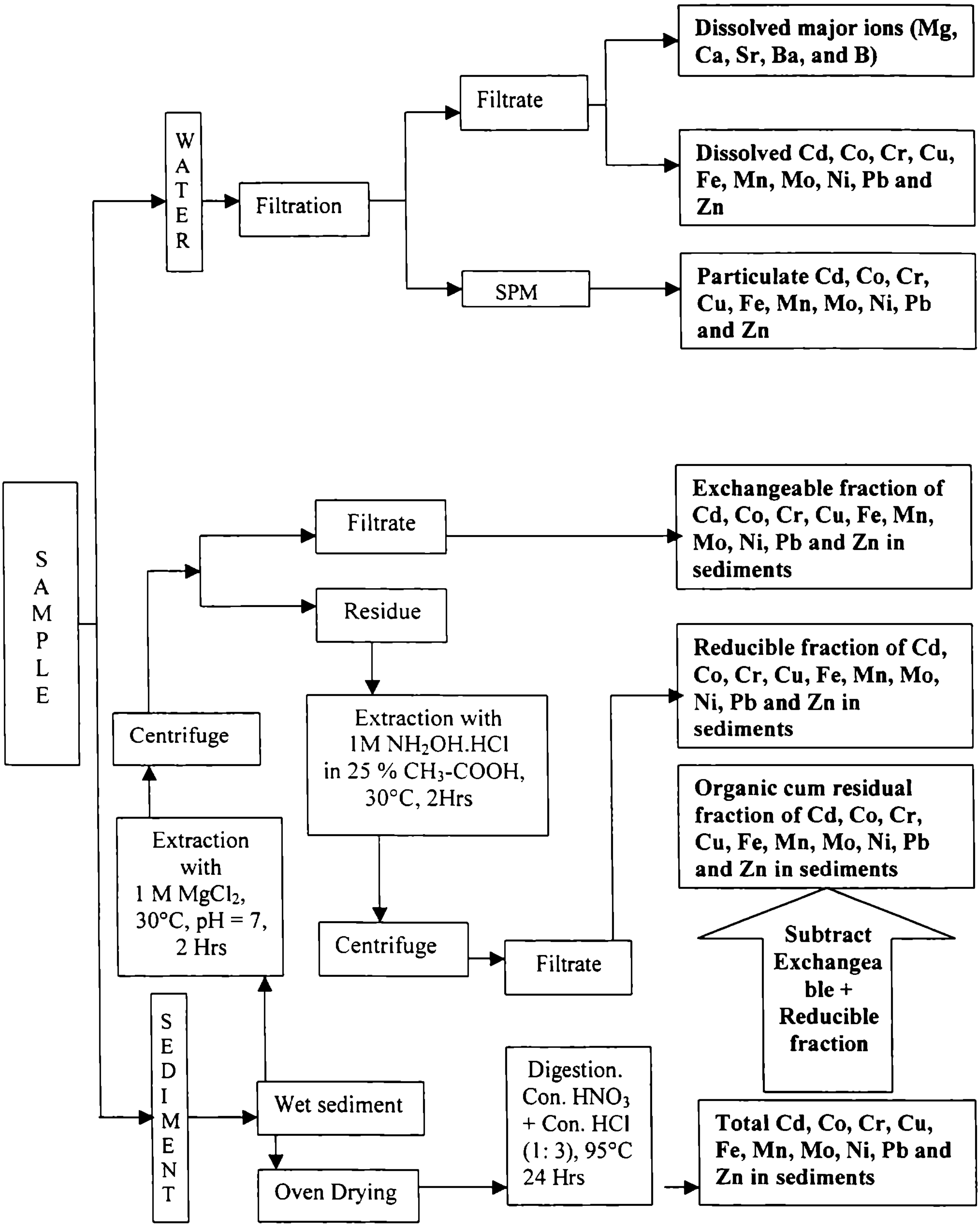


Figure 2.2 Scheme of analysis

Dissolved trace metals

Trace metal concentrations in estuarine water, although typically much higher than in open ocean water, are often sufficiently low to require some form of sample concentration before analysis. Additionally, since most estuarine studies cover the entire salinity gradient, the analytical method must account for the complex and variable matrix. One solution to the analytical problem has been to allow the dissolved metals to form complexes with organic chelating agents, extract the organo-metal complexes into an organic medium and then to back-extract the metal into an aqueous medium by decomposing the complex using inorganic acid. This method provides a pre-concentrated sample with a consistent matrix (Klinkhammer, 1980; Statham, 1985; Coffey and Jickells, 1995). After the pre-concentration, the matrix effects are sufficiently small to allow samples to be run against aqueous standard calibrations without the need for the routine use of the method of standard additions (Jickells et al., 1992; Coffey and Jickells, 1995).

The dissolved trace metal concentrations were estimated by the method described by several workers (Danielsson et al., 1978 & 1982; Bruland et al., 1979; Landing and Bruland, 1987; Martin et al., 1993; Dai and Martin, 1995; Zhulidov et al., 1997a,b). The filtrate obtained in 2.3.1 was acidified with sub-boiling distilled HNO_3 to a pH of about 2 and stored in acid washed low density polythene bottles and were used for the analyses of dissolved trace metals. The bottles were previously soaked in 5 % HNO_3 for 48 hours and then washed several times with de-ionised water and rinsed several times with Milli-Q water for minimising trace metal contamination from plastic containers. The filtered water samples were subjected to solvent extraction using ammonium-1-pyrrolidine dithiocarbamate-diethylammonium diethyl dithiocarbamate-chloroform mixture (APDC/DDDC/Chloroform) mixture after adjusting the pH of the acidified sample to 4.5 by the addition of ammonium hydroxide. The extract was then acidified with sub-boiling distilled concentrated nitric acid and the metals (cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead and zinc) were brought into the aqueous phase by equilibration with a definite volume of water and then analysed by using inductively coupled plasma atomic emission spectrometer. Analytical precision had been determined by the analyses of quadruplicates and expressed as coefficient of variation for each element: Cd 5%, Co 4%, Cr 5%, Cu 5%, Fe 4%, Mn 3%, Mo 5%, Ni 6%, Pb 6% and Zn 3% at 10 µg/l level. The accuracy of the method was evaluated by spiking 2L of water samples with salinity 10×10^{-3} and zero (fresh water) then extracting with APDC/DDDC/Chloroform mixture. Recoveries for the studied metals were Cd 95%, Co 96%, Cr 97 %, Cu 97%, Fe 98%, Mn 95%, Mo 96 %, Ni 97%, Pb 98% and Zn 98%. The recoveries were found to be same for both fresh water and saline water.

Particulate trace metals

The suspended solids collected on Whatmann membrane filter papers and stored in polythene petridishes, as described earlier, were digested with 20 ml of an acid mixture ($HClO_4$, HNO_3 and HCl in the ratio 1:1:3) (Vuorinen et al., 1986) at 90^0C for 6 hours to get the total metal in the suspended particulate matter. The acid mixture was evaporated almost to dryness. The residue was warmed with 0.1N HCl and the resultant solution was centrifuged at 4000 rpm and then made upto 25 ml with 0.1N HCl and analysed using ICP-AES (Rivaro et al., 1998). Blank corrections for filters and reagents were applied.

Sediment total trace metals

For determining the total trace metal contents in sediment, dried sediment was powdered well in an agate mortar and approximately 0.5 g of the homogenised sediment was digested with a mixture of conc. HNO_3 and conc. HCl in the ratio 1:3 (aqua regia) at 95°C for 24 hours (Johansson, 1975; Young et al., 1992). The digest was centrifuged at 4000 rpm and the supernatant liquid was further filtered, to remove particles if any, using Millipore membrane filter of pore size 0.45 μm using a plastic syringe. The syringe was then rinsed with Milli-Q water, the rinse water was added to the filtrate and the filtrate was made upto a definite volume. The made up filtrate was analysed for trace metals (cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead and zinc) using ICP-AES. Estimation of the accuracy and precision of the analysis was performed using standard addition technique and replicate analysis as detailed in dissolved trace metal analyses.

Partitioning of trace metals in sediments

The sediment was analysed for the following fractions of metals, which are schematically represented in Figure 2.2. The extractants, the sequence and the procedure followed were adopted from methods employed by Tessier et al. (1979 & 1984) and Nair et al. (1991) with some modifications.

1. ***Exchangeable fraction***
2. ***Fe/Mn oxide bound fraction or reducible fraction***
3. ***Organic cum Residual fraction***

Exchangeable fraction

This is the fraction which was extracted with 1M $MgCl_2$ at pH 7.0 (Tessier et al., 1979; Bradley and Cox, 1990; Elliot et al., 1990). 5 to 6 g aliquots of the wet sediment samples were weighed out into a beaker and allowed to equilibrate with 25 ml of 1M $MgCl_2$ at pH 7 using a mechanical shaker for two hours. The phases were separated by centrifugation. The supernatant liquid separated was analysed for trace metals by ICP-AES, using standard addition method, whereas the residue was carefully washed back into the beaker for the next sequential extraction.

Fe/Mn oxide bound fraction or reducible fraction

The residue obtained after the extraction of the exchangeable fraction was allowed to equilibrate with 25 ml of Chester and Hughes reagent (1M NH_2OH-HCl in 25% CH_3-COOH) using a mechanical shaker for two hours (Chester and Hughes 1967; Tessier et al., 1979; Yoshimura et al., 1988). The phases were separated by centrifugation at 4000 rpm and the supernatant liquid was analysed for iron-manganese bound fraction of trace metals with ICP-AES using standard addition technique.

Organic cum Residual fraction

The fraction remaining after the extraction with Chester and Hughes reagent is mainly the organic and residual fraction (Tessier et al., 1979; Bradley and Cox, 1990). This was calculated by subtracting the sum of exchangeable and reducible fractions from the total metal obtained by digestion with conc. HNO_3 and conc. HCl (1:3), i.e. Organic cum Residual fraction = Total metal in sediment (Exchangeable fraction + Reducible fraction).

2.3.4. Analyses of data

All data were subjected to statistical analyses wherever necessary. Regression analyses were performed between different trace metals and between trace metals, and different environmental variables.

CHAPTER 3

HYDROGRAPHICAL AND SEDIMENTAL CHARACTERISTICS

3.1 INTRODUCTION

Trace metals are transported to the ocean in dissolved and particulate forms by rivers. In estuaries, where river water and coastal or oceanic waters of widely different compositions are mixed, strong gradients in chemical properties occur (Burton, 1976). The variations in the hydrographical parameters in estuaries, when river water mixes with sea water, affect the transport mechanisms of dissolved and particulate components of trace metals. Generally, trace metal concentrations in sediments vary largely with sediment characteristics like grain-size, organic carbon content, sediment moisture content and sources of anthropogenic inputs. For the meticulous interpretation of metal concentrations and their diffusibility or mobility in sediments, knowledge of the sediment characteristics and other environmental features such as pH, dissolved oxygen and salinity are a prerequisite. Therefore, hydrographical parameters are vital tools while attempting to characterize the general features, distribution pattern, relative abundance and estuarine modifications of trace metals during their transport and also in the partitioning of metals in different phases, namely, water, suspended solids and sediment.

A study of the hydrographical features is essential for explaining the conditions prevailing in the estuarine environment. The general hydrographical features of Cochin backwaters have been attempted by few workers in the past, they include Ramamirtham and Jayaraman (1963), Cherian (1967), Qasim and Gopinathan (1969), Devassy and Gopinathan (1970), Josanto (1971), Wellershaus (1971), Murty and Veerayya (1972), Haridas et al. (1973), Balakrishnan and Shynamma (1976), Sankaranarayanan and Panampunnayil (1979), Sarala Devi et al. (1979), Lekshmanan et al. (1982), Balchand and Nambisan (1986), Sankaranarayanan et al. (1986), Kurup and Samuel (1987), Anirudhan (1988), KWBS (1989), Anirudhan and Nambisan (1990), Babukutty (1991), Nair (1992), Nayar (1992), Harikrishnan (1997) and Sureshkumar (1998). Most of these studies carried out were emphasized on the area around Cochin harbour. Nair and Tranter (1971) were the first to extend their observations upto the southern upstream part of the estuary (Kuttanad), though their observations were limited to two cruises, one before and the other after the monsoons. Josanto (1971) made a sincere attempt to study the salinity characteristics of the Cochin backwater system and factors that influence salt water penetration in the southern upstream part of the Cochin backwater system prior to the construction of the Thanneermukkam salinity barrier. However, KWBS (1989) monitored some preliminary water quality parameters of this water body giving more representations to the southern upstream part of the estuary (Kuttanad) and confluent rivers.

In this Chapter, a discussion on the data recorded during the survey from October 1995 to November 1996 on some hydrographical parameters like temperature, depth, pH, dissolved oxygen, salinity, suspended solids, dissolved calcium, magnesium, strontium, barium and boron, and some sedimental characteristics like texture, moisture, and organic carbon are presented. These hydrographical and sedimental characteristics are likely to influence the concentration and distribution of different trace metals and their partitioning in different environmental phases of the study area.

3.2 MATERIALS AND METHODS

Procedures have been detailed in Chapter 2.

3.3 RESULTS AND DISCUSSION

The monthly data of all the parameters discussed below are given as Annexure 1 due to the exhaustive nature of the data, whereas the station wise summary statistics, graphical representation of spatial and temporal variations, correlations etc are incorporated along with the text. The overall summary statistics on the distribution of hydrographical and sedimental parameters are given in Table 3.1.

Temperature

Water temperature is an important physical parameter as far as oceanographic studies are concerned. The mechanism whereby heavy metal toxicity increases with higher water temperatures can be explained by elevated respiratory activity (Lloyd, 1965). The absorption and release of metals by organisms can also depend on temperature. This was established for mercury, methylmercury, and phenylmercury acetate in experiments using rainbow trout (Reinert et al., 1974; Ruohtula and Miettinen, 1975). Apart from the effects of water temperature and oxygen content on the toxicity of heavy metals as a result of physiological changes in the organism, these two parameters can decisively influence heavy metal availability due to chemical processes in water and sediment (e.g., oxidizing-reducing environment). Thus, the concentration of heavy metals in interstitial waters associated with anaerobic sediments can be upto 10 times higher than in supernatant water (Reinhard and Forstner, 1976).

The temperature in this estuary showed only moderate variations, though, they were indicative to a certain extent the climatic variations in this region during the period of observation. The mean values of surface and bottom water temperatures were 29.9°C and 29.5°C with a range of values 27.0°C to 33.0°C (in both surface and bottom waters) (Table 3.1). Station

Table 3.1 Summary statistics (overall) on distribution of hydrographical and sedimental parameters.

Parameter	Min.		Max.		Mean		SD		CV	
	S	B	S	B	S	B	S	B	S	B
Temperature (°C)	27.0	27.0	33.0	33.0	29.9	29.5	1.6	1.5	5.3	5.2
pH	4.3	4.5	8.0	7.4	6.7	6.6	0.5	0.4	7.1	6.5
DO (ml/l)	3.33	1.88	7.55	7.69	5.05	4.79	0.82	0.86	16.19	18.03
Salinity (x 10^{-3})	0.05	0.05	12.08	12.34	1.25	1.38	2.61	2.75	208.28	200.35
SPM (mg/l)	1.04	1.17	97.64	109.89	9.58	19.01	17.21	19.67	179.77	103.48
Magnesium (mg/l)	1.08	1.07	520.00	509.00	53.27	58.93	113.80	122.27	213.62	207.48
Calcium (mg/l)	1.76	1.73	148.00	152.00	19.20	20.93	31.86	34.68	165.90	165.75
Strontium (µg/l)	15.80	14.20	3010.00	3150.00	316.28	342.47	618.78	666.15	195.64	194.52
Barium (µg/l)	13.40	10.50	270.00	237.00	66.38	63.55	57.47	55.86	86.57	87.89
Boron (µg/l)	3.47	3.38	1600.00	1490.00	168.04	183.18	351.89	364.01	209.41	198.71
Depth (m)	1.0		10.0		4.5		3.4		76.7	
SOC (mg/g)	1.04		47.88		26.39		12.02		45.54	
SMC (%)	20.05		63.86		40.34		9.88		24.50	

(SPM = suspended particulate matter, SOC = sediment organic carbon, SMC = sediment moisture content, SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom) wise highest annual mean temperatures were observed at station 6 (both in surface and bottom waters) (Table 3.2). Surface water temperatures were found slightly higher than bottom water temperatures (Figure 3.1). Zone wise, the average temperature was higher at zone 1 and lower at zone 3 in surface waters and higher at zone 2 and lower at zone 1 in bottom waters (Figure 3.1). Figure 3.1 also shows the seasonal variations of temperatures in the nine stations studied. The lowest temperature recorded ($27.0^{o}C$) was in the monsoon season and maximum value recorded ($33.0^{o}C$) was in the pre-monsoon season. The values, as expected, were high during pre-monsoon (February to May) and low during monsoon (June to September) seasons. The average surface temperatures at zone 1 differed more in monsoon and post monsoon seasons than in other zones.

The patterns of temperature variations observed in the present study fully agree with the earlier findings (Haridas et al., 1973; Kunjukrishnapillai et al., 1975; Silas and Pillai, 1975; Lakshmanan et al., 1982; Kurup and Samuel, 1987; KWBS, 1989). The lowering of water temperature as well as the fluctuations observed during the monsoon months may be due to the combined effect of varying quantity of influx of land run-off and monsoonal rains into the estuarine system during this period. It is relevant to mention that 60 % of the total annual rainfall (Harikrishnan, 1997) is contributed during the monsoon months (June to September) causing a considerable decrease in water temperature in this period. The shallowness of stations was largely responsible for the insignificant differences in surface and bottom water temperatures.

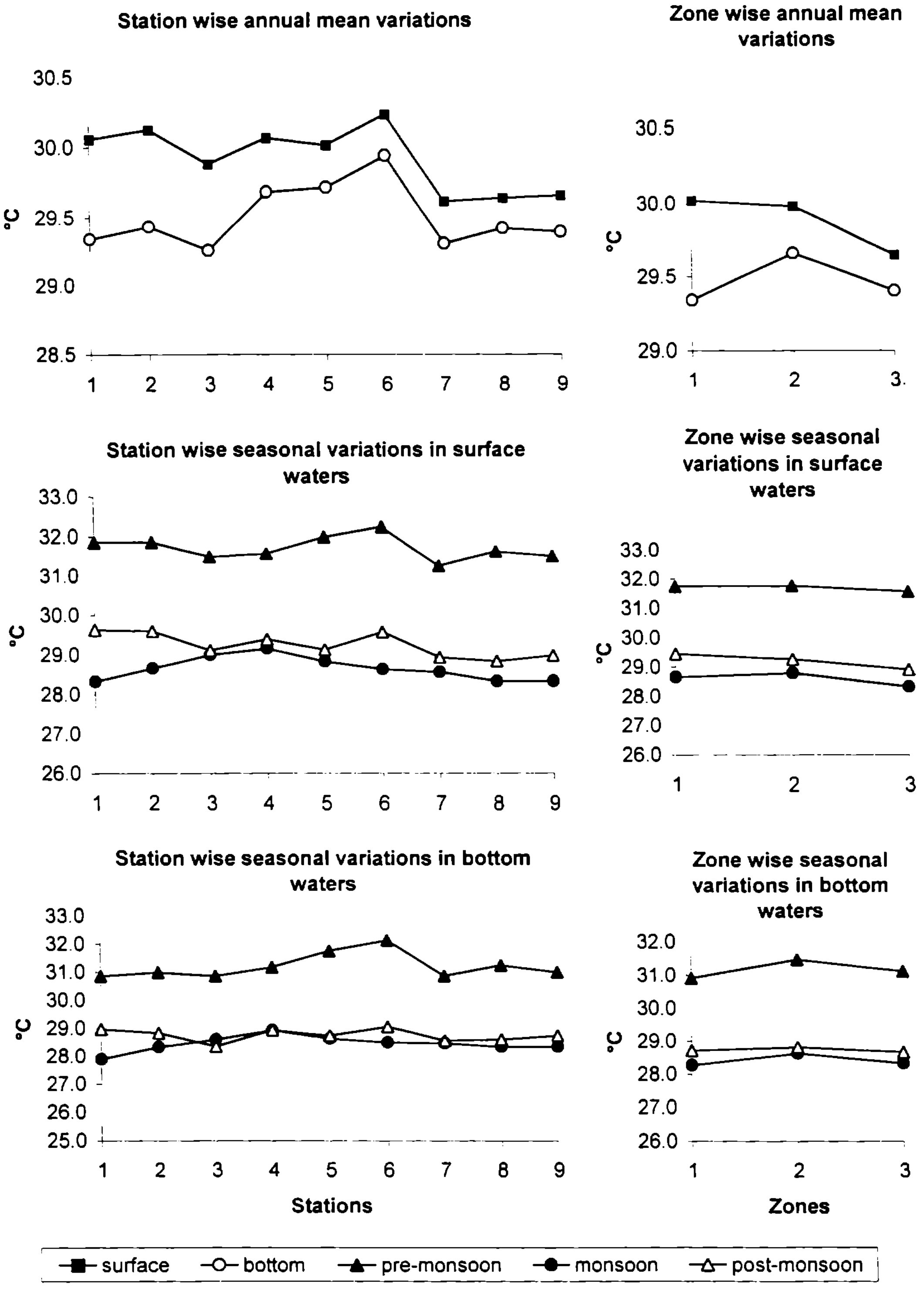
Depth

The depth of sampling sites in the surveyed area varied from 1.0 m to 10.0 m. Stations in zone 1 (stations 1, 2 and 3) were comparatively deeper and stations of zone 2 and zone 3 were shallow (Figure 3.2). The annual mean depths and the seasonal average depths are given in Table 3.2. The average depths at stations 1, 2 and 3 were 9.7 m, 9.5 m and 8.4 m

Table 3.2 Station wise summary statistics of temperatue, pH and depth.

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Temperature (°C)	1	27.5	27.0	32.5	32.0	30.1	29.3	1.5	1.5	5.7	5.1
	2	27.0	27.0	32.5	32.0	30.1	29.4	1.6	1.6	5.7	5.4
	3	28.0	27.5	32.0	31.0	29.9	29.3	1.5	1.5	5.0	5.0
	4	28.0	27.8	32.0	32.0	30.1	29.7	1.5	1.5	4.8	4.9
	5	27.8	27.5	32.0	32.0	30.0	29.7	1.7	1.7	5.8	5.8
	6	27.2	27.0	33.0	33.0	30.2	29.9	1.8	1.8	5.8	6.2
	7	27.0	27.0	32.0	32.0	29.6	29.3	1.5	1.5	5.1	5.3
	8	27.0	27.0	32.0	31.5	29.6	29.4	1.5	1.5	5.6	5.2
	9	27.0	27.0	32.0	31.5	29.7	29.4	1.4	1.4	5.4	4.8
Depth (m)	1	9.0		10.0		9.7		0.5		5.1	
	2	9.0		10.0		9.5		0.4		4.5	
	3	6.0		10.0		8.4		1.2		14.0	
	4	1.5		3.0		2.3		0.5		20.1	
	5	1.0		3.0		2.0		0.8		38.4	
	6	1.5		4.5		3.1		0.7		23.8	
	7	1.5		3.0		1.9		0.5		26.9	
	8	1.0		2.0		1.8		0.3		19.3	
	9	1.5		2.0		1.8		0.3		14.9	
pH	1	6.6	6.1	8.0	7.4	7.1	6.7	0.4	0.4	6.3	6.0
	2	6.6	6.2	7.7	7.1	7.0	6.7	0.4	0.3	5.1	4.4
	3	6.4	6.2	7.3	7.1	6.9	6.6	0.3	0.3	4.2	4.3
	4	6.2	6.1	7.3	7.2	6.7	6.6	0.3	0.4	4.7	5.4
	5	6.4	6.4	7.1	7.1	6.8	6.7	0.2	0.2	3.4	3.4
	6	5.7	5.7	7.1	7.1	6.7	6.5	0.3	0.4	5.2	5.9
	7	4.3	4.5	7.2	7.0	6.3	6.3	0.9	0.8	14.2	13.3
	8	6.2	6.1	7.2	7.0	6.8	6.6	0.3	0.3	4.4	5.2
	9	5.9	5.9	7.0	7.1	6.6	6.6	0.5	0.4	7.0	6.7

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)



Station wise annual mean variations

Zone wise annual mean variations

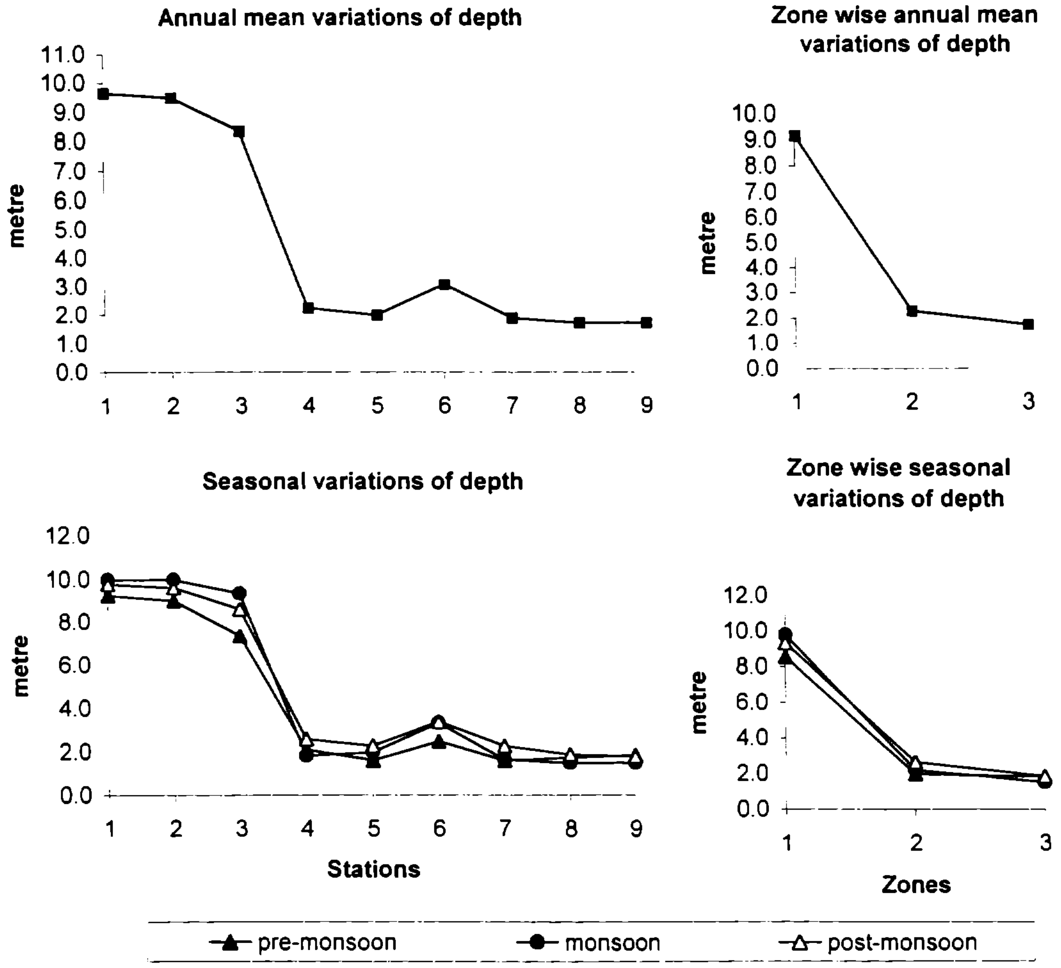
Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 3.1 Seasonal and spatial variations of temperature.


Annual mean variations of depth

Zone wise annual mean variations of depth

Seasonal variations of depth

Zone wise seasonal variations of depth

Figure 3.2 Seasonal and spatial variations of depth of water column.

respectively, whereas the average depth at stations 4 to 9 varied from 1.8 m to 3.1 m. Seasonal variations in depths at stations 4 to 9 were not very specific but at stations 1, 2 and 3, the water level increased slightly in the monsoon season with a gradual decrease in the post-monsoon and then in pre-monsoon. The increase in water level at stations 1, 2 and 3 during monsoon season may be due to the discharge of floodwater from the rivers at these stations in this season. The low water level in pre-monsoon season indicated the low flow conditions during this season.

pH

Many of the estuarine processes are directly related to the pH of the aquatic environment. pH is an important hydrographical factor indicating the level of dissolved carbondioxide in the water, which may in turn reflect the activity of phytoplankton and the level of dissolved oxygen (Skirrow, 1975). Various factors like high primary production, respiration rate, mineralization processes etc. can alter the pH of the backwater systems and are inter-linked to the changes in oxygen and carbonate concentrations. pH of the aquatic medium in an estuary also depends on the rainfall, nature of dissolved substances, discharge of effluents etc. Kunjukrishnapillai et al. (1975) had recorded high phytoplankton production during the pre-monsoon period. So the photosynthetic activity of phytoplankton during the pre-monsoon period will result in depletion of the amount of carbondioxide and an increase in pH value. The low pH during the monsoon period may be due to the large influx of run-off associated with monsoon, since the rain/river water has generally lower pH. Further, the biochemical decomposition of organic matter brought to the backwaters by monsoonal land run-off may increase the carbondioxide content and subsequently lower the pH. Natural turbulence with concomitant aeration can also influence the pH, though to a limited extent (Zingde and Desai, 1987). To a large extent, pH influences the partitioning of trace metals in water, suspended solids and sediments.

The prominent factors influencing the pH in this part of Cochin backwater system are photosynthetic activity of phytoplanktons, discharge of fresh waters from the four rivers and the extent of salinity changes during saltwater intrusion. The mean pH values of surface and bottom waters were 6.75 and 6.60 respectively (Table 3.1). During the period of this study, the pH variations were in the range 4.3 to 8.0 (in surface water) and 4.50 to 7.40 (in bottom water) (Table 3.2). Generally, the mean surface water pH was slightly higher than the bottom water pH (Figure 3.3). The station wise annual mean values showed a decreasing trend from station 1 to station 7 and then increased slightly at stations 8 and 9 (Figure 3.3). Average pH is less than 7.0 in most of the stations, which indicate a slight reducing environment in this region. Thus, lowest annual mean pH values were observed at station 7, both in surface and bottom waters, the values being 6.3 in each. The mean lower pH value at zone 2 than that of zone 1 showed that the reducing condition is more prevalent at zone 2 than at zone 1. The differences between surface and bottom water pH values were greater at stations of zone 1 than at stations of zones 2 and 3. The insignificant differences in surface and bottom water pH values at stations of zone 2 and zone 3 may be attributed to the shallowness of stations in these zones compared to the stations at zone 1.

The average seasonal values showed only slight variations. The seasonal variations observed were not uniform throughout the stations. The pre-monsoon period showed the widest range of variation (4.3 to 8.0 in surface water and 4.5 to 7.4 in bottom water), whereas the ranges of variations in the monsoon and post-monsoon seasons were comparatively less. Figure 3.3 showed that stations of zone 1 marked the highest seasonal average in pre-monsoon in the surface water, whereas stations of zone 2 and zone 3 recorded lowest seasonal average in pre-monsoon season in surface water. In bottom water, all the three zones recorded lowest seasonal average pH in pre-monsoon season. In the pre-monsoon season, the average pH values decreased at zone 2 and zone 3, both in surface and bottom waters. The monsoonal average values were lower than post-monsoon averages at zone 1 and zone 2 but at zone 3 monsoon average

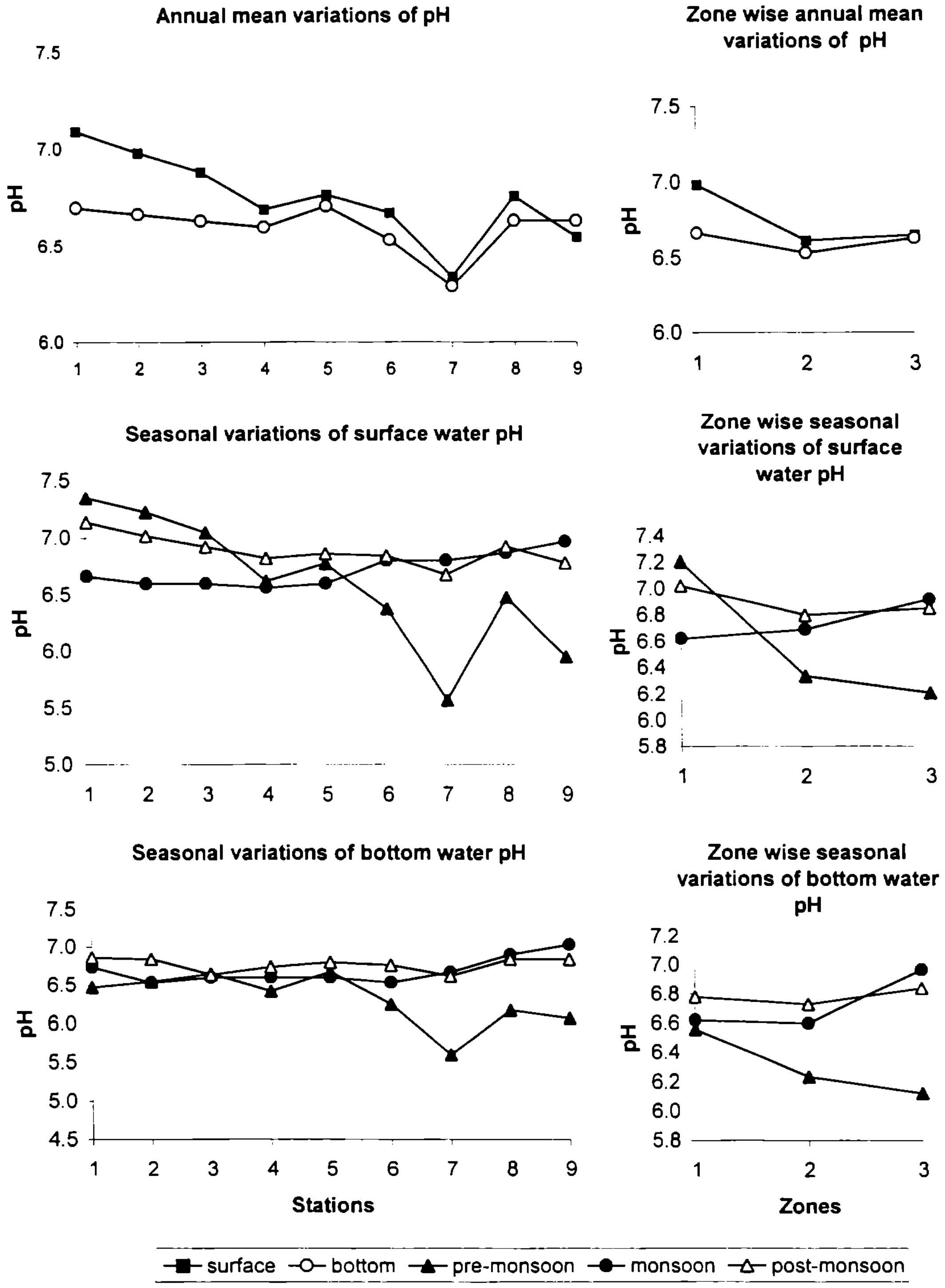


Figure 3.3 Seasonal and spatial variations of pH.

was found to be the highest in surface and bottom waters. Unlike the trend observed in pre-monsoon season, there was an increasing trend in the seasonal average pH values from zone 1 to zone 3 in monsoon season for surface waters. This trend is not observed in post-monsoon season. Instead, the zonal averages at zones 2 and 3 were almost equal but lower than that of zone 1 in surface water. In bottom water, there was a slight increase at zone 3 in post-monsoon season.

Sureshkumar (1998) who extended his study towards southern region of Kuttanad observed a range of pH variations from 4.8 to 9.5 in the area. Harikrishnan (1997) in a survey including both the southern and northern parts of the estuary reported pH values in the range 5.1 to 9.9. However, pH values above 8.0 were not observed in the present study. Compared to some earlier reports (Silas and Pillai, 1975; Kurup and Samuel, 1987; KWBS, 1989) from this part of the backwater system, the range of values was found to be higher. The pH value of river water usually increases when it mixes with saline water. This influence of saline water intrusion in the variations of pH values was not evident in this part of the study area. This is clear from the decreasing pH values in pre-monsoon season from zone 1 to zone 3. This implies that the effect of saline water intrusion in modifying pH values is outweighed by the reducing atmosphere prevailing in the pre-monsoon seasons in this part of the study area. It was also reported that the soil acidity of Kuttanad region increases very much especially in the pre-monsoon season (KWBS, 1989). The wide variations in pH especially at stations 6 to 9 in pre-monsoon period may also be attributed to the high degree of bottom churning due to the dredging of clam shell deposits (Sureshkumar, 1998). A wide variation in pH in the areas of dredging was also reported by Windom (1976). The generally observed lower pH values (less than 7.0) in most of the stations were also reported by Harikrishnan (1997) and Sureshkumar (1998).

Dissolved oxygen

Dissolved oxygen (DO) is also an important water quality parameter in assessing the extent of water pollution, and it plays a vital role in the aquatic environment as the very survival of aquatic life is linked to the availability of dissolved oxygen. The concentration of dissolved oxygen in estuarine waters depends on several factors like water temperature, partial pressure of the gas in the atmosphere, biogeochemical processes like oxidation and reduction, biochemical degradation of organic matter, respiration, photosynthesis etc. In estuarine and ocean waters, dissolved oxygen content is inversely related to temperature and salinity. The depletion in the dissolved oxygen concentration is an indication of pollution in the area. According to De Sousa and Sen Gupta (1986), study on the dissolved oxygen concentration may help to explain the various physical, chemical and biological processes taking place in the natural waters. For example, super saturation by oxygen in waters which are equilibrated with respect to non-reactive gases may suggest photosynthetic production of oxygen, and under saturation by oxygen may reflect its biological and chemical utilization for respiratory and oxidative processes (De Sousa and Sen Gupta, 1986).

The ranges of dissolved oxygen values were from 3.33 to 7.55 ml/l in surface waters and 1.88 to 7.69 ml/l in bottom waters (Table 3.3) during the period of observation. The overall mean dissolved oxygen values of surface and bottom waters were 5.05 and 4.79 ml/l respectively. The station wise variations in the annual mean concentrations of dissolved oxygen values of surface and bottom waters are depicted in Figure 3.4. In majority of cases, surface DO values were found to be higher than the bottom DO values. Except at stations 1 and 4, appreciable differences in annual mean values of DO in surface and bottom waters were observed. The zonal average of station wise annual mean values of dissolved oxygen showed a slight increase at zone 2 and a slight decrease at zone 1 in surface water. In

Table 3.3 Station wise summary statistics on dissolved oxygen, salinity and suspended particulate matter (SPM)

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Dissolved oxygen (ml/l)	1	4.28	2.81	6.93	6.62	5.08	5.09	0.92	1.02	18.06	19.96
	2	3.64	1.88	5.67	5.77	4.71	4.40	0.67	1.20	14.29	27.23
	3	4.61	3.54	6.88	4.98	5.12	4.53	0.61	0.41	11.82	8.95
	4	4.80	4.38	6.09	7.69	5.39	5.32	0.37	1.04	6.79	19.59
	5	3.74	2.99	7.55	6.05	5.12	4.70	1.20	0.83	23.43	17.62
	6	4.38	3.91	7.14	5.20	5.32	4.61	0.91	0.49	17.11	10.53
	7	3.33	4.35	6.20	6.67	4.66	5.33	0.85	0.66	18.16	12.43
	8	3.78	3.57	6.41	5.91	4.93	4.70	0.77	0.71	15.64	15.11
	9	4.20	3.34	7.06	5.40	5.10	4.47	0.77	0.75	15.14	16.78
Salinity (x 10^{-3})	1	0.07	0.07	2.15	4.57	0.38	0.61	0.68	1.31	179.47	213.10
	2	0.05	0.05	0.59	1.35	0.15	0.22	0.19	0.38	129.27	173.52
	3	0.05	0.05	0.52	0.53	0.13	0.15	0.14	0.16	110.61	105.24
	4	0.05	0.07	1.77	1.76	0.36	0.37	0.55	0.57	152.00	151.75
	5	0.05	0.07	1.63	1.91	0.43	0.47	0.59	0.66	138.71	141.48
	6	0.07	0.07	2.96	2.98	0.73	0.75	0.99	1.02	136.35	135.26
	7	0.07	0.07	7.98	8.22	1.67	1.77	2.47	2.58	148.22	145.66
	8	0.07	0.05	10.36	9.89	3.06	3.50	3.68	3.89	120.35	111.17
	9	0.08	0.06	12.08	12.34	4.38	4.53	4.96	5.13	113.21	113.29
SPM (mg/l)	1	1.78	2.06	92.92	109.89	13.86	19.18	25.80	29.21	186.16	152.24
	2	1.20	1.67	17.15	48.90	5.56	14.76	5.19	14.22	93.27	96.33
	3	1.59	7.21	22.17	59.93	6.84	24.04	5.58	18.37	81.54	76.43
	4	1.23	1.17	15.08	52.83	6.47	17.30	4.76	13.95	73.52	80.62
	5	1.04	1.59	14.20	32.38	6.15	16.35	3.68	8.95	59.86	54.72
	6	1.18	1.95	14.69	62.61	5.71	19.42	4.13	18.73	72.29	96.46
	7	1.17	1.21	95.05	100.58	14.48	26.20	26.19	28.38	180.84	108.33
	8	2.74	4.65	88.66	100.16	12.77	22.25	24.03	26.85	188.21	120.69
	9	2.58	5.54	97.64	22.54	14.33	11.56	26.36	5.57	183.91	48.21

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

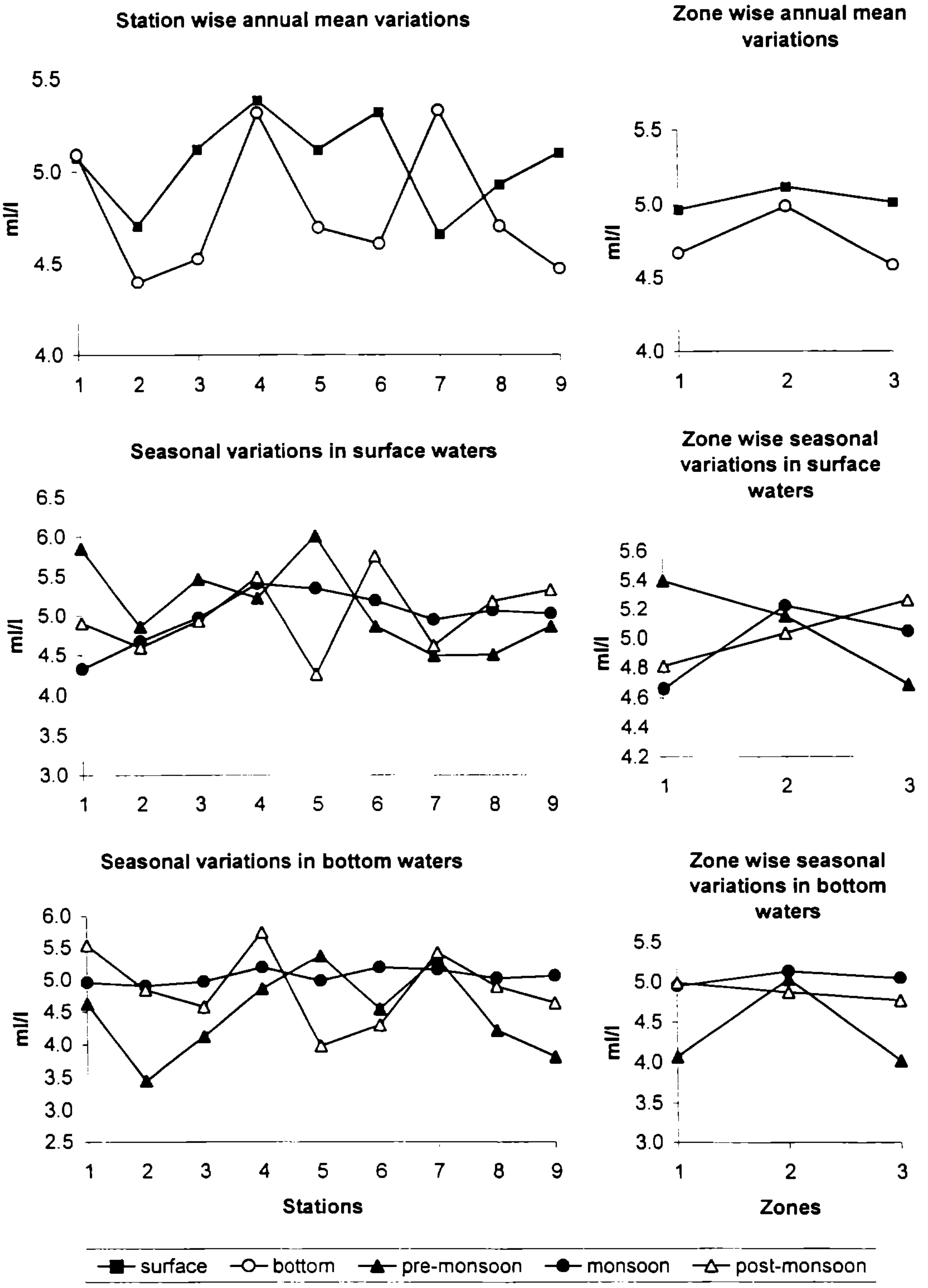


Figure 3.4 Seasonal and spatial variations of dissolved oxygen in the study area.

bottom water also, there was an increase at zone 2 but the lowest was at zone 3.

Seasonal variations of dissolved oxygen are also given in Figure 3.4. As in the case of pH, seasonal variations were not uniform throughout the stations. Surface and bottom waters also behaved differently in different seasons. In surface water, zone 1 recorded highest average value in pre-monsoon season but the lowest average in this zone was observed during the monsoon season. No marked seasonal variations in the dissolved oxygen values were observed at zone 2 in surface water. The surface water at zone 3 showed marked difference in seasonal average values; highest average value was observed in post-monsoon season and the lowest was observed during the pre-monsoon season. Thus, the trend observed in the distribution of dissolved oxygen values in surface waters were such that in pre-monsoon season, the seasonal average values decreased from zone 1 to zone 3, whereas in post-monsoon season, there was an increasing trend from zone 1 to zone 3 and in monsoon season, the values increased from zone 1 to zone 2 and then slightly decreased at zone 3.

The trend observed in bottom waters was different. The zonal average values of dissolved oxygen during the pre-monsoon season were almost equal and were notably lower at zones 1 and 3 than that of zone 2. During the post-monsoon season, there was a gradual decreasing trend from zone 1 to zone 3, whereas in monsoon season, the value increased at zone 2 and then slightly decreased at zone 3. There was not much difference between the seasonal average values at zone 1 during the monsoon and post-monsoon seasons but pre-monsoon value was considerably lower. At zone 3, the highest seasonal average was found in monsoon season and the lowest in pre-monsoon season. At zone 2, though the highest seasonal average was found in monsoon season, the lowest was found in post-monsoon season.

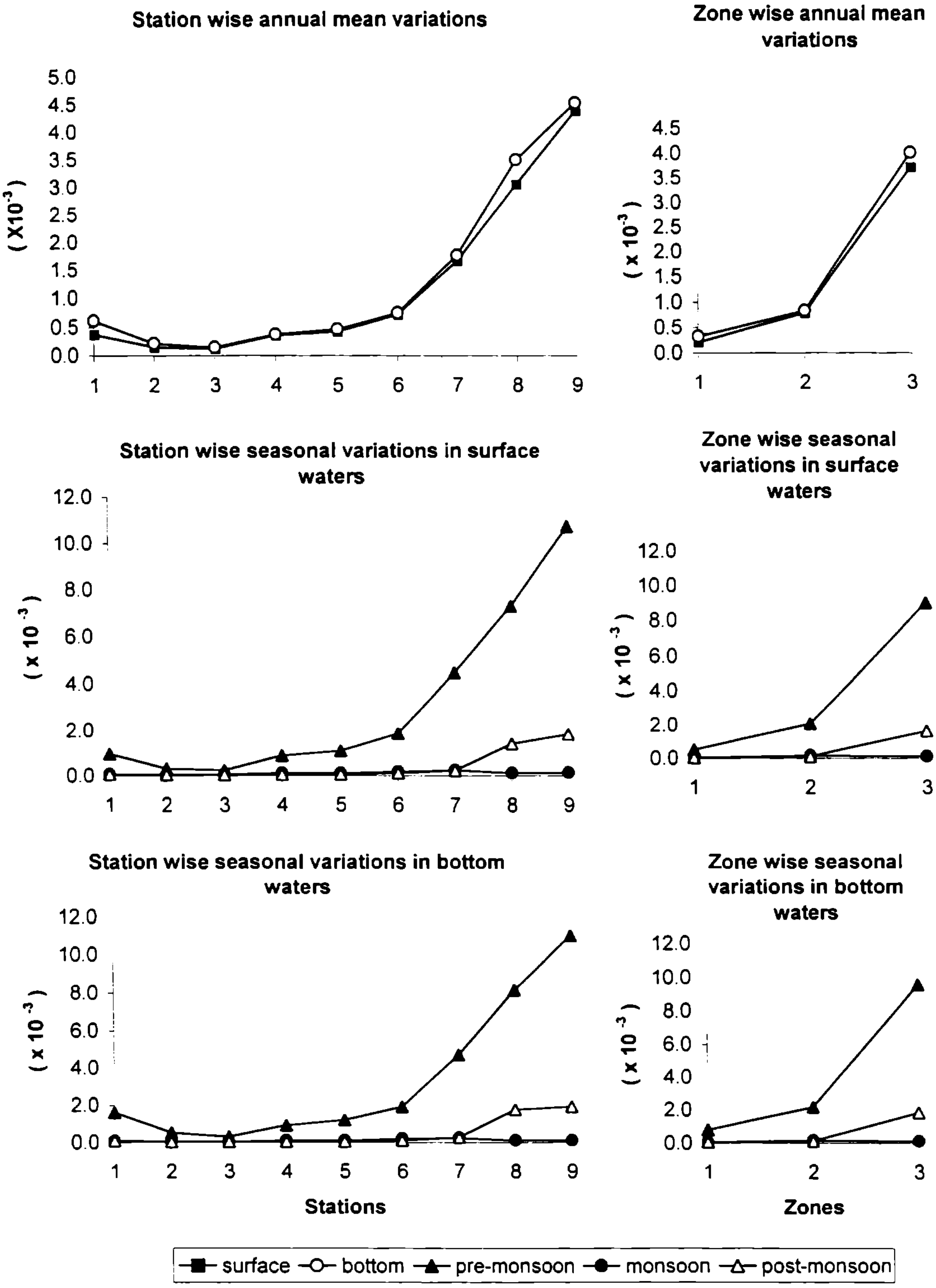
The wide range of dissolved oxygen concentrations, as observed in the present study, was also reported from Cochin Estuary by different workers. Babukutty (1991) reported dissolved oxygen values in the range 1.3 to 8.7 ml/l, whereas Sureshkumar (1998), in a study, which covered almost the entire area from Cochin to Alleppey, reported dissolved oxygen values in the range 2.2 to 9.5 ml/l. The higher DO values in the surface water may be due to the direct dissolution of atmospheric oxygen or due to photosynthesis by phytoplankton, which predominates respiration, or due to the subsurface consumption of oxygen for the oxidation of organic matter. The wind induced surface turbulence may also favour the high oxygen content in surface water. The comparatively lower dissolved oxygen values at stations 6, 7, 8 and 9 in the pre-monsoon period showed the prevailing of slightly reducing conditions in these stations as a result of the utilization of oxygen for the degradation of organic matter. This finding is further supported by the fact that these stations recorded lower pH values in the pre-monsoon season. The comparatively lower dissolved oxygen values at stations 6, 7, 8 and 9 are also related to the higher salinity values observed (discussed later) at these stations as dissolved oxygen has an inverse relationship with salinity. The generally higher DO values in surface water at zones 2 and 3 in the post-monsoon season coincide with the high primary production reported (Kunjukrishnapillai et al., 1975) during this period in the region. Thus, the spatial and temporal variations of dissolved oxygen observed in the present study can be attributed to variations in water temperature, salinity changes in pre-monsoon and monsoon seasons, photosynthetic activity of phytoplankton and oxidation of organic matter.

Salinity

In general, salinity in the marine environment is relatively constant and has comparatively little influence on the heavy metal concentrations. However, in estuaries, where fresh and salt-water intermix, salinity plays a dominant role in influencing metal concentrations in water and sediment. In sea water, the concentrations of dissolved heavy metals are generally much lower than in fresh water.

The variation in salinity in this region was of such a magnitude that the values ranged from 0.05 x 10^{-3} to 12.08 x 10^{-3} in surface waters and 0.05 x 10^{-3} to 12.34 x 10^{-3} in bottom waters (Table 3.1). Both surface and bottom waters recorded highest salinity values at station 9 (Table 3.3). The overall annual mean values in surface and bottom waters were 1.25 x 10^{-3} and 1.38 x 10^{-3} (Table 3.1) respectively. The station wise annual mean salinity values increased from station 1 to station 9, the highest being at station 9 (Figure 3.5). The trend in variation of annual mean values of salinity was such that there was only a slight increase at zone 2 but a considerable hike was observed at zone 3 (Figure 3.5). The surface and bottom water salinity did not differ much. This indicates the absence of any vertical stratification, which may be due to the shallowness of the water column in the study area.

In general, all stations recorded lowest salinities during the monsoon period (June to November) and there was a progressive increase in salinity at all stations with the advance of summer (Figure 3.5). Generally, the maximum salinity values were observed during the period March, April and May i.e. the pre-monsoon season. The highest value was 12.34 x 10^{-3} at station 9 in March. In December, January and February, stations 1 to 6 recorded salinities less than 1.0 x 10^{-3}, whereas stations 7, 8 and 9 were saline. During the period of June to November, almost a homogeneous condition prevailed throughout the surveyed area. The wide variations in salinity among seasons and stations were evident from the high coefficient of variations in the values in surface and bottom waters (208 and 200 respectively) (Table 3.1). Zone wise, zone 1 recorded a salinity value less than 1 x 10^{-3} during all seasons (Figure 3.5). Zone 2 also recorded salinity values less than one but only in monsoon and post-monsoon seasons. At zone 3, only in monsoon season, the average value was found below 1 X 10^{-3} In post-monsoon season, the average values increased to 1.63 and 1.87 x 10^{-3} in surface and bottom waters respectively, whereas in pre-monsoon


Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 3.5 Seasonal and spatial variations of salinity.

season, the average values increased to 9.02 and 9.60 x 10^{-3} in surface and bottom waters respectively.

Salinity of estuarine waters has been considered as an index of the estuarine mixing processes and the tidal effects. The reason for the observed spatial and temporal variations in salinity may be related to the intrusion of saline water into this region and changes in the discharges from river and land as a result of heavy rain during the period of south-west and north-east monsoons. From December onwards, intrusion of saline water into Kuttanad region began and saline water covered the maximum area in March, April and May. Initially, it was limited to stations 9 and 8 only. In January and February, salinity intrusion covered the area at stations 9, 8 and 7 In March, April and May, saline upto station 4, starting from station 9 and covering the area of stations 8, 7, 6 and 5, were marked. With the onset of south–west monsoon in June, the salinity in the entire region was almost completely wiped out, as also reported by KWBS (1989), Harikrishnan (1997) and Sureshkumar (1998). Thus, based on the salinity changes, the entire year can be broadly classified into three seasons, viz., December to February, March to May and June to November. December to February is the season of increasing salinity, while March to May is the season of peak salinity and June to November is the season of low salinity. In fact, salinity appeared as the most variable water quality parameter in the study area. The salinity barrier at Thanneermukkam and the mode of its operations significantly influences the spatial and temporal distributions of salinity in the area. Table 3.4 gives 15 years record on the closing and opening of the shutters at the Thanneermukkam salinity barrier. In a study of the bottom salinity characteristics of the Cochin backwater system, before the commissioning of the salinity barrier at Thanneermukkam, Josanto (1971) observed that bottom water salinities varied from 18 x 10^{-3} to 22 x 10^{-3} in the southern upstream part (the present study area), on the contrary, the variations observed during the present study was from the fresh water condition to 12.34 x 10^{-3} which was slightly higher than the data reported by Harikrishnan (1997) (0 to 8 x 10^{-3}) and Sureshkumar (1998) (0 to 8 x 10^{-3}). Thus, the spatial and temporal distribution pattern of salinity in the study area

Table 3.4 Opening and closing dates of shutters at Thanneermukkam salinity barrier

Year	Closing date	Opening date	No. of closure days
1983 - 1984	December 10, 1983	June 8, 1984	181
1984 - 1985	December 26, 1984	May 26, 1985	151
1985 - 1986	December 30, 1985	Jule 14, 1986	166
1986 - 1987	December 4, 1986	June 4, 1987	182
1987 - 1988	January 4, 1988	April 30, 1988	117
1988 - 1989	December 10, 1988	May 24, 1989	165
1989 - 1990	December 14, 1989	May 26, 1990	163
1990 - 1991	November 13, 1990	April 17, 1991	155
1991 - 1992	December 12, 1991	April 14, 1992	124
1992 - 1993	December 15, 1992	April 8, 1993	114
1993 - 1994	December 18, 1993	April 18, 1994	121
1994 - 1995	December 12, 1994	April 18, 1995	127
1995 - 1996	December 22, 1995	April 22, 1996	122
1996 - 1997	December 15, 1996	April 9, 1997	115
1997 - 1998	December 30, 1997	May 11, 1998	132

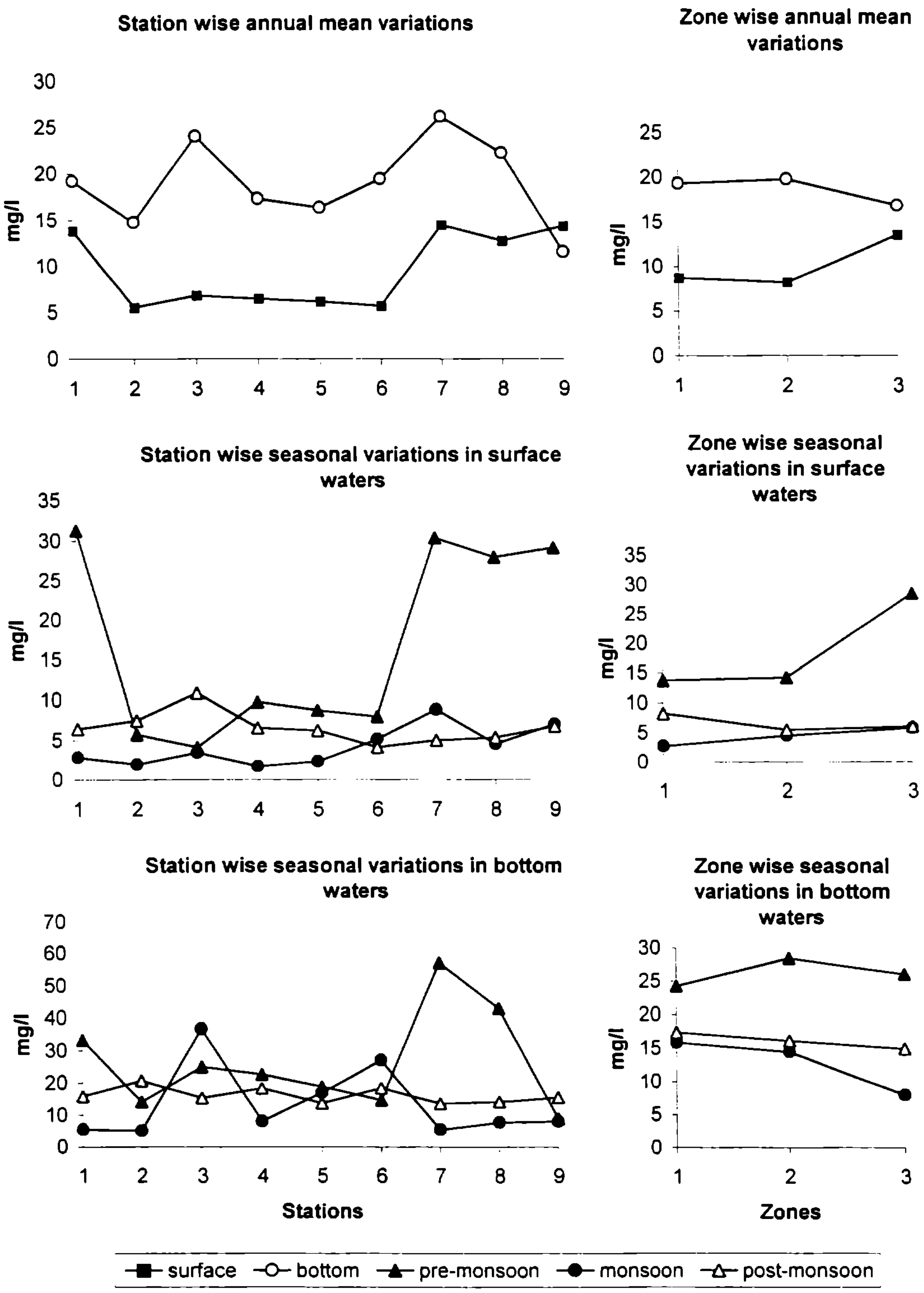
(Source: Office of the Executive Engineer, Mechanical division, Thanneermukkam Project, Department of Irrigation, Govt. of Kerala) clearly showed that a total change in the distribution of salinity in the southern upstream part of the Cochin backwater system has taken place since the commissioning of the salinity barrier at Thanneermukkam. The slight variations in the recently reported salinity values can be attributed to the changes in the operation schedule of the salinity barrier (Kurup et al., 1992).

Suspended particulate matter (SPM)

Suspended particles play a significant role in regulating the chemical form, distribution, and deposition of many oceanic constituents including trace metals. This is particularly true in coastal and estuarine waters where dissolved and particulate runoff from rivers interact with sea water. Some elements in particulate form are transported to the oceans, via river runoff, where they are desorbed at the fresh water - sea water interface (Grieve and Fletcher, 1977; Feely et al. 1981). Others are adsorbed onto the surfaces of suspended particles and are subsequently removed to the sediments as the particles settle (Grieve and Fletcher, 1977; Feely et al. 1981). Many trace metals occur in sea water in association with one or more solid phases (i.e. terrigenous particles from river runoff and winds, biogenic materials, detrital organic matter etc.), or in various chemical forms (i.e. as an adsorbed cation, as an exchangeable cation, as a structural component of the particle, or as part of a coating on the particle). The importance of suspended solids in the estuarine geochemistry of trace metals is related to at least three factors: (1) The suspended matter has a large specific surface area and consequently a large capacity for trace element adsorption/desorption reactions (Boyden et al., 1979; Rae and Aston, 1982), (2) Suspended solids are closely related to the biological uptake of trace elements as filter feeders often indiscriminately ingest suspended matter (Bligh, 1972; Rae and Aston, 1982) and (3) The estuarine transport of trace metals is strongly influenced by the behaviour of suspended solids (Cline et al., 1973; Rae and Aston, 1982).

The SPM values ranged between 1.04 mg/l to 97.64 mg/l in surface waters and 1.17 mg/l to 109.89 mg/l in bottom waters (Table 3.1). The mean value of suspended particulate matter recorded in the bottom water (19.01mg/l) is about twice that recorded in the surface water (9.58 mg/l) (Table 3.1). Stations 5 and 4 recorded the lowest values of suspended solids in surface and bottom waters respectively, whereas stations 9 and 1 recorded the highest values in surface and bottom waters respectively (Table 3.3). The concentrations of suspended particulate matter varied widely, surface waters showing more fluctuations (coefficient of variation 179) than bottom waters (coefficient of variation 103) (Table 3.1). Generally, the suspended solids in the bottom waters were found to be higher than in the surface waters (Figure 3.6). No definite trend in the annual mean values of suspended solids was observed among stations. The annual mean concentrations of suspended solids in the bottom waters at stations 2, 3, 4, 5 and 6 were comparable and lower than the annual mean concentrations at stations 1, 7, 8 and 9. The distribution of suspended particulate matter was such that the zonal average of annual mean values did not differ much at zones 1 and 2 in surface waters, whereas the annual mean value at zone 3 was much higher. In bottom water, though the zonal average at zones 1 and 2 were almost equal, zone 3 recorded lower zonal average.

In surface waters, except at stations 2 and 3, the highest seasonal average was recorded in the pre-monsoon season. The highest seasonal values recorded in the surface waters at stations 1, 7, 8 and 9 were notably much higher (approximately about 5 times) than the highest values recorded at stations 2, 3, 4, 5 and 6. The lowest seasonal average in the surface waters from stations 1 to 5 and at station 8 was observed in the monsoon season, while at stations 6, 7 and 9, the lowest values were observed in the post-monsoon season (Figure 3.6). The seasonal loads of suspended solids in the bottom waters were not as specific as that of surface waters. Stations 1, 4, 5, 7 and 8 recorded highest values in the pre-monsoon period, station 2 showed highest values in the post-monsoon period and stations 3 and 6 recorded highest values in monsoon period.



Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 3.6 Seasonal and spatial variations of suspended particulate matter(SPM).

In general, the comparatively higher suspended particulate matter concentrations in the pre-monsoon and post-monsoon seasons may be due to the high primary production and zooplankton production in this season (Kunjukrishnapillai et al., 1975). Babukutty and Chacko (1995) had reported a mean suspended particulate matter concentration of 18.62 mg/l from the northern part of the Cochin estuarine system that is comparable to the mean value (14.30 mg/l) observed in the present study. The higher concentrations of suspended particulate matter in the bottom waters may be due to the resuspension of sediments at the bottom. The generally observed uniform concentration of suspended particulate matter in the study area indicated that the backwater system is physically less dynamic.

Dissolved major elements

Major elements or ions in sea water are those having a concentration greater than one ppm and have very low geochemical reactivity (Riley and Chester, 1971). The relative concentrations of the major ions in sea water bear a constant ratio to one another, (ie, constancy of composition) though the total concentrations of individual ions vary from place to place in the sea (Culkin and Cox, 1966; Riley and Tongudai, 1967). This means that the ratios of major ions to chlorinity do not vary significantly in oceans. The constancy of the composition is attributed to the balance between the rate of addition and the rate of removal (Riley and Chester, 1971). The study on the distribution of major elements in the Kuttanad backwaters was also undertaken for a better understanding of the trace metal behaviour in the region.

One approach that has proved to be of value in studying the fate of a dissolved constituent, entering an estuarine system, is to compare its observed distribution with that predicted for simple mixing of water bodies during which the constituent is conserved. If the behavior of a compound or ion is such that there is a linear relationship between its concentration and the degree of mixing between the end members of the mixing series, then this behavior is described as conservative or non-interactive. The term, non-interactive is used in this sense in relation to the concentration as measured analytically and refers in most circumstances to interactions that alter the distribution of a constituent between particulate phases and solution. If such interactions occur to a significant extent, they should be detected through non-linearity in the plot of concentration against a suitable index of mixing. This approach appears most informative for a constituent which has a marked opposite concentration gradient to that of salinity (Burton, 1976), since this represents a situation in which major river input is subjected to a continuous series of altered conditions. With the reverse situation, the material entering in river water is swamped early in mixing by that present in the sea water. The sea water mixing in an estuary, however, can also be subjected to conditions under which its composition may be modified by interactions. In this approach, the index of mixing most usually employed has been salinity (Burton, 1976). Chlorinity or chlorosity values are fundamentally more satisfactory parameters as indices of mixing.

Significant deviations from conservative behavior may result through interactions involving removal of the dissolved constituent by precipitation, through uptake by particulate phases already present, or through addition by dissolution of, or exchanges with, the solid phases (Burton, 1976; Ghosh et al., 1991). Removal of water by evaporation or its direct introduction in rainfall could conceivably be of importance in unusual localised situations. The assessment of behavior during mixing by examining plots of concentration of constituent against a mixing index appears straightforward, but in practice, difficulties can arise in satisfactorily defining the end members. The most obvious problem stems from possible variations in concentration between different fresh water inputs to an estuary.

Dissolved magnesium

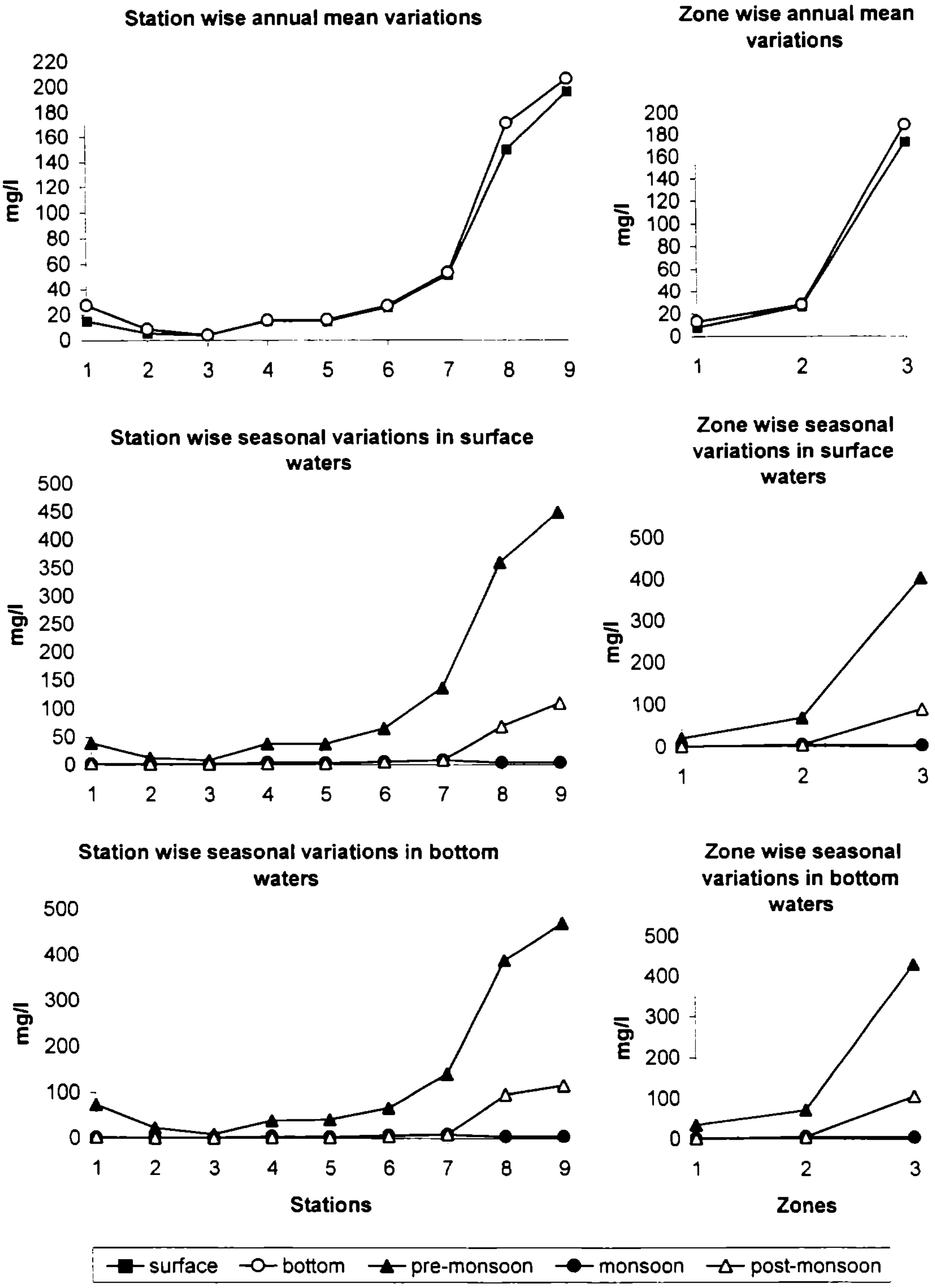
Magnesium is the second most abundant cation in sea water, which has an average concentration of 1209 mg/l. The river water contains an average concentration of 4.1 mg/l (Livingstone, 1963). The principal source of dissolved Mg in the ocean is sub aerial weathering on the continents. The most probable processes by which Mg is removed from sea water are carbonate formation, ion exchange, gluconite formation, Mg-Fe exchange and burial of interstitial water.

Concentrations of dissolved magnesium in the study area were found to be in the range 1.08 mg/l to 520 mg/l in surface waters and 1.07 to 509 mg/l in bottom waters (Table 3.1). The overall mean of surface and bottom water concentrations of dissolved magnesium was 53.27 mg/l and 58.93 mg/l respectively (Table 3.1). The concentrations were found to vary widely among seasons and stations, which were evident from the high coefficient of variations in the recorded values (213 and 207 for surface and bottom waters respectively) (Table 3.1). The station wise minimum, maximum, annual mean concentrations, standard deviations and coefficient of variations are given in Table 3.5. The lowest annual mean concentration was observed at station 3 (4.29 mg/l) and highest annual mean concentration was at station 9 (206.42 mg/l). Though, the minimum value observed at each station fall within a short range (1.07 mg/l to 1.87 mg/l), the maximum values showed a wide range (12.30 mg/l to 520 mg/l). The trend observed in the variations of annual mean concentrations was such that initially the values showed a decreasing trend from station 1 to station 3 and then showed an increasing trend towards station 9 (Figure 3.7). The surface and bottom water concentrations did not differ much. This may be due to the shallowness of the stations. The zonal average value of annual mean concentrations (Figure 3.7) at zone 3 was found to be remarkably higher than the values observed at zones 1 and 2.

Table 3.5 Station wise summary statistics on dissolved magnesium and Mg : Cl ‰ ratio.

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Magnesium (mg/l)	1	1.71	1.70	94.60	226.00	15.31	27.27	29.03	64.33	189.54	235.92
	2	1.13	1.10	24.90	62.00	5.77	9.03	7.75	17.51	134.34	193.92
	3	1.08	1.07	12.30	12.90	4.29	4.32	4.07	4.22	95.02	97.65
	4	1.52	1.55	69.50	69.00	15.39	15.69	23.02	23.63	149.62	150.66
	5	1.30	1.27	66.20	77.40	15.04	16.17	21.92	24.61	145.80	152.19
	6	1.87	1.77	108.00	116.00	25.69	26.75	33.76	35.50	131.41	132.74
	7	1.38	1.55	179.00	211.00	51.59	53.52	65.29	70.43	126.55	131.60
	8	1.64	1.75	477.00	460.00	149.86	171.22	171.72	186.36	114.59	108.84
	9	1.82	1.79	520.00	509.00	196.50	206.42	214.35	221.59	109.09	107.35
Mg : Cl ‰ ratio	1	0.068	0.065	0.127	0.183	0.092	0.092	0.020	0.036	21.39	39.79
	2	0.067	0.069	0.274	0.181	0.118	0.103	0.061	0.036	51.20	34.59
	3	0.038	0.035	0.396	0.196	0.118	0.093	0.094	0.044	79.94	46.67
	4	0.072	0.072	0.191	0.171	0.110	0.104	0.039	0.036	35.71	34.34
	5	0.031	0.033	0.200	0.208	0.102	0.092	0.050	0.044	48.81	47.81
	6	0.046	0.042	0.148	0.126	0.090	0.086	0.029	0.023	32.12	27.00
	7	0.026	0.020	0.118	0.129	0.076	0.075	0.024	0.027	31.82	36.43
	8	0.064	0.069	0.168	0.236	0.089	0.103	0.026	0.045	29.47	43.65
	9	0.010	0.062	0.125	0.114	0.076	0.085	0.028	0.016	36.71	19.28

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)


Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 3.7 Seasonal and spatial variations of dissolved magnesium.

Seasonal variations were characterised by remarkable increase in dissolved magnesium concentrations during the pre-monsoon periods in both surface and bottom waters (Figure 3.7). The concentrations in monsoon and post-monsoon periods did not vary much in stations 1 to 7 In stations 8 and 9, though concentration in monsoon period remained steady, the post-monsoon concentrations were considerably higher than the monsoonal concentration. Tripathy et al (1990) observed a similar seasonal variation of dissolved magnesium in the Rushikulya Estuary (Orissa, India) with a maximum value (910 mg/l) in the pre-monsoon season and a minimum value (0.28 mg/l) in the monsoon season. The higher values in the pre-monsoon period were due to the intrusion of saline water during this period in the region. During the monsoon period, the entire region became fresh water zone, which accounts for the lowest magnesium value in this period. The values in this period remained less than 10 mg/l. In the post-monsoon season also, stations 1 to 7 remained almost as a fresh water zone, which explains the lower values of magnesium in these stations in the post-monsoon period. The intrusion of saline water into stations 8 and 9 began from the post-monsoon period and this explained the high magnesium concentrations at stations 8 and 9 during the post-monsoon period. Figure 3.7 shows that stations 1, 2 and 3 recorded the lowest values in the monsoon season. These are the stations that located at the upstream part of the estuary and receive the maximum riverine influxes. The trend observed in the variation of dissolved magnesium in the pre-monsoon season is almost in accordance with the trend observed for salinity variations in these stations. This is evident from the highly significant positive correlation of dissolved magnesium with salinity ($r = 0.958$ and 0.964 respectively for surface and bottom waters, $n = 108$, $p << 0.001$). This observation suggests that the major controlling factor in the spatial and temporal distribution of dissolved magnesium in this part of the Cochin backwater system is the salinity variations in the region.

Definite seasonal and temporal variations were observed in the magnesium chlorinity ratio. Unlike the seasonal trend observed for dissolved magnesium concentrations where seasonal maximum was observed in the pre-monsoon season, the ratio of magnesium to chlorinity generally showed seasonal hike in the post-monsoon season (Figure 3.8) except at stations 3 and 8 in surface waters and at 1 and 8 in bottom waters. The station wise annual mean values ranged from 0.076 to 0.118 in surface waters and 0.075 to 0.103 in bottom waters (Table 3.5). The spatial distribution of dissolved Mg concentrations and Mg-chlorinity ratios were different. Generally, there was a decreasing trend of the ratio from stations 2 to 7 followed by a slight increase at station 8 and a further decrease at station 9 (Figure 3.8) contrary to the increasing trend observed from stations 1 to 9 in the case of dissolved Mg. These results suggest that there was considerable input of Mg into the backwater system during the post-monsoon period. The source of this magnesium may be from the excessive amount of fertilizers being used in the paddy fields, which reach the backwater system along with the run off from the paddy fields during the post-monsoonal showers. Narvekar et al. (1981) had observed such addition of magnesium during the entire period of observation in Mindola River Estuary (Gujarat). The magnesium chlorinity ratio is almost a constant in sea water due to its conservative behaviour and is found to be 0.067 (Riley and Chester, 1971). But in coastal and estuarine waters where fresh water modifies the concentrations of various elements, the ratio is not found to be a constant. Narvekar et al. (1983) found conservative behaviour for magnesium in the Ambica Estuary (India). Similarly, conservative behaviour was also reported from Cauvery Estuary (India) by Ramanathan et al. (1988). The wide variations in the Mg-chlorinity ratios observed in the present study also suggest that the behaviour of magnesium in the southern upstream part of Cochin backwater system is not conservative in nature. Such wide variations in Mg Cl ‰ ratio (0.033 to 2.760) was also observed in the Rushikulya Estuary by Tripathy et al. (1990). Tripathy et al. (1990) also observed that the values of Mg Cl ‰ ratio under high salinity regime remained close to the value (0.067) reported for sea water. In the present study, an examination of the trend in the variation of the annual mean values of Mg Cl ‰ ratios showed that the variations from the oceanic value (0.067) is more in the fresh water regimes and the values tend to be more closer to the oceanic values towards the mixing zone. Semi-

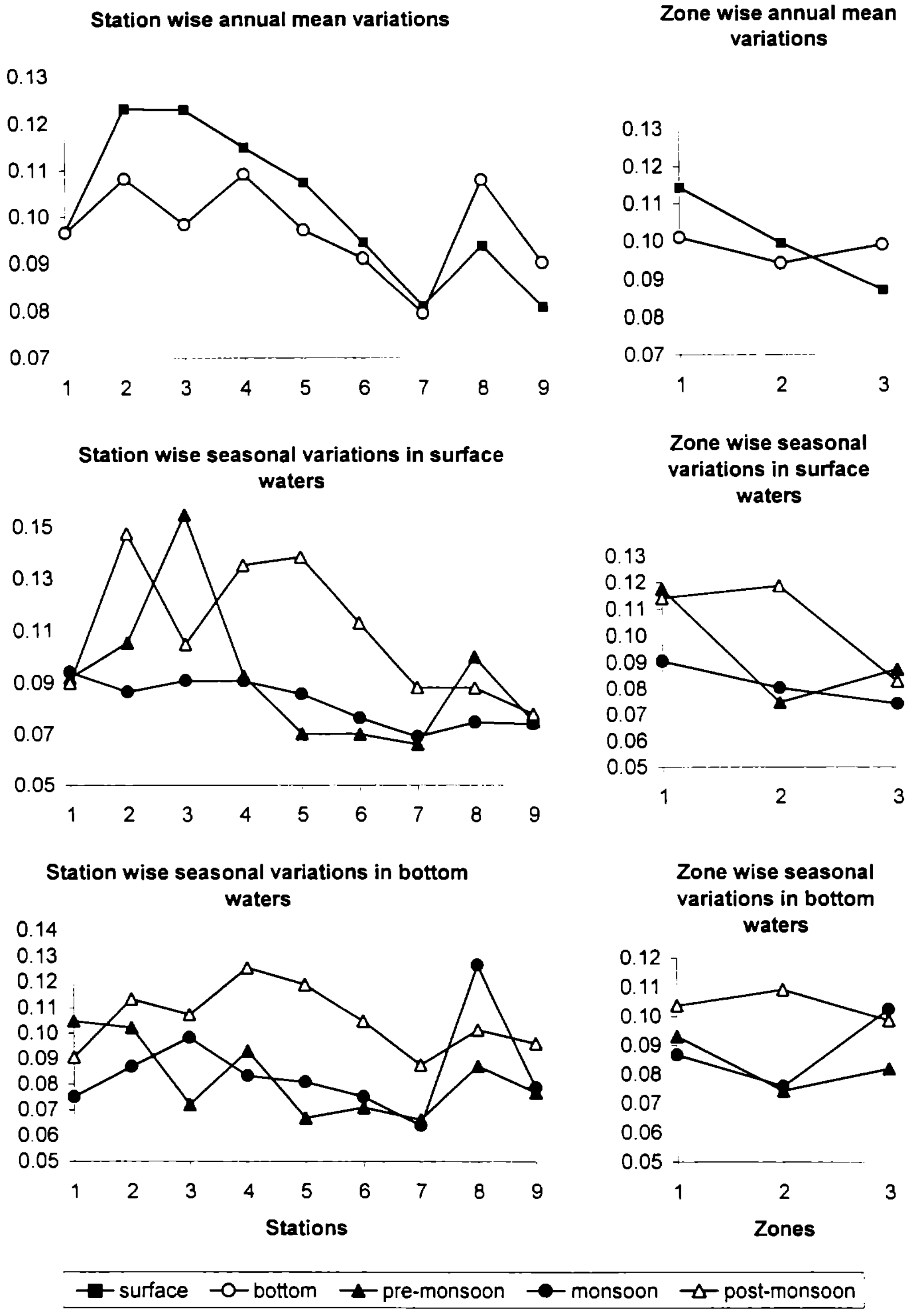


Figure 3.8 Seasonal and spatial variations of dissolved Mg : Cl‰ ratio.

conservative behaviour of magnesium was also reported from Hugly Estuary (Calcutta, India) by Ghosh et al. (1991). As observed in the present study, Ghosh et al. (1991) also found that the semi-conservative behaviour was more in the low saline region and it decreased with increase in chlorinity and this behaviour of Mg in the Hooghly Estuary was attributed to biological uptake, precipitation and ion-exchange processes on clay minerals. The non-conservative behaviour of an element in mixing zone may be due to ion exchange, variation in ionic strength, adsorption and biological uptake (Liss, 1976). In the present case also, it can be inferred that the behaviour of Mg in the Kuttanad waters is influenced by ion-exchange processes on clay minerals, biological uptake, precipitation, adsorption and variation in ionic strength in addition to anthropogenic inputs.

Dissolved calcium

The average concentration of calcium in sea water is 413 mg/kg. Due to its conservative behaviour, calcium bears a constant ratio with chlorinity (0.021) in sea water. The average concentration of calcium in river water is 15.0 mg/kg. Culkin and Cox (1966) observed a higher concentration of calcium in the deeper water than in the surface water. This increase is mainly due to the dissolution of precipitated calcium carbonate in bottom water. Land drainage, rate of biological uptake, precipitation and dissolution processes and characteristics of shallow system modify the calcium concentrations in coastal, estuarine and lagoon waters (Sugandhini Naik and Reddy, 1980). There is a marked dominance of calcium in river waters contrasting with that of magnesium in sea water.

Dissolved concentrations of calcium during the period of survey varied from 1.76 mg/l to 148 mg/l in surface waters and 1.73 to 152 mg/l in bottom waters. The highest dissolved calcium concentration (152 mg/l) as in the case of magnesium was observed at station 9. The overall mean values of dissolved calcium in surface and bottom waters were 19.20 mg/l and 20.93 mg/l respectively (Table 3.1). This is about 2.8 times higher than the average concentration of dissolved magnesium observed in the present study. Dissolved calcium concentrations also showed wide variations in values (coefficient of variation 166). The station wise minimum, maximum, annual mean concentrations, standard deviations and coefficient of variations are given in Table 3.6. Station 3 recorded the least fluctuation in dissolved calcium concentrations. The annual mean concentrations showed a decreasing trend from station 1 to station 3 and then found increasing towards station 9. Thus, the trend observed in the variations of annual mean concentrations of dissolved calcium was similar to that of magnesium. As in the case of magnesium, the difference between surface and bottom water concentrations was not very significant, probably due to the shallowness of the water body.

The variations in seasonal concentrations are given in Figure 3.9. Like magnesium, all stations showed highest values in the pre-monsoon period and the concentrations at stations 1 to 7 did not vary much during monsoon and pre-monsoon periods. At stations 8 and 9, the post-monsoon period showed considerably higher values than the monsoon period. The higher values observed at all stations during pre-monsoon period and the higher values at stations 8 and 9 in the post-monsoon period were attributed to the intrusion of saline water during these periods in the region. The salinity dependency of dissolved calcium concentration was also evident from the good correlation of dissolved calcium with salinity ($r = 0.963$ and 0.964 for surface and bottom waters respectively, $n = 108$, $p << 0.001$). During monsoon and post-monsoon seasons, all stations except stations 8 and 9 in post-monsoon became fresh water zones. Tripathy et al. (1990) observed calcium concentrations in the Rushikulya Estuary (Orissa, India) varying from 49.68 to 430 mg/l where the chlorinity varied from 0.28×10^{-3} to 18.77×10^{-3} The author also observed high values in the pre-monsoon season and low values in the monsoon season due to the variations in salinity, as observed in the present study.

As in the case of magnesium, seasonal and temporal variations were also observed in the Ca-Cl ‰ ratios (Figure 3.10). The general trend

Table 3.6 Station wise summary statistics on dissolved calcium and Ca : Cl ‰ ratio.

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Calcium (mg/l)	1	2.18	2.03	33.40	72.40	7.69	11.47	9.78	20.06	127.19	174.95
	2	1.84	1.76	10.90	22.90	4.59	5.82	3.29	6.31	71.67	108.50
	3	1.95	1.87	12.33	11.80	5.32	4.92	3.85	3.36	72.45	68.25
	4	2.17	2.34	30.30	28.80	9.46	9.61	9.11	9.40	96.29	97.85
	5	2.05	2.02	28.40	31.70	9.81	10.40	8.98	9.83	91.52	94.51
	6	2.42	2.31	43.20	44.60	15.55	15.56	14.55	14.37	93.52	92.39
	7	1.97	2.12	61.60	69.60	20.12	20.64	22.36	23.13	111.13	112.10
	8	1.76	1.73	125.00	124.00	43.82	52.09	47.63	54.06	108.69	103.78
	9	1.83	1.73	148.00	152.00	56.46	57.83	60.24	62.73	106.70	108.48
Ca : Cl ‰ ratio	1	0.028	0.029	0.141	0.198	0.093	0.088	0.036	0.052	38.658	58.94
	2	0.034	0.031	0.339	0.282	0.150	0.136	0.080	0.064	53.066	47.38
	3	0.044	0.043	0.511	0.301	0.177	0.137	0.125	0.071	70.841	51.78
	4	0.031	0.029	0.261	0.253	0.131	0.123	0.077	0.072	58.527	58.76
	5	0.027	0.029	0.271	0.278	0.123	0.118	0.080	0.081	65.357	68.45
	6	0.027	0.023	0.227	0.192	0.099	0.092	0.063	0.055	63.731	59.90
	7	0.009	0.008	0.149	0.120	0.064	0.058	0.043	0.039	67.236	67.43
	8	0.022	0.021	0.086	0.192	0.048	0.061	0.024	0.051	49.302	82.83
	9	0.011	0.019	0.078	0.101	0.038	0.044	0.022	0.025	56.253	57.28

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

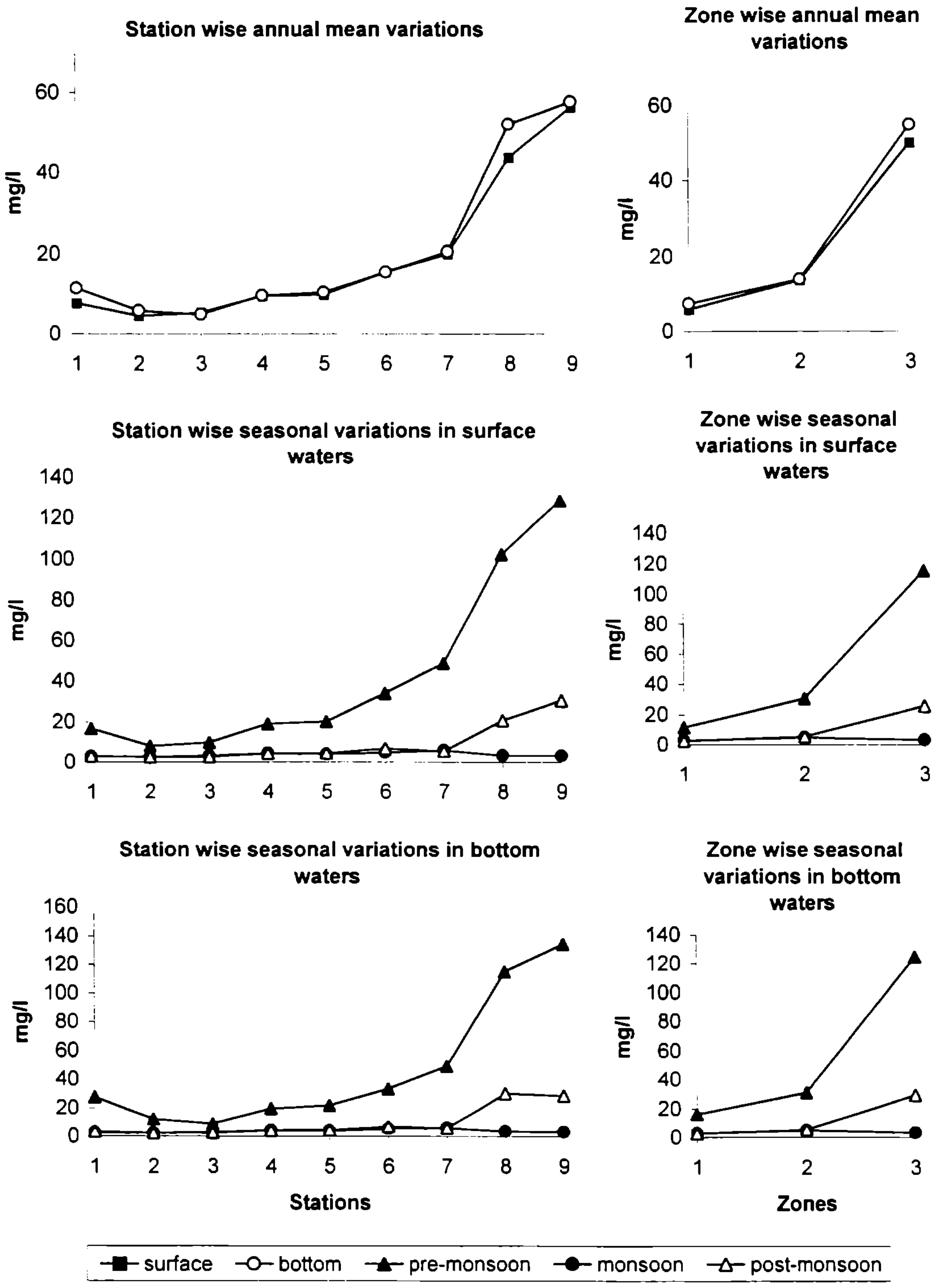
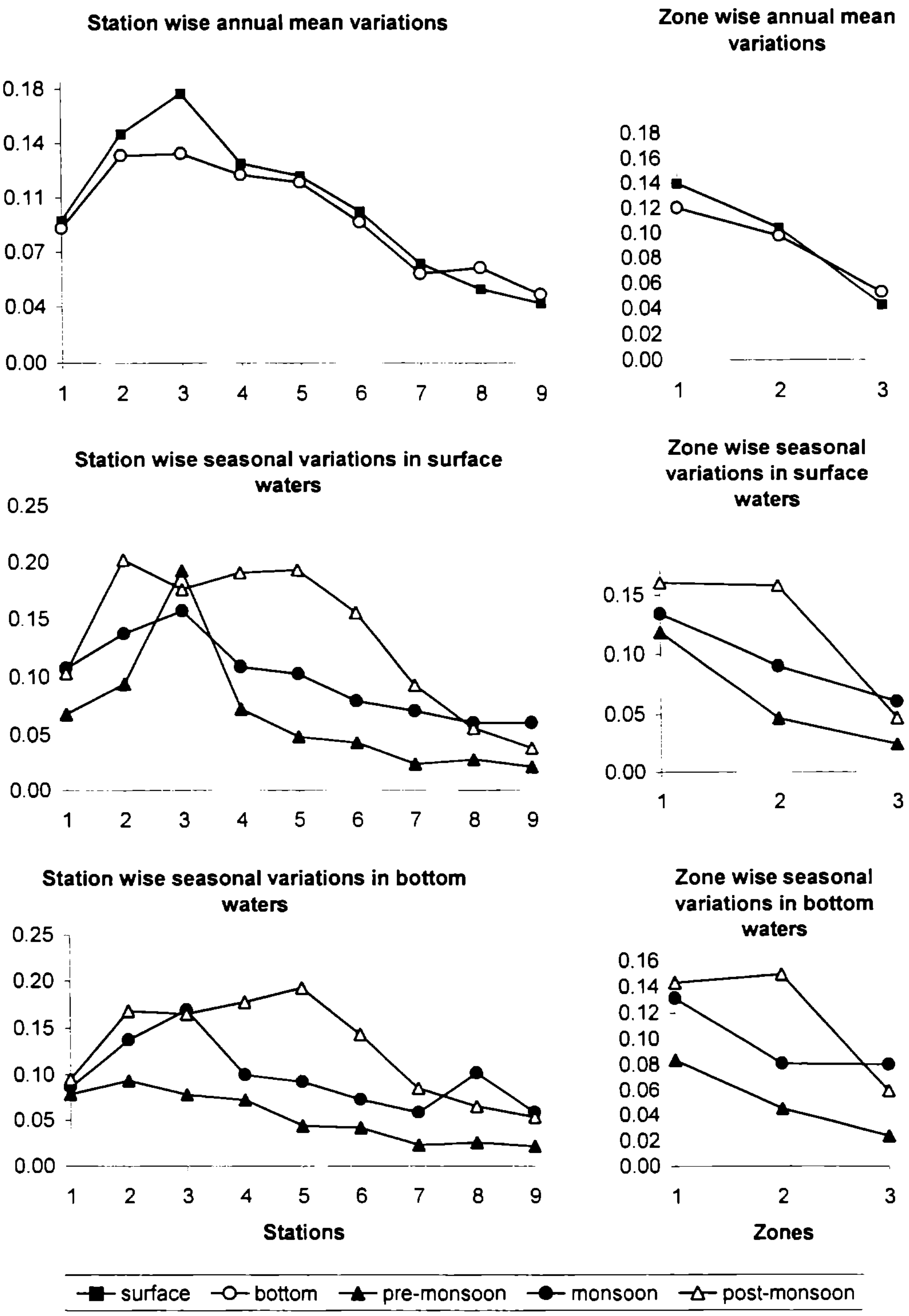


Figure 3.9 Seasonal and spatial variations of dissolved calcium.



Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 3.10 Seasonal and spatial variations of dissolved Ca : Cl‰ ratio.

was that post-monsoonal values were higher than the pre-monsoonal and monsoonal values, especially in stations 4, 5, 6 and 7 (zone 2). This type of post-monsoonal hike was observed in the case of magnesium also. The lowest seasonal average was recorded in pre-monsoon season except the value in surface water at station 3. The seasonal trend was more evident in the case of calcium than in the case of magnesium. The station wise summary statistics are given in Table 3.6. Unlike the trend observed in the distribution of dissolved calcium, the ratio of calcium to chlorinity showed a gradual decreasing trend from station 3 to station 9 after an initial increase from station 1 (Figure 3.10). Almost a similar type of variation was observed in the case of magnesium-chlorinity ratio also, except the small hike at station 8. The post-monsoonal hike in the calcium-chlorinity ratio, as observed in the case of Mg-chlorinity ratio, again confirms that there is considerable input of calcium in this season into the water body along with magnesium which again may be associated with the pre-monsoonal influxes from the paddy fields where excessive quantity of fertilizers are being used for agricultural purposes.

Thus, in general, the wide variations in the Ca-Cl ‰ ratios and the post-monsoonal hike confirms that the behaviour of calcium, as observed in the case of magnesium, is not conservative in this part of the Cochin backwater system. The wide variations in Ca Cl ‰ ratio, as observed in the present study, was also reported from the Rushikulya Estuary (0.011 to 0.920) by Tripathy et al. (1990). They also observed that except in monsoon season, the Ca Cl ‰ ratio remained close to the values reported for sea water and the deviation during the monsoon season was assigned to the severe dilution of estuarine water by fresh water input into the system. In the present study also, it was found that Ca Cl ‰ ratio deviated more from the oceanic value in the fresh water conditions and the ratio tends to be closer towards oceanic value in the mixing zone. The deviation of Ca Cl ‰ ratio in the fresh water conditions, especially during monsoon and post-monsoon periods, is attributed to the severe dilution effect of estuarine water by massive ingress of fresh water into the system. This is clearly evident from Figure 3.10 that the seasonal average values during the pre-monsoon season at stations 7, 8 and 9 showed values very close to 0.021. Semi-conservative behaviour of calcium was also reported (Ghosh et al., 1991) from Hooghly Estuary. Processes like biological uptake, precipitation and ion-exchange on clay minerals were attributed for the semi-conservative behaviour of calcium. Narvekar et al. (1981) had found addition of calcium over the entire period of observation in a study of Mindola River Estuary (Gujarat). Sen Gupta and Sugandhini Naik (1981) found semi-conservative behaviour for calcium in Mandovi and Zuari River Estuaries and the same was attributed to the involvement of calcium in the bio-geochemical cycles of the estuary. The semi-conservative behaviour of calcium in the present study also can be due to some or all of the above factors discussed in addition to anthropogenic inputs.

Dissolved strontium

Strontium is a fairly common element, replacing calcium or potassium in igneous-rock minerals in minor amounts. The carbonates (strontianite) and sulphates (celestite) are common in sediments. Solubility product ($\approx 10^{-6.5}$ at 25°C) of strontium sulphate (celestite) quoted by Sillen and Martell (1964) is nearly two log units more negative than the corresponding solubility product for gypsum and suggests that celestite solubility might be having an important control on strontium concentrations. The strontium concentration in most natural waters does not approach the solubility limit of either strontianite or celestite.

The overall mean values of strontium in surface and bottom waters were 316.28 µg/l and 342.47 µg/l respectively (Table 3.1). Similar to that of calcium and magnesium, dissolved strontium also showed high fluctuations in concentrations among seasons and stations (coefficient of variations 196 and 195 respectively in surface and bottom waters). The highest value observed was at station 9 and the lowest value at station 2 (Table 3.7). The highest and lowest annual mean concentrations were also observed at stations 9 and 2 respectively. The spatial variations of dissolved

Table 3.7 Station wise summary statistics on dissolved strontium and Sr : Cl ‰ ratio.

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Strontium (µg/l)	1	20.8	20.2	610.0	1330.0	108.7	174.9	180.5	373.9	166.1	213.8
	2	16.5	14.2	157.0	373.0	49.0	68.7	46.7	102.9	95.4	149.9
	3	15.8	16.4	200.4	108.0	55.2	45.8	55.8	34.5	101.1	75.4
	4	19.6	20.8	416.0	401.0	114.3	115.1	139.3	141.7	121.9	123.0
	5	19.2	18.4	390.0	437.0	111.4	120.4	136.3	150.5	122.4	125.0
	6	22.7	21.4	675.0	693.0	191.0	196.1	216.8	222.7	113.5	113.6
	7	18.9	20.0	1020.0	1160.0	321.8	325.7	384.6	401.0	119.5	123.1
	8	19.6	20.1	2360.0	2420.0	802.2	878.9	899.6	982.6	112.1	111.8
	9	21.2	20.1	3010.0	3150.0	1092.9	1156.6	1192.5	1251.9	109.1	108.2
Sr : Cl ‰ ratio	1	0.434	0.409	1.274	1.886	0.928	0.881	0.270	0.435	29.05	49.36
	2	0.463	0.481	3.134	2.418	1.382	1.224	0.721	0.517	52.18	42.19
	3	0.408	0.392	8.309	2.533	1.810	1.193	2.113	0.596	116.73	49.92
	4	0.430	0.418	2.258	2.060	1.175	1.106	0.559	0.519	47.56	46.95
	5	0.248	0.259	2.316	2.477	1.033	1.006	0.580	0.609	56.10	60.58
	6	0.326	0.298	1.853	1.570	0.910	0.853	0.457	0.389	50.26	45.59
	7	0.154	0.119	1.333	1.313	0.695	0.643	0.338	0.337	48.65	52.48
	8	0.410	0.241	0.957	2.180	0.632	0.780	0.178	0.538	28.07	69.05
	9	0.101	0.392	0.776	1.177	0.538	0.624	0.204	0.218	37.90	34.95

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

strontium were very much similar to that of magnesium and calcium. The annual mean of dissolved strontium concentrations showed a decreasing trend towards station 3 and then an increasing trend from station 3 to station 9 (Figure 3.11). The insignificant differences in surface and bottom water concentrations were mainly due to the shallowness of the stations.

Like that of magnesium and calcium, dissolved strontium also exhibited distinct seasonal variations, the pre-monsoon season showing the highest values (Figure 3.11). Wide variations in concentrations were observed in this season. Stations 1 to 7 had more or less similar concentrations in the monsoon and post-monsoon seasons, but at stations 8 and 9, the post–monsoon season recorded appreciably higher concentrations than the monsoon season. During the pre-monsoon period, concentrations at stations 2 and 3 were slightly lower than that of station 1, but gradually increased from station 4 to 9, reaching the maximum at station 9. This trend can also be observed in the station wise annual mean concentrations.

The average concentration of Sr in stream water was reported to be 60 µg/l (Martin and Whitfield, 1983). Culkin and Cox (1966) reported an average of 7.8 mg/l in the range 7.4 to 7.9 mg/l from sea water, whereas Riley and Tongudai (1967) reported an average of 8.1 mg/l in the range 7.8 to 8.5 mg/l. The observed seasonal variations in dissolved strontium concentrations were in accordance with the salinity variations in the area. Higher values of strontium in pre-monsoon season and at stations 8 and 9 in post-monsoon season were attributed to the increase in salinity at these stations during pre-monsoon and post-monsoon seasons. Since the entire area became a fresh water regime during monsoon season, dissolved strontium values in this season were found very low, within the range 20.5 to 70 µg/l. Thus, it appears that the major controlling factor in the distribution of strontium in the estuary is the intrusion of saline water into the region. The salinity dependency of dissolved strontium is further supported by the excellent correlation of dissolved strontium with salinity (r = 0.962 and 0.961

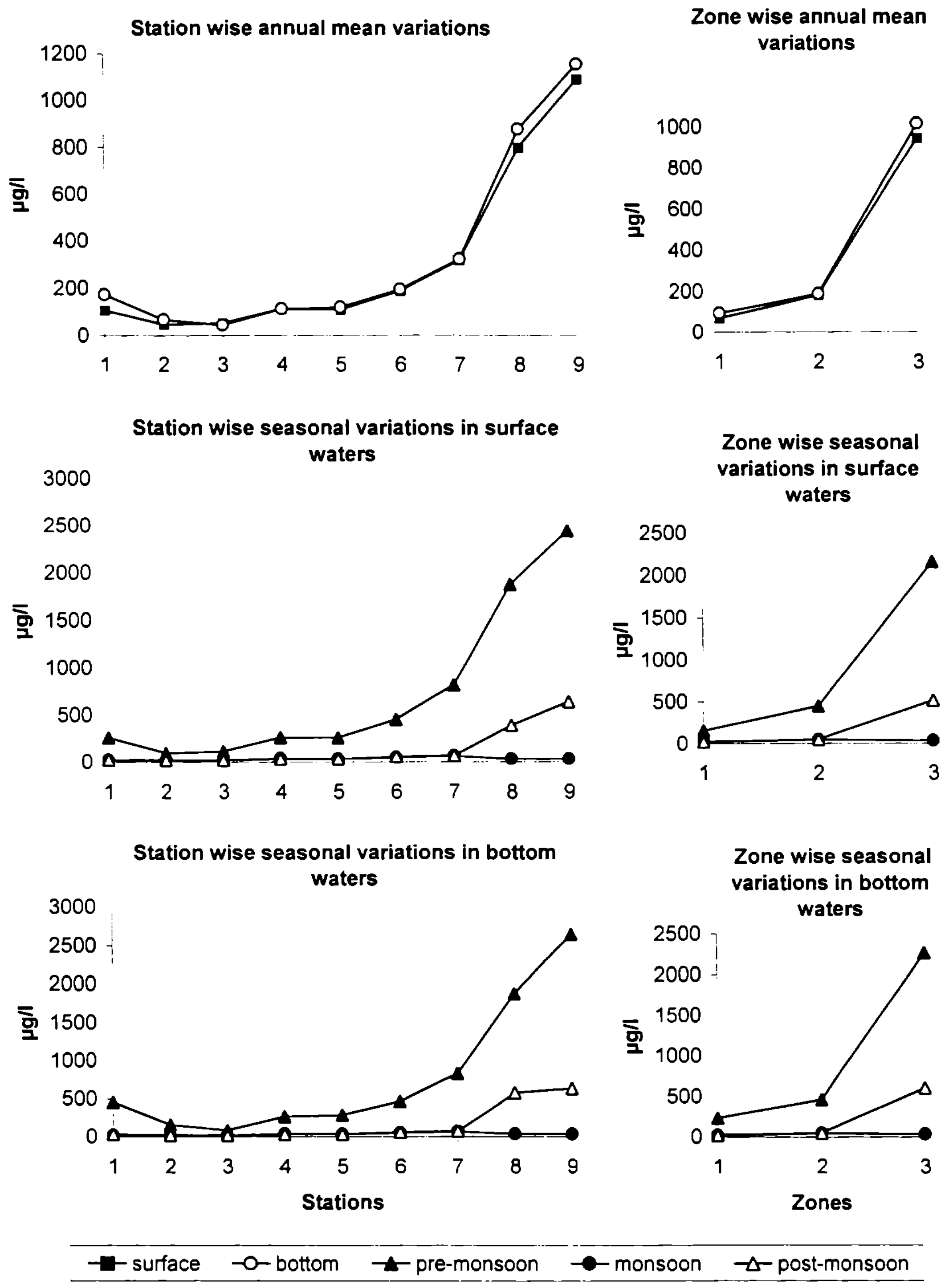


Figure 3.11 Seasonal and spatial variations of dissolved strontium.

respectively for surface and bottom waters respectively, $n = 108$, $p << 0.001$).

The Sr-Cl ‰ ratios were found to fall within the range 0.101 to 8.309×10^{-3} in surface waters and 0.119 to 2.533×10^{-3} in bottom waters. Sr-Cl ‰ ratios in the range 0.41 to 0.47×10^{-3} were reported from different oceans by Culkin and Cox (1966). As in the case of magnesium and calcium, seasonal and temporal variations were observed in the distribution of dissolved strontium also (Figure 3.12). Generally, higher values were observed in the post-monsoon season and lower values in the pre-monsoon season. An exceptional case was station 3 where the pre-monsoonal average was found to be the highest. Similar observations were made in the case of magnesium and calcium. Station wise summary statistics are also given in Table 3.7 The variations observed in the station wise annual mean concentrations (Figure 3.12) were more or less the same as that observed for magnesium and calcium i.e., there was a gradual decrease towards station 9 after an initial increase from station 1 to 2 or 3. This trend was observed in all seasons. The seasonal hike in the ratio of strontium to chlorinity during post-monsoon period confirms anthropogenic addition of strontium into the region during this period.

Dissolved barium

Barium is somewhat more abundant in igneous rocks than strontium, whereas, the carbonate rocks contain considerably less barium than strontium. Barium ions have a larger radius than strontium ions and probably cannot enter the crystal lattices of the carbonates of lighter alkaline earth metals. The solubility of barium carbonate is about the same as that of calcite (Sillen and Martell, 1964). A likely control over the concentration of barium in natural water is the solubility of barite ($BaSO_4$), which is a fairly common mineral. The solubility product for this material is nearly 10^{-10} (Sillen and Martell, 1964) and at sulphate molar activities near 10^{-4} ($\approx$10 mg/l) or

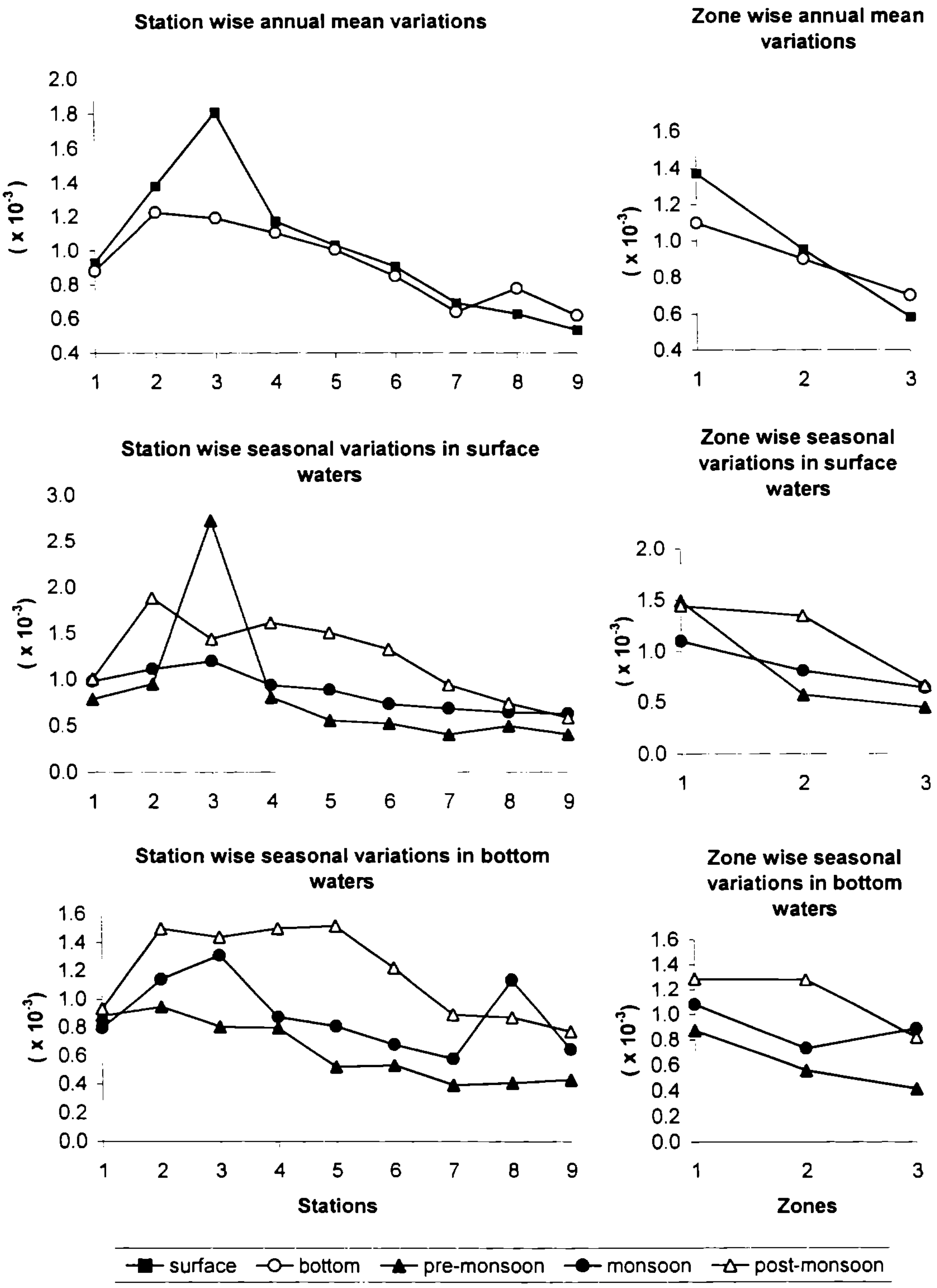


Figure 3.12 Seasonal and spatial variations of dissolved Sr : Cl‰ ratio.

10^{-3} (≈100 mg/l), the corresponding equilibrium molar activities of Ba^{2+} would be 10^{-6} or 10^{-7} (≈ 0.14 mg/l ≈ 0.014 mg/l) respectively (Sillen and Martell, 1964). Another factor that seems to influence the concentration of barium in natural water is adsorption by metal oxides or hydroxides.

Barium concentrations during the survey period were found to vary within the range 13.40 to 270 µg/l in surface waters and 10.50 to 237 µg/l in bottom waters (Table 3.1). Of the five major dissolved elements studied, barium recorded the lowest abundance with mean values in surface and bottom waters of 66.38 µg/l and 63.55 µg/l respectively. Again, among the five dissolved major elements studied, barium recorded the least fluctuations in values (coefficient of variations 86 and 87 in surface and bottom waters respectively) (Table 3.1). Stations 3 and 2 recorded the lowest two annual mean concentrations for dissolved barium (Table 3.8), like that of magnesium, calcium and strontium. In contrast to magnesium, calcium and strontium that showed highest annual mean concentrations at station 9, barium recorded highest annual mean concentration at stations 7 and 6 for surface and bottom waters respectively (Figure 3.13). After station 3, the trend observed was slightly different from that of magnesium, calcium and strontium. From station 3 onwards, the values showed an increasing trend, reached maximum at station 7 and then decreased towards station 9. Like magnesium, calcium and strontium, barium also showed clear seasonal variations (Figure 3.13). All stations recorded highest values during the pre-monsoon period, both in the surface and bottom waters. The recorded highest values in surface and bottom waters were observed during the pre-monsoon period (April). No distinguishable variability was observed in the distribution of barium during monsoon and post-monsoon seasons.

The appreciable increase in the values of dissolved barium concentrations during pre-monsoon season and the slightly higher values observed during the post-monsoon season at zone 3 can be attributed to the higher salinity values observed at these stations. This is also confirmed by the significant correlation of barium with salinity (r = 0.567 and 0.587 for

Table 3.8 Station wise summary statistics on dissolved barium and Ba : Cl ‰ ratio.

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Barium (µg/l)	1	24.5	19.4	211.0	222.0	74.1	65.6	59.3	59.8	80.0	91.2
	2	24.2	22.3	99.9	112.0	43.9	43.1	22.2	29.6	50.6	68.5
	3	25.0	20.7	84.0	92.7	40.1	43.8	16.6	26.7	41.4	60.8
	4	19.1	17.2	211.0	208.0	66.4	63.2	65.5	68.6	98.6	108.4
	5	20.7	17.7	166.0	168.0	64.7	58.3	53.4	50.4	82.4	86.4
	6	19.7	21.3	177.0	187.0	79.2	83.7	66.3	72.1	83.8	86.2
	7	18.8	17.9	270.0	237.0	93.4	82.2	90.2	73.1	96.6	89.0
	8	14.9	10.5	189.0	178.0	69.8	66.5	58.0	56.7	83.1	85.2
	9	13.4	12.1	131.0	129.0	65.9	65.5	49.5	49.3	75.1	75.3
Ba : Cl ‰ ratio	1	0.179	0.088	3.596	1.846	1.410	0.936	0.991	0.636	70.29	67.98
	2	0.244	0.132	2.918	2.900	1.740	1.448	0.992	0.837	57.03	57.83
	3	0.201	0.265	3.068	2.350	1.635	1.323	0.976	0.685	59.72	51.75
	4	0.218	0.202	1.655	1.329	0.944	0.752	0.527	0.371	55.83	49.30
	5	0.120	0.110	3.255	1.567	1.015	0.794	0.888	0.514	87.47	64.66
	6	0.106	0.109	1.162	1.040	0.598	0.555	0.365	0.323	61.08	58.12
	7	0.043	0.035	1.230	1.128	0.452	0.394	0.376	0.347	83.33	88.00
	8	0.021	0.023	0.898	1.646	0.287	0.354	0.289	0.497	100.66	140.45
	9	0.018	0.017	0.648	1.025	0.219	0.270	0.256	0.318	116.61	117.58

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

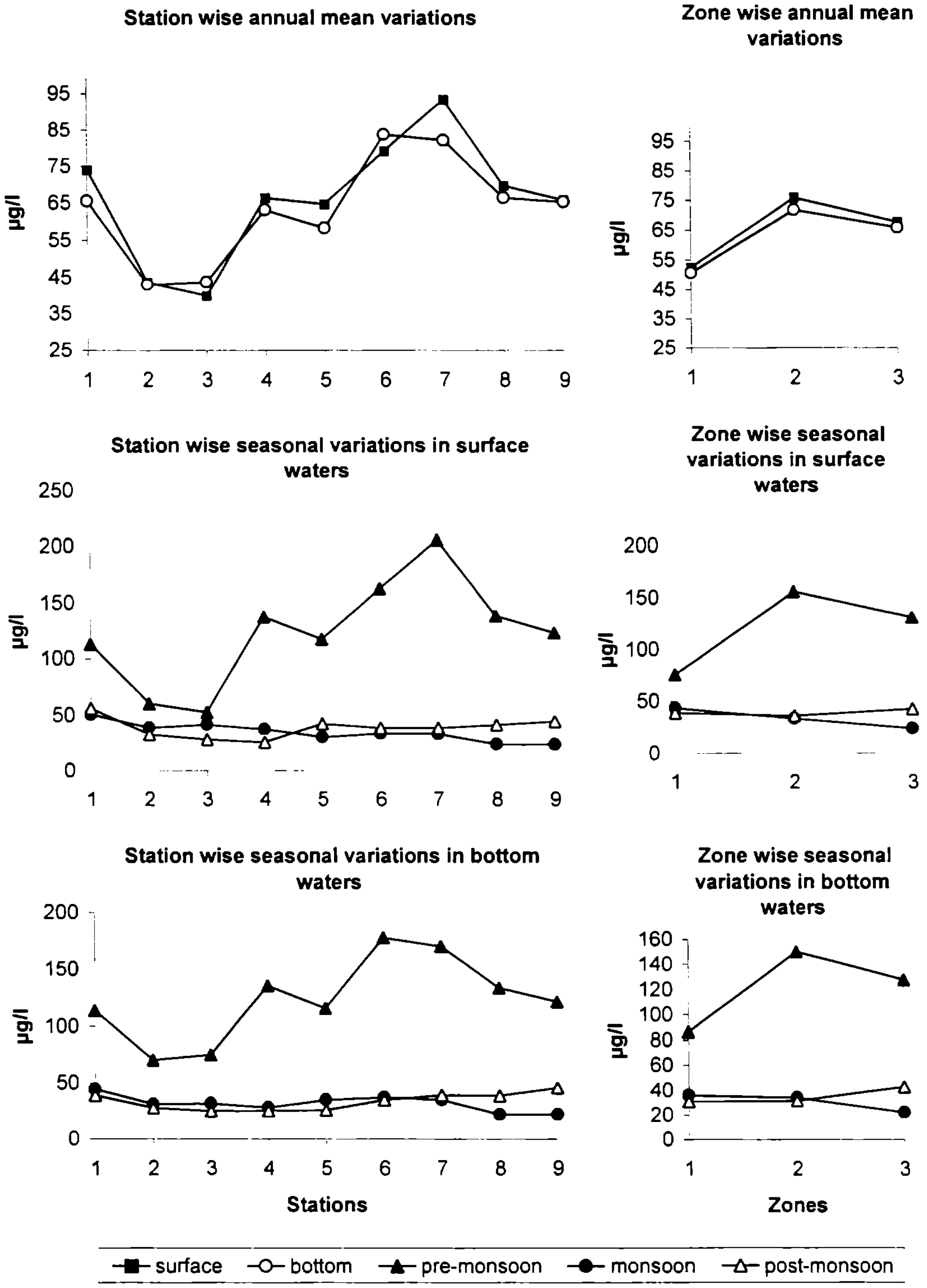


Figure 3.13 Seasonal and spatial variations of dissolved barium.

surface and bottom waters respectively, $n = 108$, $p < 0.001$). A marked difference observed between barium and the other major elements like magnesium, calcium and strontium is that the correlation coefficient of barium with salinity is comparatively less than the correlation of magnesium, calcium and strontium with salinity ($r = > 0.95$). This implies that the behaviour of barium in the study area is slightly different from the behaviour of other major elements like Mg, Ca and Sr, though salinity is the major controlling factor for the distribution of barium in the study area.

The Ba Cl ‰ values were found to fall within the range 0.018 to 3.596 x 10^{-3} in surface waters and 1.025 to 2.900 x 10^{-3} in bottom waters (Table 3.8). The station wise annual mean variations were found to be maximum at station 2 and the trend observed was that the value increased from station 1 to 2 and then decreased gradually to station 9 (Figure 3.14). Comparing the annual mean variations with Mg, Ca and Sr-chlorinity ratios, a clear peak of the Ba Cl ‰ ratio was observed in the fresh water station (station 2). Seasonal variations were clearly evident in the case of barium-chlorinity ratios. The pre-monsoonal averages were clearly less than the averages in monsoon and post-monsoon seasons in all the stations (Figure3.14). Calcium and strontium exhibited somewhat similar behaviour, but in the case of magnesium it was not very clear. The monsoonal and post-monsoonal values did not differ very much, though the values at some stations showed a slight increase.

The general regression equation for dissolved barium concentration (µg/kg) against chlorinity is, Ba = 21.80 Cl ‰ + 49.45. The slope of the equation gives the average barium-chlorinity ratio (0.0218 x 10^{-3}) and the intercept on the barium concentration axis gives the effective zero salinity end member concentration (Coffey et al., 1997). In other words, the Y intercept gives the calculated riverine end member dissolved barium concentration which is equal to 49.45 µg/kg. This value is well comparable with the value (45 µg/l) reported by Durum and Haffty (1963) from the larger rivers of North America. Coffey et al. (1997) in their study of the behaviour of dissolved barium in six estuarine systems in the U.S.A and Europe found the

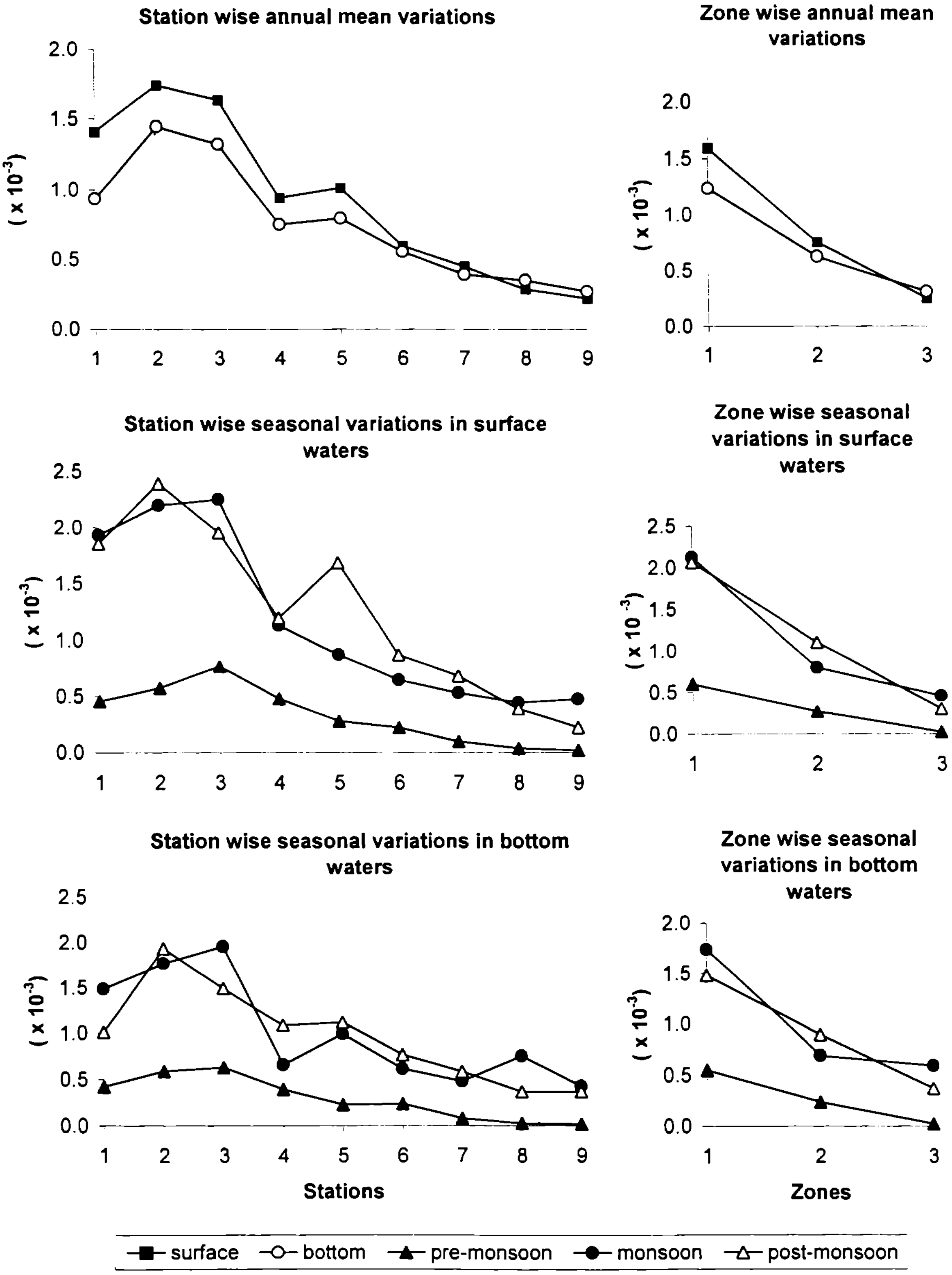


Figure 3. 14 Seasonal and spatial variations of dissolved Ba : Cl‰ ratio.

effective zero salinity end member concentration varying from 26 µg/l to 162 µg/l. This shows that riverine dissolved barium concentrations vary among estuaries. This variability may be anthropogenic in origin or differences in catchment rock type, weathering rates and river flow. Figure 3.14 shows that the Ba Cl ‰ ratio peaks at the fresh water stations 2, 3 and 1. This suggests that release of barium takes place when river water enters the fresh water zone of the estuary. The seasonal variation indicates that this addition is more during the monsoon and post-monsoon seasons. The release of barium can be due to the desorption from river borne suspended particulate matter. Carroll et al. (1993) observed that in the Ganges-Brahmaputra system, particulate material deposited in the lower reaches during high flow season subsequently released barium as saline water moved upstream under low flow summer conditions. The decreasing trend of Ba Cl ‰ ratio during the pre-monsoon season from station 3 to station 9 indicates that removal of Ba in the estuary takes place during the pre-monsoon season in the low salinity region when fresh water mixes with saline water. Coffey et al. (1997) found that removal of dissolved barium takes place at low salinities yielding a concentration minimum at salinity of about 2 in the Schelde, Delaware and Maurice River Estuaries as well as Canary Creek. But in the same study, no barium removal at low salinity was found from Humber Estuary. Also, no removal of dissolved barium was observed from the Ganges-Brahmaputra (Carroll et al., 1993).

Dissolved boron

Boron is an essential micronutrient element for the growth of phytoplankton. However, the tolerance range between toxicity and deficiency of boron is narrow and due to this it can be a pollution hazard in the productive areas of the estuary. Boron is considered as a major element in sea water and its concentrations is 4.5 mg/kg at a salinity 35 ‰. The dissolved boron concentration in river water is about 10 µg/l i.e., the concentration in sea water is about 450 times greater than the average amount in river water. In sea water, boron exists as boric acid and borate. At the pH of sea water, the boric acid and borate remain almost unionised. Cations like Na^+, Mg^{2+} and Ca^{2+} are found to show ion pairing with boron in sea water (e.g., $NaB(OH)_4$, $MgB(OH)_4^+$ $CaB(OH)_4^+$ (Byrene and Kester, 1974) On the assumption that sediments will take up an amount of boron roughly proportional to the dissolved boron level of the water from which they are deposited, it has often been suggested that the boron content of sediments and sedimentary rocks may be used as an indicator of paleosalinity. Measurements of the relationship between dissolved boron and salinity in suites of estuarine samples should throw light on the suggestion of Rajagopal et al. (1981) that boron uptake occurs in estuaries during the mixing of sea and river waters. Boron shows considerable inter-estuarine variability with respect to the removal during the mixing process (Rajagopal et al., 1981).

In the present study, dissolved boron concentrations were found to vary from 3.5 to 1600 µg/l in surface waters and 3.4 to 1490 µg/l in bottom waters (Table 3.1). The recorded mean values of dissolved boron in surface and bottom waters were 168 and 183 µg/l respectively. Similar to that of Mg, Ca etc., boron also showed wide fluctuations seasonally and temporarily as is evident from the high coefficient of variations (209 and 199 in surface and bottom waters respectively). Station 3 recorded the lowest annual mean concentration and the highest annual mean concentration was recorded at station 9 in both surface and bottom waters. The trend observed in the spatial variations of the annual mean concentrations of dissolved boron was almost similar to that observed in the case of Mg, Ca and Sr.

From the seasonal average values (Figure 3.15), it can be seen that all stations recorded the lowest seasonal average of dissolved boron concentrations in the monsoon period. The pre-monsoon period was characterised by the remarkably higher concentration of dissolved boron in both surface and bottom waters. The seasonal average values during pre-monsoon period showed a decreasing trend from station 1 to station 3 and then showed a gradual increasing trend from station 3 to station 9. These

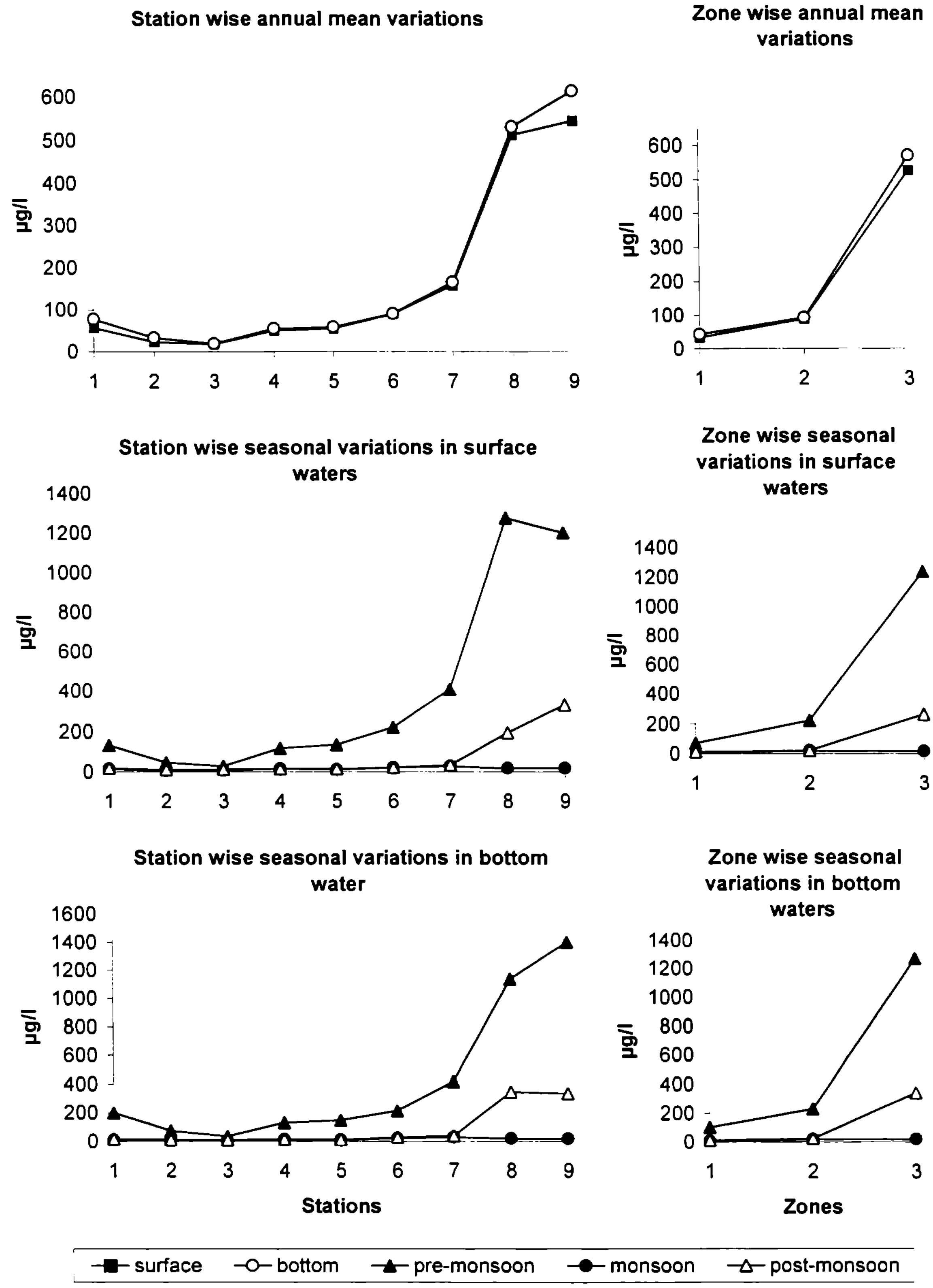


Figure 3.15 Seasonal and spatial variations of dissolved boron.

observations were well in agreement with the salinity distributions in the region during this period. Dissolved boron concentrations and salinity values were found to have good correlations ($r = 0.917$ and 0.964 in surface and bottom waters respectively, $n = 108$, $p << 0.001$). From the coefficient of variation (Table 3.9), it is clear that station 3 was the least affected and station 9 was the most affected ones due to the influence of sea water intrusions. Thus, in the case of boron also saline water intrusion into the region is the major controlling factor which determines the distribution of boron in the study area.

Shirodkar et al. (1982) had reported concentrations in the range 1.17 to 4.74 mg/kg with an average value of 3.33 mg/kg of inorganic boron in the Arabian Sea. Rajagopal et al. (1981) found that the concentrations of boron in the Zuari Estuary (Goa) varied from 0.02 to 5.42 mg/kg corresponding to a chlorinity variation of 0.28 ‰ to 19.76 ‰. The comparatively high values reported from these studies were due to the survey conducted in high saline regions. Liddicoat et al. (1983) reported conservative behaviour of boron in Tamar Estuary (S.W. England).

The average dissolved B-Cl ‰ ratio in sea water is 0.231×10^{-3} (Riley and Chester, 1971). In the present study, considerable variations in B:Cl ‰ ratio (0.063×10^{-3} to 1.918×10^{-3}) was observed (Table 3.9) when compared to oceanic values. The distribution of dissolved boron concentration and B-Cl ‰ ratio showed distinct difference. Comparing Figures 3.15 and 3.16, it can be seen that when the annual mean concentration of dissolved boron showed a decreasing trend form station 1 to 3 followed by a gradual increase towards station 9, annual mean values of B-Cl ‰ ratio showed a decreasing trend from station 2 to 9. This type of a decreasing trend was also observed in the case of Mg, Ca, Sr and Ba. A slight increasing tendency at station 8 was observed in the case of Mg also. In the monsoon season in which the entire region becomes fresh water zone, the boron-chlorinity ratio was above 0.3×10^{-3} (except at station 7 where the ratios were 0.249 and 0.234×10^{-3} in surface and bottom waters respectively). In the pre-monsoon period, the seasonal average of B-Cl ‰

Table 3.9 Station wise summary statistics on dissolved boron and B : Cl ‰ ratio.

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Boron (µg/l)	1	13.6	7.0	277.0	571.0	57.5	78.0	83.4	163.1	145.2	209.1
	2	3.5	3.4	85.5	192.0	23.6	33.6	27.6	53.8	116.7	159.9
	3	4.3	3.4	48.6	56.2	18.6	19.7	13.8	16.2	74.2	82.0
	4	7.4	5.0	225.0	230.0	50.9	55.7	70.0	74.7	137.5	134.1
	5	7.8	8.3	220.0	250.0	55.5	59.4	75.5	84.4	136.0	142.2
	6	9.1	8.7	388.0	363.0	90.4	90.9	118.4	110.2	131.0	121.1
	7	4.8	7.1	572.0	632.0	158.7	166.1	196.0	206.7	123.5	124.5
	8	13.7	12.1	1600.0	1410.0	512.6	531.0	602.9	558.6	117.6	105.2
	9	12.7	11.7	1470.0	1490.0	544.6	614.2	624.5	659.8	114.7	107.4
B : Cl ‰ ratio	1	0.235	0.150	1.101	0.957	0.610	0.406	0.278	0.234	45.57	57.70
	2	0.222	0.247	1.708	1.918	0.624	0.620	0.455	0.520	72.92	83.84
	3	0.152	0.130	1.860	1.503	0.623	0.529	0.498	0.378	79.94	71.42
	4	0.233	0.207	1.080	1.021	0.502	0.517	0.274	0.285	54.68	55.22
	5	0.113	0.115	1.073	1.334	0.452	0.418	0.276	0.311	61.06	74.36
	6	0.145	0.129	0.677	1.699	0.380	0.468	0.166	0.420	43.84	89.70
	7	0.073	0.063	0.654	0.685	0.327	0.337	0.177	0.213	54.28	63.11
	8	0.245	0.237	0.703	1.537	0.387	0.473	0.160	0.379	41.39	80.29
	9	0.074	0.214	0.666	1.183	0.298	0.378	0.157	0.268	52.80	70.87

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

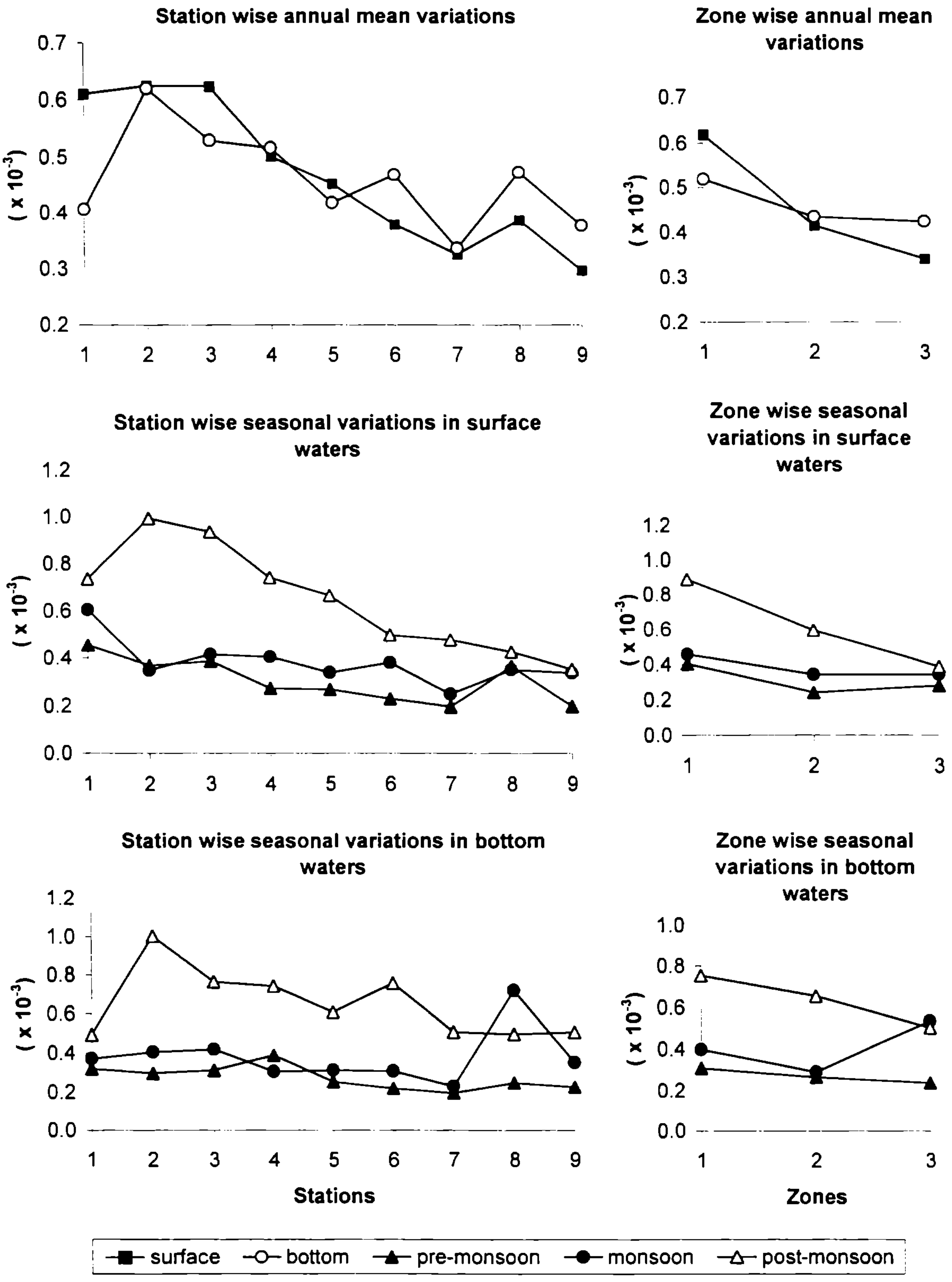


Figure 3.16 Seasonal and spatial variations of dissolved B : Cl‰ ratio.

ratio decreased from stations 4 to 9. During this season, salinity values were found to increase from stations 4 to 9. In other words, conservative behaviour of boron was observed from stations 4 to 9 in the pre-monsoon season as the B-Cl ‰ values were much closer to 0.231×10^{-3} during this period. The seasonal average values were found to be the highest in post-monsoon season. In this period, the average values were found to vary from 0.353 to 1.005×10^{-3} During this period also, the whole region remained as fresh water zone (except stations 8 and 9 which showed very low seasonal average salinities in the range 1.41 to 1.95 ‰).

From a study in the Alde Estuary by Liss and Pointon (1973), the relationship between boron and salinity was found to be non-linear, indicating a removal of 25-30 % of the boron entering the estuary from sea water. In contrast, Hosokawa et al. (1970) found no removal of boron in their survey of the Chikugogawa Estuary, nor was any observed by Liss and Pointon (1973) in a study of the estuary of the River Beaulieu in England. In a study of the well mixed Mindola River Estuary (Gujarat), Narvekar et al. (1981) found that boron is preferentially removed over entire tidal cycle. High and low B:Cl ‰ ratios indicate addition as well as removal of boron. In the present study, it was found that the relationship of boron with chlorinity is non-linear and there was addition of boron, rather than removal (except at stations 4 to 9 in pre-monsoon season) especially in monsoon and post-monsoon seasons and from stations 1 to 3 in pre-monsoon season. This shows that boron is getting added to the water column of the study area from some other sources. Addition of boron can be due to the in situ production or due to addition from external sources or both. The former includes oxidation of organic matter, weathering of rocks and endothermal release of boron from sediments (Narvekar et al., 1981; Shirodkar and Singbal, 1992). The latter includes external sources such as industrial effluents and or sewage discharges either drained directly or indirectly into the study area and the land drainage. The correlation coefficient (r) values between boron and dissolved oxygen, though negative in most of the cases, were not significant in surface waters, but, significant ($r = -0.261$, $n = 108$, $p < 0.01$) in bottom waters. This suggests that the oxidation of organic matter in surface sediments may be contributing to a certain extent in the addition of boron to the water column. River water contains on an average 10 -13 µg/l of boron, so it need not necessarily contain high boron unless and until the river water flows over the bed rock containing boron and is therefore, not a significant contributing factor. In shallow and turbulent waters, the boron released from sediments due to the endothermic reactions shows high values in bottom waters. In the present case, the mean value of dissolved boron in the bottom waters was found slightly higher (183 µg/l) than in surface waters (168 µg/l) and one possible reason for this may be the release of boron from surface sediments into the shallow water column due to endothermic reactions. Another alternate source of boron could be the sewage discharges and the land drainage, especially from the vast areas of agricultural lands where excessive quantity of fertilizers and pesticides are being used for agricultural purposes.

Boron-chlorinity ratio in the Zuari Estuary, Goa (Rajagopal et al., 1981) was found to vary from 0.186 to 0.351 x 10^{-3} Shirodkar et al. (1982) had reported a B-Cl ‰ ratio in the range 0.06 to 0.241 x 10^{-3} with an average value of 0.173 x 10^{-3} in the Arabian Sea. While working on boron chemistry in the eastern Arabian Sea, Shirodkar and Singbal (1992) found B:Cl ‰ ratio varying from 0.202 to 0.269 x 10^{-3} in the coastal region and from 0.171 to 0.238 x 10^{-3} in the off shore region. In the present study, it was found that, the mean values of B-Cl ‰ ratio in surface and bottom waters did not differ much, the values being 0.467 and 0.461 x 10^{-3} The almost similar values of B-Cl ‰ ratios in surface and bottom waters showed that evaporation loss from surface waters as reported by Savenko (1977) and utilization of boron in surface waters by phytoplankton as reported by Igelsrud et al. (1938) were not clearly evident in this region. This may be due to the shallowness of the water body. Ghosh and Jana (1993) from a study of the Hugli Estuary (India) observed a semi-conservative nature for boron (B Cl ‰ ratio 0.231 ± 0.115 x 10^{-3}). In the present study also a semi conservative behaviour was observed for boron. The semi-conservative behaviour can be attributed to the colloidal co-precipitation of inorganic boron with silica, and the probable conversion of inorganic boron to organic complex form by carbohydrate and mannitol excreted by phytoplankton during the periods of high phytoplankton production (Ghosh and Jana, 1993).

Texture analysis of sediments

The distribution pattern of sediments in an estuary depends on several factors such as sediment sources, the texture of the sedimentary material supplied, the bottom topography of the basin and general hydrographical features (Veerayya and Murty, 1974). In this part of the Cochin estuarine system, the bulk of the sedimentary material is being supplied by the four rivers, Pamba, Manimala, Meenachil and Achencovil (Figure 2.1), mainly in the south-west and north-east monsoon seasons, by way of bedload as well as suspended load (Veerayya and Murty, 1974).

Grain size analysis is a fundamental procedure in sedimentology and limnology and it gives basic information on the sediment composition and depositional environment. Also, changes in the particle size distribution are a good proxy for changing hydrodynamic conditions within a watershed. Natural sediments consist of particles of varying 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 (> 63μm), silt (4 – 63 μm) and clay (<4 μm) sizes (Krumbein and Pettijohn, 1938). The relative abundance of the above grain size groups was analysed on surficial sediment samples of selected months (representing the three seasons) from the surveyed area and the results are given in Table 3.10 along with their textural classifications (Folk et al., 1970) and the seasonal variations are presented in Figure 3.17 Seasonal and spatial variations in the three size fractions of the sediments were clearly observable from the data. The percentage distributions of different size fractions of sediments indicated the existence of partitioning between sand, silt and clay fractions.

Sediments of stations at zone 3 mainly consisted of sand fraction (Figure 3.17). The percentage of sand in this zone was above 70 in all the

Table 3.10 Size composition of sediments

Stations	Seasons	Nature of sediment	Sand (> 63 µm)	Silt (4 - 63 µm)	Clay (< 4 µm)
1	**Pre-monsoon**	Sandy mud	40.51	24.73	34.76
	Monsoon	Sandy mud	20.24	49.98	29.78
	Post-monsoon	Sandy mud	38.65	36.95	24.40
2	**Pre-monsoon**	Mud	7.70	47.53	44.77
	Monsoon	Sandy mud	10.01	36.89	53.10
	Post-monsoon	Muddy sand	56.69	25.64	17.67
3	**Pre-monsoon**	Mud	9.58	48.14	42.28
	Monsoon	Mud	8.36	40.11	51.53
	Post-monsoon	Silty sand	38.97	46.15	14.87
4	**Pre-monsoon**	Mud	6.09	50.31	43.60
	Monsoon	Sandy mud	17.79	48.46	33.75
	Post-monsoon	Sandy mud	26.71	44.34	28.94
5	**Pre-monsoon**	Sandy mud	36.74	27.44	35.82
	Monsoon	Sandy mud	23.56	32.87	43.57
	Post-monsoon	Sandy silt	47.81	38.17	14.02
6	**Pre-monsoon**	Sandy silt	40.05	52.08	7.87
	Monsoon	Sandy silt	44.66	39.59	15.75
	Post-monsoon	Sandy mud	44.17	35.69	20.14
7	**Pre-monsoon**	Sandy silt	72.62	23.12	4.26
	Monsoon	Muddy sand	65.28	13.85	20.87
	Post-monsoon	Silty sand	56.75	31.01	12.24
8	**Pre-monsoon**	Sand	94.60	4.76	0.64
	Monsoon	Clayey sand	86.95	1.47	11.58
	Post-monsoon	Muddy sand	84.49	9.91	5.60
9	**Pre-monsoon**	Sand	91.06	7.39	1.55
	Monsoon	Muddy sand	71.72	14.50	13.78
	Post-monsoon	Muddy sand	88.41	6.34	5.25

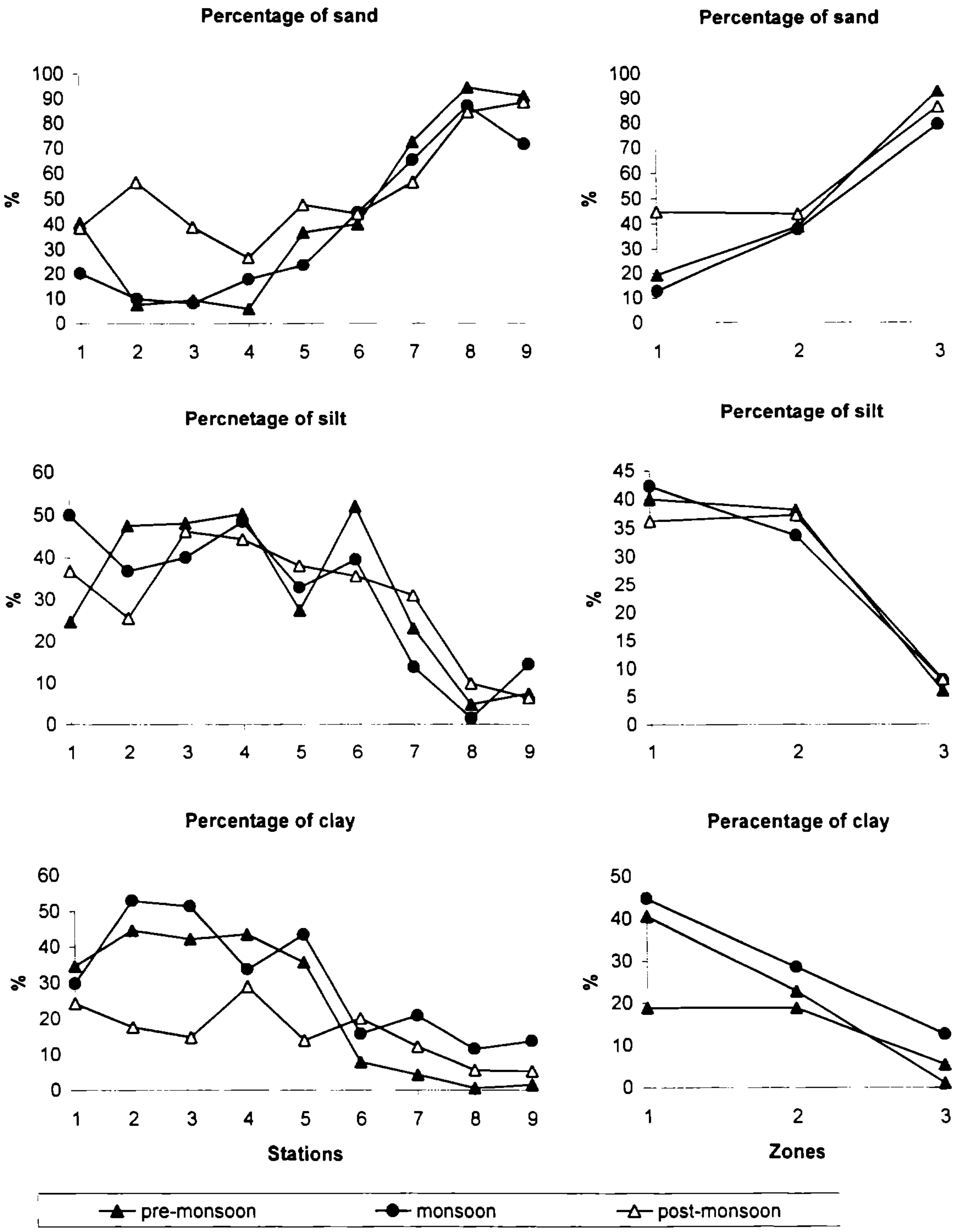


Figure 3.17 Seasonal and spatial variations of texture of sediments.

seasons. In pre-monsoon period, it crossed above 90% and the seasonal minimum was observed in the monsoon season. The lowest percentage of sand was observed at stations 2, 3 and 4 in the pre-monsoon and monsoon periods. In the post-monsoon period, stations 1, 3 and 4 showed the lowest values. The general trend observed was that the percentage of sand increased from station 4 to station 9. Another trend observed was that stations 2, 3, 4 and 5 showed higher percentage of sand in the post-monsoon season, whereas in the pre-monsoon and monsoon seasons the values were almost comparable. Station 6 was found to have least variation in sand percentage during the three seasons (40 to 44 %). Post-monsoon season recorded lowest seasonal average of sand in all the three zones (Figure 3.17). Seasonal variations were not very marked at zone 2 but, zone 1 recorded marked seasonal variations with highest values in post-monsoon season. Unlike this, zone 3 recorded highest seasonal average in pre-monsoon season. The relative variations in the percentage of sand at different zones were in the order Z1 < Z2 < Z3 during the pre-monsoon and monsoon seasons. During the post-monsoon season, the relative variations in different zones were $Z_1 \approx Z_2 < Z_3$.

Seasonal variations in silt percentage were observed but the trend was not uniform in all the stations (Figure 3.17). The lowest silt percentage was observed at zone 3 in all the seasons (1.47 to 14.5 %) and the highest silt percentage was observed at zone 1 during the monsoon and pre-monsoon seasons. During the post-monsoon season, zones 1 and 2 showed almost equal values of silt percentage. The riverine stations at zone 1 recorded the maximum seasonal average during the monsoon season. The lowest in this zone was observed in post-monsoon season. Zone 2 was less silty during monsoon period than in the other two seasons. In this zone, pre-monsoonal and post-monsoonal values did not differ much. The relative variation of the percentage of silt in different zones were in the order Z1 > Z2 > Z3 during pre-monsoon and monsoon seasons, while in post-monsoon season, the order was Z2 < Z1 < Z3.

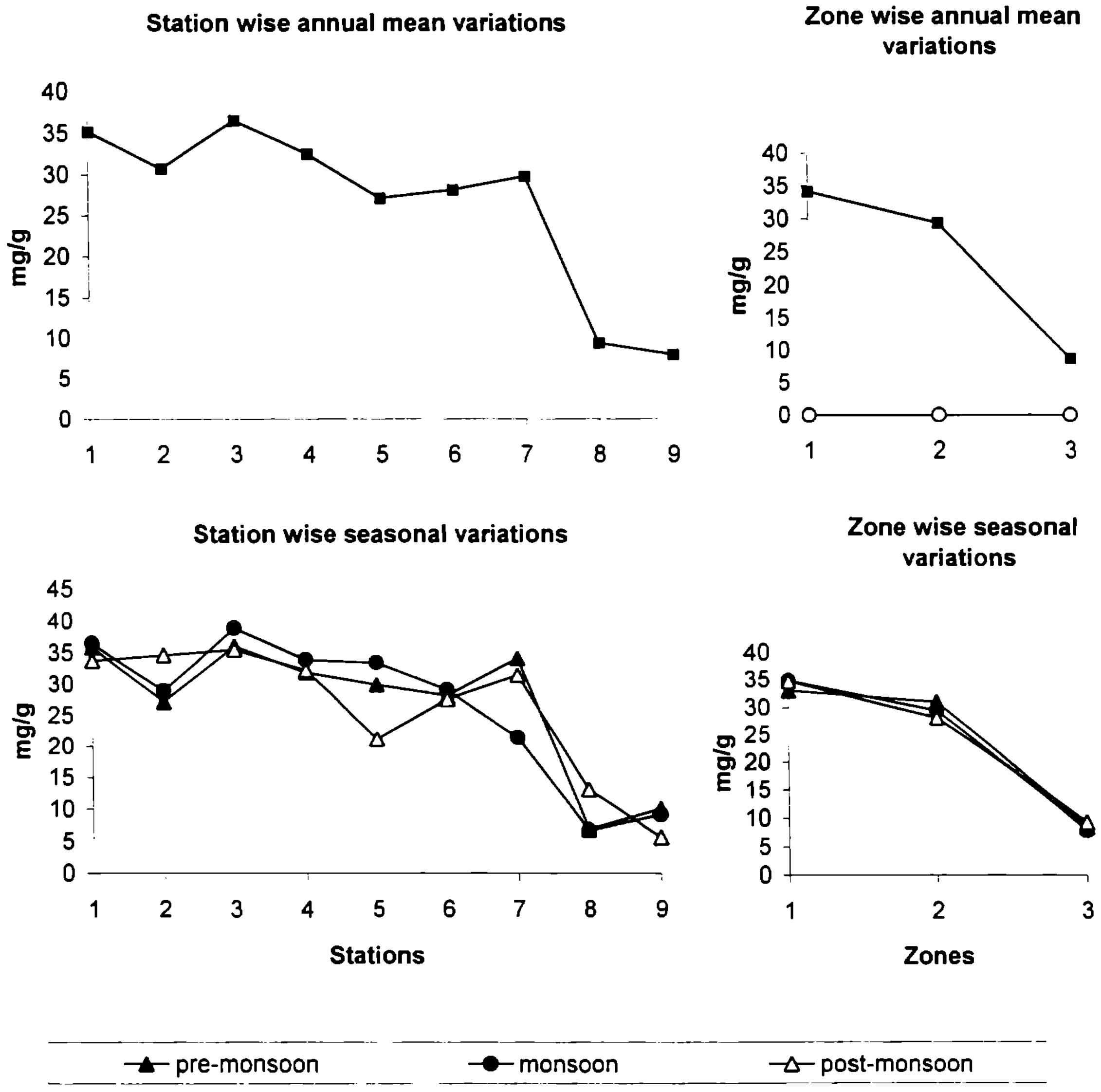
Clay acts as nucleation centres for Fe/Mn oxides in the fresh water region (Forstner, 1977) and during estuarine mixing as well as centers for the flocculation and precipitation of dissolved and colloidal organic matter during estuarine mixing (Aston and Chester, 1973; Sholkovitz, 1976). Percentage of clay, in the present study, varied from 0.64 to 53.10 (Figure 3.17). Stations 8 and 9 (zone 3) showed the lowest values in all the seasons (Figure 3.17). The percentage of clay was found to be highest during monsoon season in most of the stations. During this season, the clay content in sediments decreased sharply from zone 1 to zone 3. The relative variations observed in clay content in different zones during pre-monsoon season was similar to that observed during monsoon season but the values were comparatively less. During the pre-monsoon season, the values observed at stations 1 to 5 were much higher than the values recorded at stations 6 to 9. A similar trend was observed in the monsoon season also, but the range of values at stations 7 to 9 was found slightly higher (11.58 % to 20.87 %) and at stations 1 to 5, the range was 29.78 % to 53.10 %. The distribution of clay content in sediments in the post-monsoon season was found to be different from that observed in monsoon and pre-monsoon seasons. Stations 1 to 5 recorded lowest seasonal average in post-monsoon season, whereas at stations 6 to 9, the clay content in sediments was higher during the monsoon and post-monsoon seasons than that observed in pre-monsoon season. Unlike the trend observed in pre-monsoon and monsoon seasons, the clay content at zone 2 increased slightly from zone 1 and then decreased to zone 3.

The higher percentage of sand and the corresponding decrease in the percentage of silt and clay at zone 3 is due to the operation of the shutters of the Thanneermukkam salinity barrier. Opening of the shutters, partially or fully causes water to flow at high velocities, carrying the fine-grained fractions of the sediments namely clay and silt. From the spatial distribution pattern of different grain sizes of sediment particles, it appears that the siltation due to the four rivers is affected mainly at stations 1 to 6. As observed in the present study, high percentage of silt (upto 69 %) was also reported from the nearshore stations of Hooghly Estuary by Sasamal et al. (1986). The fine grained sediment particles in suspension, especially clay fractions, carried by the four rivers got deposited or flocculated mainly at stations 2 to 5. Relatively slow movement of water in this area and the shallowness of the water column favour the sedimentation of finer (silt and clay) particles.

Sediment organic carbon (SOC)

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 organic matter in the sedimentary environment of Cochin Estuary was reported by Murty and Veerayya (1972) and Sankaranarayanan and Panampunnayil (1979). However, these studies were confined to the northern part of the Cochin estuarine system.

In most of the unpolluted estuaries, organic carbon content of the bottom sediments is less than 50 mg/g. However, in areas, where organic pollutants are high organic carbon content of surface sediments often exceeds 50 mg/g. The distribution of organic carbon content in the study area exhibited distinct spatial variations and was found within the range 1.04 mg/g to 47.88 mg/g with a mean value of 26.39 mg/g (Table 3.1). These values are generally less than the proposed limit for a polluted estuary. The variation of station wise annual mean values is depicted in Figure 3.18. In



Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations

Zone wise seasonal variations

Figure 3.18 Seasonal and spatial variations of organic carbon in sediments.

general, a decreasing trend was observed in the station wise annual mean values of sediment organic carbon from station 1 to station 9. Stations at zones 1 and 2 recorded relatively higher values, four to five times greater than the values observed at stations of zone 3. Table 3.11 gives station wise summary statistics of sediment organic carbon. The highest two annual mean values were recorded at station 3 and station 1 (36.58 mg/g and 35.22 mg/g respectively) and the lowest two annual mean values were recorded at stations 9 and 8 (7.98 mg/g and 9.42 mg/g respectively).

Seasonal variations were noticed but those variations were not very distinct and were not uniform throughout the stations. On a zonal basis, average at zone 1 was found slightly higher in the monsoon and post-monsoon seasons than in the pre-monsoon season. At the same time, the highest seasonal average at zone 2 was found during pre-monsoon season. At zone 3, a different trend was found with the post-monsoon and monsoon seasons recording the highest and lowest seasonal averages respectively.

In a survey of Cochin backwater system from Cochin to Alleppey, Murty and Veerayya (1972) observed that organic matter content of sediments ranged from 1.0 to 60.0 mg/g. In another study of Cochin Estuary, Padmalal and Seralathan (1995) observed that organic carbon in sediments varied from 1.3 mg/g to 59.1 mg/g. High range of organic carbon was also reported from other parts of Cochin Estuary by Sankaranarayanan and Panampunnayil (1979) (7.4 to 38.4 mg/g), Nair (1992) (0.18-34.98 mg/g) and Jayasree (1993) (0.63 to 71.44 mg/g). The comparatively higher organic carbon content in sediments from stations 1 to 6 (except at station 2) may be due to the combined result of river run-off, domestic sewage and industrial effluent and also due to the settling of organic detritus of the overlaying water column. Terrestrial inputs of organic matter from the nearby paddy fields also contribute much to the organic load in the sediment. Lower organic carbon content of zone 3 was associated with the prominent coarse sandy sediment fractions of this region. Correlation study of organic carbon content with the texture of sediment showed that particle size had an inverse relationship with sedimentary organic carbon. The good negative correlation of sediment

Table 3.11 Station wise summary statistics on organic carbon and moisture contents of sediments

Parameter	Stations	Min.	Max.	Mean	SD	CV
Organic carbon (mg/g)	**1**	24.35	42.52	35.22	4.96	14.09
	2	11.09	39.39	30.77	9.60	31.19
	3	26.00	47.88	36.58	6.12	16.73
	4	28.89	36.91	32.53	2.16	6.63
	5	9.88	36.81	27.11	7.81	28.81
	6	18.74	38.76	28.08	6.49	23.10
	7	10.33	39.56	29.78	7.85	26.35
	8	3.03	36.56	9.42	9.14	97.03
	9	1.04	22.38	7.98	6.08	76.14
Moisture content (%)	**1**	36.82	56.53	45.99	5.82	12.65
	2	26.94	54.43	45.49	7.48	16.45
	3	40.79	54.06	48.60	4.42	9.09
	4	40.33	50.52	46.39	3.07	6.61
	5	29.32	50.96	42.50	6.50	15.31
	6	37.64	49.23	41.04	3.12	7.60
	7	29.50	47.95	39.50	5.01	12.69
	8	20.05	63.86	28.93	11.95	41.32
	9	20.34	33.32	24.62	3.87	15.73

(SD = standard deviation, CV = coefficient of variation)

organic carbon with sand (-0.791) showed that the comparatively lower organic carbon content at stations 8 and 9 was primarily due to the sandy nature of the sediments at these stations. It was also found that the organic carbon content in the study area was highly positively correlated with the silt (r = 0.794) and clay fractions (r = 0.614) of the sediment. Association of higher content of organic matter with the finer fractions of sediments in the Cochin backwater system was also reported by Murty and Veerayya (1972). A linear relationship between organic matter and sediment particle size was reported by many other workers (Nayar, 1992; Padmalal and Seralathan, 1995; Abdulla Bava, 1996). The sediments of stations 1 to 7 were mainly silty-clay and clayey-silt. Nair (1992) observed a general increase in organic carbon content during the pre-monsoon season than in the monsoon season in a comparatively more dynamic part of the Cochin backwater system. The insignificant seasonal variations of organic carbon at the above stations assume the preservation of organic matter through sedimentation and incorporation into the clayey-silt and silty-clay sediments. Mohan (1997) observed higher percentage of organic carbon in the clay fractions of the sediment than in the bulk fractions in a study of the Vellar Estuary (Tamil Nadu). Higher concentrations of sediment organic carbon in the riverine and estuarine region may be explained as due to the high organic (biological) productivity in the entire region may be due to the high input of organic load into the fresh water region from the rivers, and from the adjacent paddy fields.

Moisture content of sediment

Moisture content in sediments varied from 20.1 % to 63.9 % and maximum and minimum values were observed at station 8 (Table 3.11). Table 3.11 also gives station wise summary statistics of sediment moisture content. Seasonal and spatial variations were observed in the moisture content. The highest station wise annual mean of moisture content was observed at station 3 (48.9 %). Station 3 was also characterized by minimum variability in moisture content (coefficient of variation 9). The station wise annual mean values of moisture content increased from 46 % at station 1 to 48 % at station 3 and then decreased gradually to station 7 (39.6 %) followed by an abrupt decrease at stations 8 and 9 (29.6 % and 24.4 % respectively) (Figure 3.19). Seasonal variations could be seen from Figure 3.19. It was found that seasonal variations were not uniform among stations. Higher percentage of moisture was found in the sediments from stations 1 to 5 (except station 2). Generally, stations 8 and 9 (zone 3) recorded the lowest values in all the seasons. During the pre-monsoon season, there was a gradual decrease in the percentage of moisture from station 1 to station 9. This trend was observed in monsoon season also, except a small decrease at station 2. The comparatively lower percentage of moisture contents at stations 8 and 9 were associated with the sandy nature of sediments found at these stations. This is evident from the good negative correlation of moisture with sand percentage ($r = -0.845$, $n = 27$). The correlations of moisture with the percentages of silt and clay fractions of the sediment was found to be 0.822 and 0.681 respectively ($n = 27$). Moisture content also showed significant positive relationship with organic carbon ($r = 0.956$, $n = 27$). From the above discussion, it appears that the variation in moisture content could be attributed to the variation in sediment texture and organic carbon.

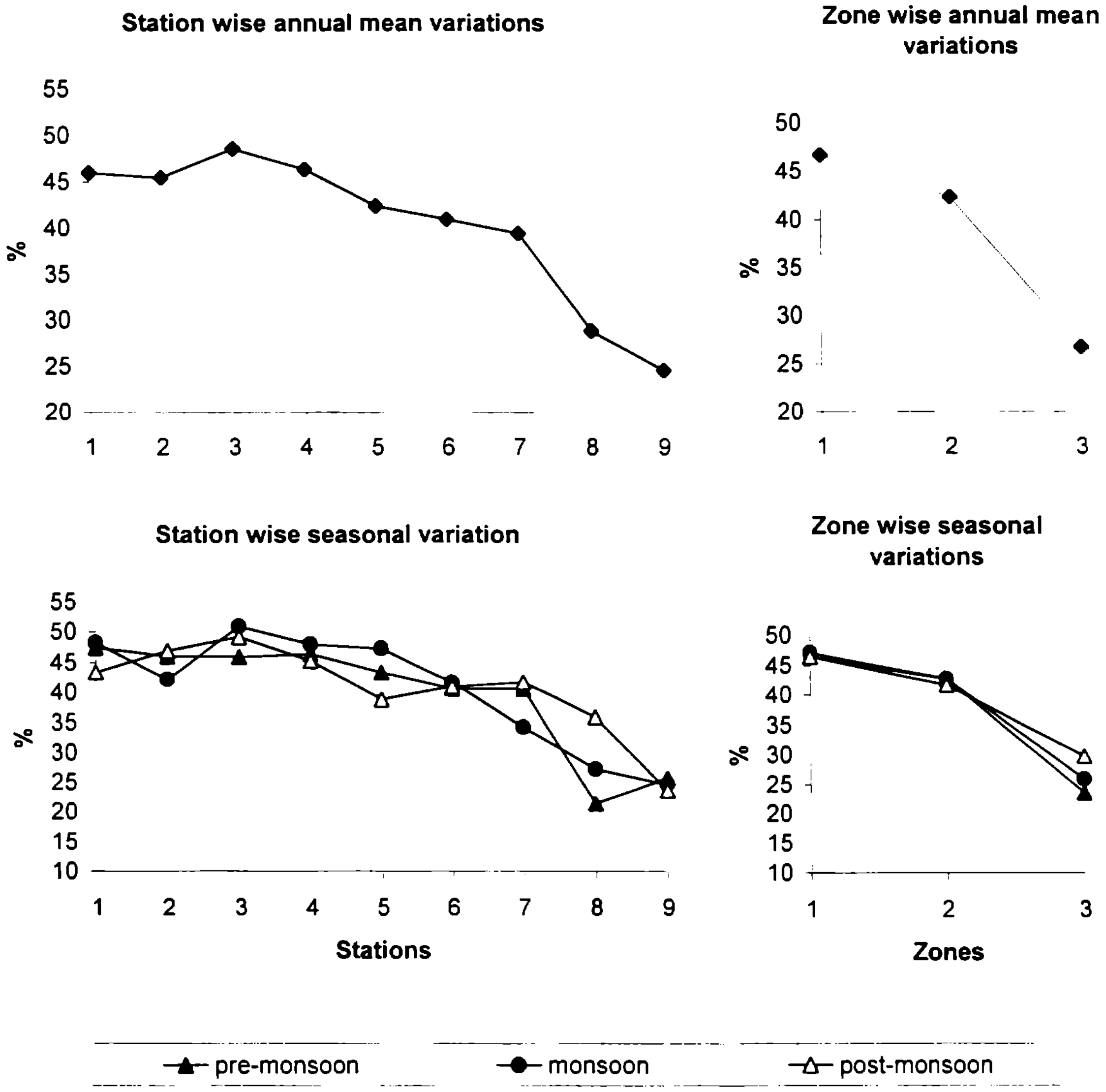


Figure 3.19 Seasonal and spatial variations of moisture in sediments.

CHAPTER 4

DISSOLVED TRACE METALS

4.1 INTRODUCTION

Numerous studies on the distribution and behaviour of trace 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 same estuary. Factors which have been demonstrated to be important in controlling trace metal behaviour include estuarine flushing time (Morris, 1990; Owens and Balls, 1997), complexation with dissolved inorganic (Comans and van Dijk, 1988; Owens and Balls, 1997) and organic (van den Berg et al., 1987; Owens and Balls, 1997) species, and interactions with suspended solids (Turner et al., 1993; Benoit et al., 1994; Owens and Balls, 1997) 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 trace metals; for different metals, the factors may not be the same. The variations in the concentrations of trace constituents among the individual rivers can be very wide. Such complexity generally means that survey work must be completed in every estuary of interest before confident predictions regarding trace metal behaviour can be made.

The rationale for studying trace metals in estuaries may be purely geochemical, or may be linked to studies on the distribution and fate of metals of anthropogenic origin. In Western Europe and North America, the latter type of study has resulted in a disproportionate amount of effort being directed towards estuaries near industrialised cities. Relatively few studies have examined the scarcer, more pristine, temperate estuaries (Danielsson et al., 1983). An improved understanding of trace metal behaviour in such environments is valuable in assessing the extent to which natural cycles are perturbed or enhanced in a system where there is appreciable anthropogenic input.

Trace metals in sea water occur in many different chemical and physical forms, or species. The bio-availability, toxicity, reactivity, and ultimate fate of trace metals depend on their speciation. For example, many studies have shown that most organisms are sensitive only to some sub-fraction of filtrate metal species, usually the free-dissolved ion (aquo complexes). For this reason, it is important to know how metal ions partition between particles and solution, as a first step in better understanding the potential impact on aquatic organisms.

Many workers like Danielsson (1980), Moore (1981), Duinker and Nolting (1982), Paul and Pillai (1983a), Satyanarayana et al. (1985a), Campbell et al. (1988), Windom et al. (1988), Harper (1991), Laslett and Balls (1995), Dassenakis et al. (1997), Kremling et al. (1997) and Owens and Balls (1997) have reported the distribution of trace metals in water column. Concentrations of chemical species of selected heavy metals (Cu, Zn, Hg, Cd and Pb) were determined in surface waters from a series of coastal sites in Bahrain, U.A.E. and the Sultanate of Oman by Fowler et al. (1984).

Data on concentration of dissolved trace metals are scarce from Indian coastal/estuarine waters. As a part of the programme of estimation of trace metals from some of the World Oceans, Chester and Stoner (1974) reported levels of zinc, nickel, manganese, cadmium, copper and iron from the Indian Ocean areas. Danielsson (1980) analysed dissolved fraction of Cd, Cu, Fe, Ni, Pb and Zn in the western Indian Ocean waters. In 1980, Braganca and Sanzgiry (1980) studied the trace metal levels in the coastal and offshore regions of the Bay of Bengal. These authors (Sanzgiry and Braganca, 1981) also carried out investigations on the trace metals in the Andaman Sea. Rajendran et al. (1982) investigated the trace metal contents, both dissolved and particulate forms, in the western Bay of Bengal. Sanzgiry and Moraes (1979) reported the trace metal levels in the Laccadive Sea. Satyanarayana and Murty (1990) have made a detailed study on the distribution patterns of dissolved trace metals (Ni, Zn, Cd, Cu, Mn, Pb and Fe) in inshore and offshore regions of Bay of Bengal. Matkar et al. (1981) studied the distribution of Zn, Cu, Mn and Fe in the Bombay harbour. Venugopalan and Ramdas (1975) conducted studies on the distribution of dissolved, particulate and sedimentary iron in Vellar Estuary. Shibu et al. (1990) and Ouseph (1992)) had carried out investigations on the trace metal levels in Cochin Estuary. These studies were concentrated on the northern part of the Cochin estuarine system and no data are available on trace metal concentrations from the southern upstream part of the Cochin back water system.

4.2 MATERIALS AND METHODS

Details have been given in Chapter 3.

4.3 RESULTS AND DISCUSSION

The monthly data on dissolved trace metals (Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn) are given as Annexure 2 and the overall summary statistics of dissolved trace metals are given in Table 4.1. Values of some

Table 4.1 Overall summary statistics on the distribution of dissolved trace metals (µg/l)

Metal	Min.		Max.		Mean		SD		CV	
	S	B	S	B	S	B	S	B	S	B
Cd	0.40	0.23	6.10	5.75	2.58	2.77	1.10	1.17	42.71	42.18
Co	0.06	0.06	4.36	3.97	0.73	0.77	0.93	0.95	127.15	123.54
Cr	0.10	0.08	6.45	7.15	2.58	2.84	2.12	2.13	81.94	74.84
Cu	0.30	0.61	8.85	7.85	2.08	2.30	1.31	1.19	62.86	51.96
Fe	9.80	23.80	394.00	346.00	75.34	70.86	57.10	55.59	75.79	78.46
Mn	0.05	0.13	117.50	67.00	2.17	2.65	12.10	10.17	556.76	383.54
Mo	0.01	0.02	9.65	10.25	1.74	1.94	2.46	2.64	141.43	136.46
Ni	0.29	0.47	17.15	18.15	3.93	4.33	3.65	3.89	92.78	89.75
Pb	0.59	1.49	39.15	40.95	10.40	10.86	8.03	8.49	77.17	78.16
Zn	1.73	2.26	387.50	97.00	12.10	9.65	37.38	11.87	308.95	123.08

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

dissolved trace metal concentrations reported from different parts of the world are given in Table 4.2. The relative abundance of dissolved trace metals observed in the present study was in the order Fe > Zn > Pb > Ni > Cr > Cd > Mn > Cu > Mo > Co.

4.3.1 Dissolved cadmium

Cadmium fluxes and cycling in the environment have been reviewed by Friberg et al. (1974), Nriagu (1980a) and Bruland (1983). The average concentration of cadmium in natural water is 0.4 µg/l. Like mercury, cadmium has also been shown to pose a real health threat to human populations, which receive a high level of exposure. Itai-itai disease, which is almost certainly related to cadmium poisoning, was first observed in the inhabitants of the Jinzu River basin in Japan towards the end of the second world war (Tsuchiya, 1981). In this case, the cadmium had been transported to the river from the Kanoucoka mine, which produced mainly zinc as well as small quantities of lead and cadmium (the distributions of cadmium and zinc in the environment are invariably linked). Cadmium has no known physiological role in the human body (Friberg et al., 1974). Therefore, the intake of cadmium causes accumulation in the body. Kidney is the worst affected part, and one third of cadmium in the body gets accumulated in kidney. This, together with its long half-life in biological system, makes cadmium as one of the most toxic metals (Craig, 1986).

The anthropogenic sources of cadmium in the environment include the primary uses of cadmium in electroplating other metals or alloys for protection against corrosion, in photographic industries and in the manufacture of storage batteries, glass ceramics, pigments and some biocides. Cadmium is of considerable environmental and health significance because of its increasing mobilisation and toxicity to many life forms. It was

Table 4.2 Values of some dissolved trace metals reported from other parts of the world (µg/l)

Location	Cd		Co		Cr		Cu		Fe		Reference
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
World river average										700	Linvingstone (1963)
World average of Sea water										10	Linvingstone (1963)
World river average								7		670	Burton and Liss (1974)
Rhine and North Sea	0.01 - 0.27						0.7 - 3.20				Duinker and Kramer (1977)
World river average								10		40	Martin and Meybeck (1979)
Coastal region of Bay of Bengal							2.8 - 7.2	5.6		66.3	Braganca and Sanzgiry (1980)
Indian Ocean	0.01 - 0.10						0.08 - 0.48	0.23	0.15 - 10.0	0.83	Danielsson (1980)
Yarra river, Australia	0.21 - 0.47						3.0 - 6.40	6.40			Hart and Davies (1981)
Hudson river estuary, U.S.A.	0.1 - 0.36						2.7 - 3.40	3.40			Klinkhammer and Bender (1981)
Bombay Harbour Bay							2.6 - 7.34	5.5	5.0 - 17.7	9.9	Matkar et al. (1981)
Inshore region of Western Bay of Bengal							3.5 - 6.2	5.37	12.1 - 28.3	19	Rajendran et al. (1982)
Tees estuary							0.5 - 7.0				Taylor (1982)
Gota river							1.0 - 1.4		25.0 - 75.0		Danielsson et al. (1983)
World river average		0.02						1.5			Martin and Whitfield (1983)
Cochin estuary, South India.	0.1 - 3.40						1.0 - 30.6				Paul and Pillai (1983a)
Elbe estuary							0.5 - 7.0				Mart et al. (1985)
Wadge Bank region(Arabian Sea)	0.09 - 1.69						0.2 - 2.17				George (1986)
Inshore region of Bay of Bengal							0.37 -6.18	2.87	0.98 - 14.8	3.9	Satyanarayana and Prabhakara Murty (1990)
Cochin estuary, South India	0.4 - 8.00	3.72					1.3 - 6.4	3.6			Shibu et al. (1990)
Continental shelf of Pakistan	1 - 87.0				1.0 - 54.0		1.0 - 545.0		10.0 - 126.0		Tariq et al. (1994)
San Francisco Bay					0.11 - 0.43						Abu-Saba and Flegal (1995)
Ob-Irtysh Rivers (Russia)					0.06 - 0.34		1.83 - 4.81				Moran and Woods (1997)
Coromandal coast, India	0.30 - 66.80		ND - 9.60				0.31 - 50.70				Govindasamy and Azariah (1999)
Tay river	0.003 - 0.02						0.59 - 1.56				Owens and Balls (1997)

Table 4.2 (Contd.) Values of some dissolved trace metals reported from other parts of the world (µg/l)

Location	Mn		Ni		Pb		Zn		Reference
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
World river average								20	Linvingstone (1963)
World average of Sea water									Linvingstone (1963)
World average of Sea water		0.4							Turekian (1969)
World river average		7				3			Burton and Liss (1974)
Rhine and North Sea							2.0 - 7.5		Duinker and Kramer (1977)
Rhine estuary					300 - 1100				Duinker and Nolting (1977)
World river average		8.2		2.2		1		30	Martin and Meybeck (1979)
Coastal region of Bay of Bengal		8.8					6.7 - 15.3	10.1	Braganca and Sanzgiry (1980)
Indian Ocean			0.18 - 1.0	0.52	0.02 - 0.18	0.07	0.20 - 13.80		Danielsson (1980)
Yarra river, Australia							15.0 - 55.0		Hart and Davies (1981)
Hudson river estuary, U.S.A.							2.40 - 22.0		Klinkhammer and Bender (1981)
Bombay Harbour Bay	0.48 - 4.51	2.78					2.65 - 33.92	14.54	Matkar et al. (1981)
Inshore region of Western Bay of Bengal	1.0 - 7.0	3.57	2.7 - 15.0	6.19			3.75 - 46.3	25.4	Rajendran et al. (1982)
Tees estuary							1.0 - 117		Taylor (1982)
Gota river			0.7 - 0.90		10 - 200		6.0 - 7.0		Danielsson et al. (1983)
World river average		8.2		0.5		0.1		30	Martin and Whitfield (1983)
Cochin estuary, South India.							1.3 - 156.0		Paul and Pillai (1983a)
Severn estuary					1000 - 3000				Morris (1984)
Elbe estuary					40 - 400				Mart et al. (1985)
Wadge Bank region(Arabian Sea)					0.23 - 4.57				George (1986)
Inshore region of Bay of Bengal	0.92 - 6.42	2.8	0.21 - 2.25	1.33	1.4 - 3.74		ND - 6.85	3.16	Satyanarayana and Murty (1990)
Cochin estuary, South India.							13 - 116	42.9	Shibu et al. (1990)
Continental shelf of Pakistan	1.0 - 55.0		10.0 - 264.0		20 - 530		110 - 2358		Tariq et al. (1994)
Tweed estuary(U.K)					40 - 170				Laslett (1995)
Wear estuary					58 - 550				Laslett (1995)
Mersey estuary					32 - 880		1.5 - 17.0		Laslett (1995)
Tees estuary					54 - 820				Laslett (1995)
Tyne estuary					57 - 1100				Laslett (1995)
Humber estuary					23 - 620				Laslett (1995)
Tay river	2.28 - 8.95		0.22 - 0.66				0.61 - 3.60		Owens and Balls (1997)
Coromandal coast, India			ND - 14.60				9.0 - 130.6		Govindasamy and Azariah (1999)
Vellar estuary, South India								25.51	Senthilnathan and Balasubramanian (1997)

also reported that the geochemistry of Cd is closely associated with the behaviour of Zn in the environment (Alloway, 1990).

Cadmium is relatively mobile in aquatic systems, existing 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^-, SO_4^{2-} (Moore, 1991). Since the $^{+}2$ valency state predominates in fresh water, redox potential has little effect on speciation (Moore, 1991).

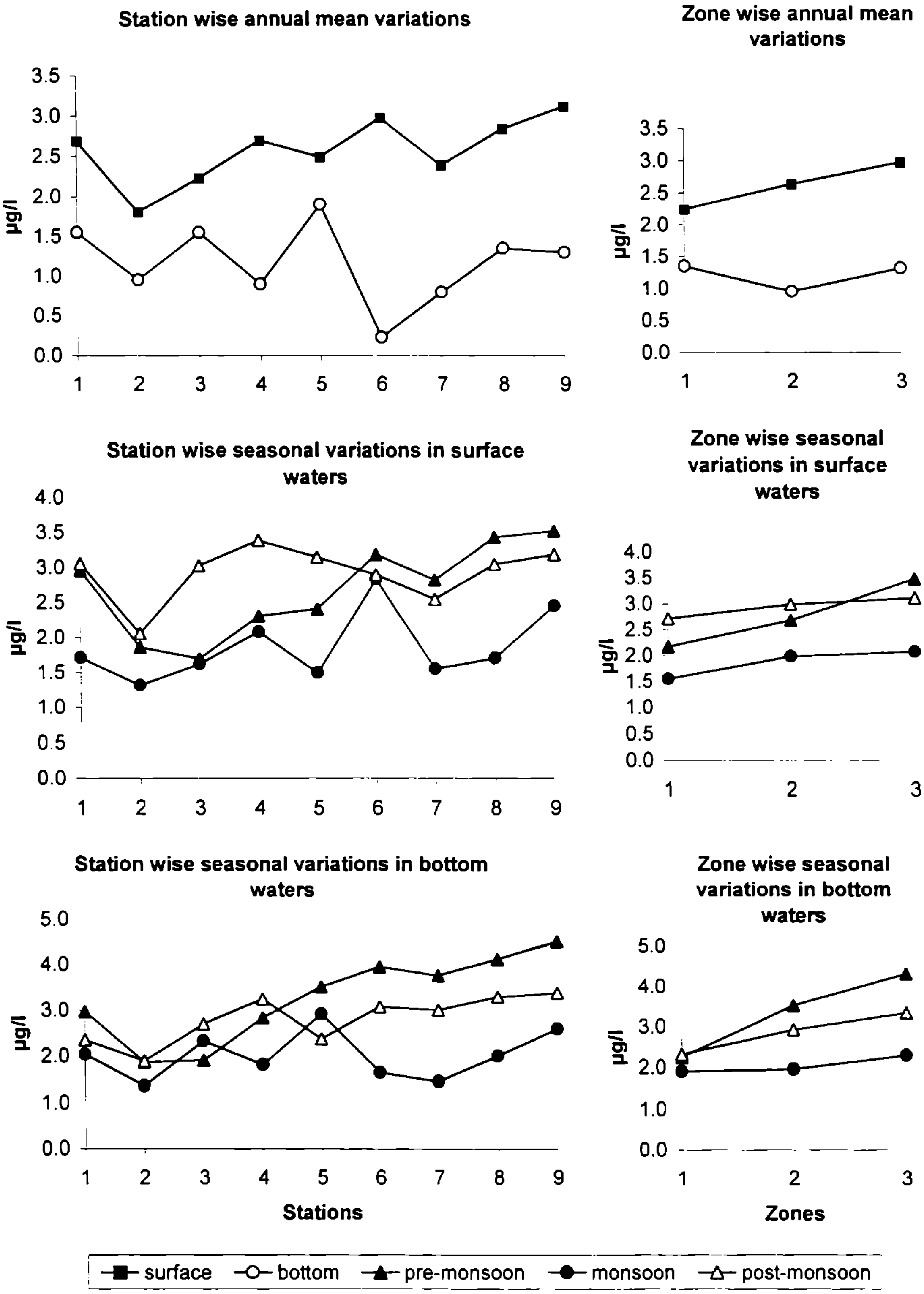
Dissolved concentration of cadmium in the surveyed area was found to vary from 0.40 to 6.10 µg/l in surface waters and 0.23 to 5.75 µg/l in bottom waters, with a mean value of 2.58 µg/l in surface water and 2.77 µg/l in bottom water (Table 4.1). Dissolved concentration of Cd showed the minimum variability, which is evident from the low coefficient of variance (42) among the 10 metals studied (Table 4.1). Station wise annual mean concentrations were in the range 1.81 µg/l to 3.12 µg/l for surface waters and 0.23 to 1.90 µg/l in bottom waters (Table 4.3). Lowest and highest annual mean concentrations were observed at stations 2 and 9 respectively for surface waters and at stations 6 and 5 respectively for bottom waters (Figure 4.1). All stations recorded higher annual mean concentrations in surface waters. In surface waters, the annual mean concentrations generally showed an increasing trend from station 2 to station 9. Zonal mean of dissolved cadmium concentrations (Figure 4.1) was maximum at zone 3 and minimum at zone 1 in surface waters, whereas in the case of bottom waters, zones 1 and 3 recorded almost equal value but a decrease was observed at zone 2.

Seasonal variations were observed (Figure 4.1) and it can be seen that in surface waters, the lowest seasonal averages were recorded in all the stations in the monsoon season and in bottom waters also, most of the

Table 4.3 Station wise summary statistics on dissolved cadmium and cobalt (µg/l)

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Cadmium	**1**	1.60	1.55	4.45	3.15	2.69	2.49	0.87	0.52	32.17	20.79
	2	1.05	0.96	2.90	2.45	1.81	1.76	0.63	0.39	34.63	22.03
	3	1.32	1.55	4.11	4.25	2.24	2.35	0.98	0.89	43.90	38.02
	4	1.70	0.90	4.30	4.36	2.70	2.76	0.91	1.07	33.84	38.83
	5	1.19	1.90	4.60	5.40	2.49	2.90	0.96	0.99	38.36	34.26
	6	0.40	0.23	6.10	5.75	2.98	3.02	1.46	1.61	48.91	53.42
	7	0.45	0.80	4.50	4.75	2.39	2.88	1.17	1.26	49.04	43.61
	8	1.05	1.35	5.10	5.10	2.84	3.25	1.23	1.21	43.33	37.16
	9	1.00	1.30	4.95	5.15	3.12	3.57	1.25	1.37	40.07	38.45
Cobalt	**1**	0.08	0.06	1.40	1.81	0.47	0.54	0.43	0.61	92.68	114.06
	2	0.09	0.07	2.64	3.02	0.71	0.76	0.85	0.97	120.60	129.06
	3	0.07	0.07	3.21	3.97	0.79	0.88	1.07	1.29	135.11	146.30
	4	0.09	0.10	3.21	3.50	0.78	0.87	1.09	1.24	140.08	142.75
	5	0.07	0.06	3.72	3.76	0.91	0.97	1.30	1.35	141.81	138.27
	6	0.07	0.08	4.36	2.60	0.86	0.70	1.22	0.79	141.51	112.65
	7	0.06	0.10	1.52	1.95	0.53	0.64	0.53	0.61	99.81	94.48
	8	0.07	0.12	2.41	2.85	0.73	0.79	0.86	0.84	117.64	106.34
	9	0.14	0.06	3.17	2.62	0.83	0.78	0.93	0.78	112.03	100.31

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)



Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 4.1 Seasonal and spatial variations of dissolved cadmium.

stations recorded lowest seasonal averages in this season. This trend is more visible on a zonal basis (Figure 4.1). Highest seasonal average was observed in the post-monsoon season at zone 1 and zone 2 and in the pre-monsoon season at zone 3 in surface waters. In bottom waters, zone 1 recorded almost equal values in pre-monsoon and post-monsoon seasons but zones 2 and 3 showed a distinct hike in dissolved Cd concentrations in the pre-monsoon season. During the entire seasons, zone 1 recorded lowest values in surface and bottom waters and there was an increasing trend towards zone 3, especially in pre-monsoon and post-monsoon seasons. This increase in the dissolved concentration of cadmium at zone 3 and zone 2 may be due to the complexation of cadmium with chloride ions at increased salinity of these zones during pre-monsoon and post-monsoon seasons.

Martin and Whitfield (1983) reported that the average concentrations of dissolved cadmium in river and ocean waters are 0.02 and 0.01 µg/l respectively. The behaviour of cadmium in the aquatic environment has been investigated by several workers and its preference to remain in the dissolved phase (75 to 90 %) rather than in the particulate phase has been established (Hall et al., 1996; Millward and Glegg, 1997). In a study of the continental shelf of Pakistan, Tariq et al. (1994) observed cadmium concentrations varying from 1 to 87 µg/l. The higher values of Cd observed in the above study were mainly observed at stations where anthropogenic activities are high like Karachi harbour and the mouth of river Indus. Babukutty (1991) reported dissolved Cd concentrations in the range 0.28 to 2.15 µg/l with station wise annual mean concentrations in the range 0.45 to 1.04 µg/l from the northern part of the Cochin estuarine system. Compared to this, the range and mean values of dissolved cadmium found in the present study were slightly higher. One probable reason for the comparatively higher concentration of dissolved cadmium observed in the present study is the use of large quantity of phosphatic fertilizers for agricultural purposes in the study area. Elbaz-Poulichet et al. (1987) reported high concentration of cadmium in the Rhone River due to extensive use of phosphatic fertilizers in the catchment area. A general increase in dissolved cadmium concentrations with increasing salinity was observed which is evident from the higher concentrations of dissolved cadmium during pre-monsoon and post-monsoon seasons, especially at zone 3 (Figure 4.1). Zone 3 is characterised by the intrusion of saline water during pre-monsoon and post-monsoon seasons (Figure 3.5). Similar observations of increasing Cd concentration with increasing salinity have been made in estuaries world-wide, e.g. Rhone and Haunghe (Elbaz-Poulichet et al., 1987), Cochin Estuary (Shibu et al., 1990), the Forth (Laslett, 1993) and Gironde and Tay Estuary (Owens and Balls, 1997). The generality of the Cd-salinity relationship in diverse estuarine environments has been attributed to the formation of stable soluble complexes between Cd and chloride ions, which are abundant in saline water (Comans and van Dijk, 1988). It is thought that the desorption of cadmium, which depends on a number of variables, occurs first and is followed by the formation of the chloro-complexes which prevent its re-adsorption onto particles (Elbaz-Poulichet et al., 1987). It has been reported that the dissolved fraction of cadmium exhibits a maximum in the mid-estuarine reaches (salinity 18 - 25 ‰) due to the dissolution from particulate phase (Duinker, 1986; Windom et al., 1988). Short term variability in estuarine environments can greatly affect dissolved and suspended particulate metal concentrations (Laslett, 1995). Increased fresh water run-off may effectively dilute those metals discharged from point sources. The depletion in the concentrations of dissolved cadmium during the monsoon season may also be due to the dilution of the estuarine water with fresh water run-off from the rivers. Pohl et al. (1998) observed that distribution of dissolved cadmium in the Oder and Peene Rivers and in the Southern Pomeranian Bight was linked to phytoplankton growth. The authors observed a 50 % removal of dissolved cadmium from the water column during the summer season. The influence of biogenic cycling on seasonal variations of Cd has been discussed in shelf areas (Kremling and Pohl, 1989), Arctic regions (Pohl et al., 1993) and coastal areas (Schneider and Pohl, 1996). The lower values of dissolved cadmium observed in the present study in surface waters at zones 1 and 2 during pre-monsoon and monsoon seasons can also be attributed to the influence of biogenic cycling. Figure 4.1 shows that there is a noticeable increase in dissolved concentration of cadmium in bottom waters in the pre-monsoon season especially at zones 2 and 3. This is attributed to the mineralization processes taking place in recently sedimented biogenic particulates. Such an observation was also made by Kremling et al. (1997) from the Mecklenburg Bights of the Baltic Sea.

4.3.2. Dissolved cobalt

Cobalt is relatively scarce in the earth's crust, but the human body requires vitamin B_{12}, which is a cobalt (III) complex to form haemoglobin. In fact, cobalt is widely distributed throughout the human body, without excessive concentration in any particular organ or tissue (Forstner and Wittmann, 1983). Having the ability to occupy low symmetry sites in enzymes, cobalt (II) is an enzyme activator. Total environmental flux of cobalt is relatively low compared to most trace metals. Anthropogenic emissions, largely the burning of fossil fuels, account for approximately 55% of cobalt in the air; the primary natural sources to the atmosphere are wind-borne soil particles and sea salt dispersion.

In fresh water, the dominant species 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 sea water. Cyanocobalamin, or vitamin B_{12}, is a cobalt co-ordination compound found in surface waters, sediments, and other substrates such as sewage sludge (Moore, 1991). Numerous plants and micro-organisms use vitamin B_{12} as their primary source of cobalt. Theis et al. (1988) demonstrated that the concentration of dissolved metal was significantly correlated with pH and the concentration of suspended solids in the water.

In the present study, dissolved concentrations of cobalt were found to vary from 0.06 µg/l to 4.36 µg/l in surface waters and 0.06 µg/l to 3.97 µg/l in bottom waters (Table 4.1). The concentration of dissolved cobalt showed much more variability than that of Cd (coefficient of variation 127 and 123 respectively for surface and bottom waters). Co was found to be the least abundant dissolved trace metal with a mean concentration of 0.73 µg/l and 0.77 µg/l in surface and bottom waters respectively (Table 4.1). The station wise annual mean concentrations varied from 0.47 µg/l (station 1) to 0.91 µg/l (station 5) for surface waters and from 0.54 µg/l (station 1) to 0.97 µg/l (station 5) for bottom waters (Table 4.3). The station wise annual mean values showed an increasing trend from station 1 to station 5 followed by a decrease to station 7 and a further increase to station 9 (Figure 4.2). The above trend was observed as a common feature for both surface and bottom waters. Most of the stations showed slightly higher annual mean concentrations of dissolved Co in bottom water. Zone wise, zone 1 recorded lowest concentration of dissolved cobalt in surface and bottom waters and zone 2 and 3 recorded almost equal values (Figure 4.2).

Unlike cadmium, the dissolved concentrations of cobalt were relatively much higher at all the stations in both surface and bottom waters during the monsoon season when compared to that of pre-monsoon and post-monsoon seasons (Figure 4.2). During the same season, the values generally showed an increasing trend from station 1 to station 5, followed by a decrease towards station 7 and a further increase towards station 9. In the

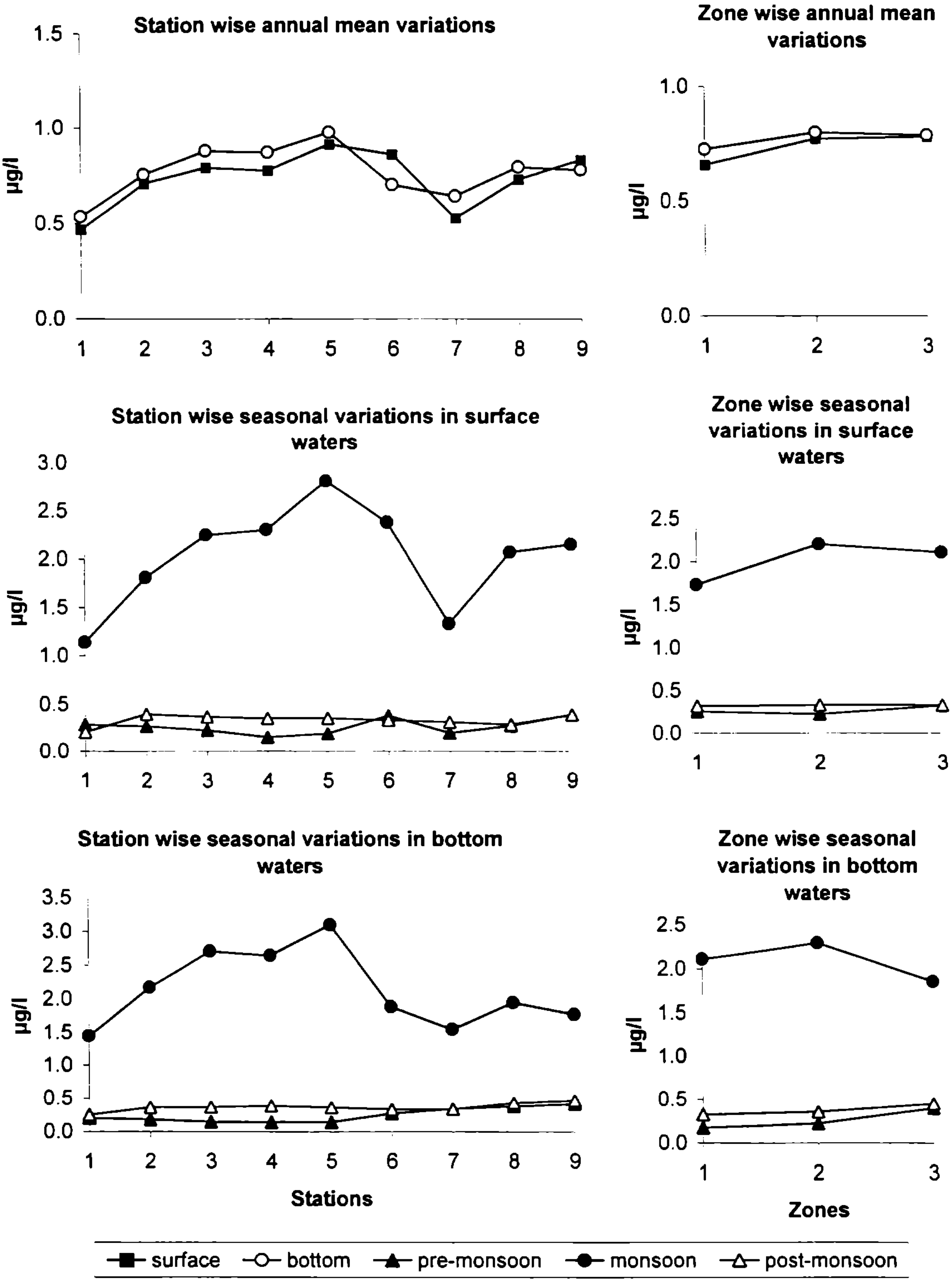


Figure 4.2 Seasonal and spatial variations of dissolved cobalt.

monsoon season, the highest seasonal average was observed at zone 2 in both surface and bottom waters; the lowest zonal average in the surface water was at zone 1 (Figure 4.2) but in bottom water it was observed at zone 3. The seasonal average values in pre-monsoon and post-monsoon periods did not differ much but still pre-monsoon season recorded relatively lower values in most of the stations.

Total cobalt in fresh waters is generally below 1 µg/l, increasing to 10 µg/l in highly industrialised or mining areas. For example, residues in a stream in Czechoslovakia averaged to 1 µg/l with a range of 0.2-5 µg/l (Vymazal, 1984). Although similar results (0.6-5 µg/l) were reported for a lake in Nigeria (Sridhar, 1986), much higher concentrations (8-15 µg/l) were found in the Hindon River in northern India (Ajmal et al., 1987), which receives wastes from several municipalities located along its course. Cobalt occurs in extremely low concentrations in marine waters, often below 10 ng/l. Higher levels have been recorded in the open ocean, but these are probably due to the contamination by phytoplankton and other organisms that metabolise vitamin B_{12}.

The relatively higher concentrations of dissolved cobalt observed in the monsoon season may be associated with the river and land runoff entering the estuary during the heavy rain in monsoon season. Increased fresh water runoff may cause higher concentrations of those metals leached by terrestrial weathering (Boyden et al., 1979). Moreover, increased river flow during the monsoon season may cause increased sediment resuspension and injection of interstitial waters into the overlying waters (Boughriet et al., 1992). It appears that salinity has influence in the distribution of dissolved cobalt in this area as there is a slight increase in the concentration of dissolved cobalt at zone 3 during the pre-monsoon season. The low fresh water flow in the pre-monsoon season facilitates the sorptive equilibrium to attain faster. The relatively lower values of dissolved cobalt in the pre-monsoon season may be attributed to greater adsorption onto suspended particulate matter and increased biological uptake. The lower values of dissolved cobalt during the pre-monsoon period can also be attributed to the lower solubility and mobility of cobalt due to the precipitation of Co as CoS under the generally prevailing sub-oxic condition in the sediments during the pre-monsoon season and may limit the solubility and mobility of cobalt in water (As described by Lapp and Balzer, 1993). Thus, it can be seen that monsoonal runoff is a major source of input of dissolved cobalt into the estuary.

4.3.3 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, 1983). Generally, the mammalian body can tolerate 100-200 times its total body content of chromium without harmful effects, Cr (VI) compounds are approximately 100 times more toxic than Cr (III) salts (Forstner and Wittmann, 1983). The stomach acidity leads to the reduction of Cr (VI) to Cr (III) of which gastrointestinal absorption is less than 1%

Estimates of the total anthropogenic discharges of chromium to surface waters range from 45 x 10^3 to 239 x 10^3 M.T./year (Nriagu and Pacyna, 1988). The primary sources include domestic waste water from both central and non-central sources, manufacturing processes involving metals, and dumping of sewage sludge. Atmospheric fallout is another important source of chromium in surface water (upto 16 x 10^3 M.T./year). Coastal marine sources are dominated by input from rivers and, to a lesser degree, dredging sludge and dumping of industrial wastes.

Total Cr is generally detected at low concentrations in fresh water (1 µg/l to 6 µg/l). The principal forms of Cr in fresh water include $CrOH^{2+}$ $Cr(OH)_2^{+}$ and $Cr(OH)_4$ Cr^{6+} on the other hand, is water soluble, always existing in solution as a component of a complex anion (Moore, 1991). The anionic species varies with pH, and may be chromate (CrO_4^{2-}), hydroxychromate ($HCrO_4^{-}$), or dichromate ($Cr_2O_7^{2-}$) (Moore, 1991). Dichromate is rare at circumneutral pH, and only becomes common in acidic waters (At pH > 6.5, most Cr^{6+} is present as the chromate ion). Chromium exists in natural waters primarily in the III and VI oxidation states (Elderfield, 1970). In oxygenated waters, the dominant redox species is a tetrahedral oxyanion (CrO_4^{2-}), which has a low affinity for deprotonated oxide surfaces that accounts for its nearly conservative distribution in estuarine waters (e.g. Cranston and Murray, 1980). Reduced Cr(III) is present as a hydrolysed cation, $Cr(OH)_3$ or $Cr(OH)_2^{+}$ These species are very particle reactive which accounts for the non-conservative distribution of Cr(III) in estuarine waters (Cranston and Murray, 1980).

In the present study, dissolved chromium was found in the range 0.10 to 6.45 µg/l in surface waters (at stations 8 and 7 respectively) and 0.08 (station 2) to 7.15 µg/l (station 9) in bottom waters (Table 4.4). The mean values in surface and bottom waters were 2.58 µg/l and 2.84 µg/l respectively (Tables 4.1). The station wise annual mean concentrations were in the range 1.75 µg/l (station 8) to 3.41 µg/l (station 5) in surface waters and 2.23 µg/l (station 2) to 3.47 µg/l (station 9) in bottom waters (Table 4.4). An increasing trend in the annual mean concentrations of dissolved chromium was observed (Figure 4.3) from zone 1 to zone 3 in bottom waters, whereas in surface water, the lowest annual mean was observed at zone 3 and the

Table 4.4 Station wise summary statistics on dissolved chromium and copper (μg/l)

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Chromium	**1**	0.12	0.47	5.85	6.35	2.17	2.65	2.16	2.18	99.70	82.19
	2	0.13	0.08	6.25	6.00	2.75	2.23	2.48	2.07	89.99	93.03
	3	0.15	0.09	6.30	6.20	3.01	2.82	2.32	2.26	77.15	80.12
	4	0.20	0.29	6.20	6.25	2.81	3.29	2.38	2.18	84.94	66.23
	5	0.29	0.09	6.20	6.05	3.41	2.86	2.29	2.28	67.10	79.75
	6	0.13	0.63	6.35	6.60	2.84	2.57	2.29	2.26	80.63	88.01
	7	0.22	0.20	6.45	6.90	2.34	2.54	2.28	2.38	97.61	93.78
	8	0.10	0.12	4.63	6.90	1.75	3.16	1.38	2.01	78.99	63.56
	9	0.17	0.77	5.00	7.15	2.19	3.47	1.37	1.93	62.47	55.63
Copper	**1**	1.00	1.17	3.27	3.51	1.97	2.09	0.68	0.76	34.70	36.22
	2	0.90	0.95	8.85	4.35	2.65	2.41	2.47	1.02	93.28	42.27
	3	0.82	0.77	5.25	3.17	2.59	1.82	1.60	0.77	61.95	42.47
	4	0.97	1.04	4.22	7.85	2.06	2.49	0.98	1.78	47.56	71.50
	5	0.77	1.03	4.20	3.61	2.04	2.13	0.92	0.91	45.05	42.78
	6	0.30	0.84	3.55	4.19	1.94	2.50	1.21	1.10	62.60	44.16
	7	0.47	0.61	5.50	4.12	1.93	2.36	1.35	1.13	70.11	48.02
	8	0.71	0.61	2.63	5.70	1.73	2.36	0.62	1.61	35.85	67.91
	9	0.56	0.94	4.53	5.10	1.80	2.52	1.02	1.45	56.68	57.39

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

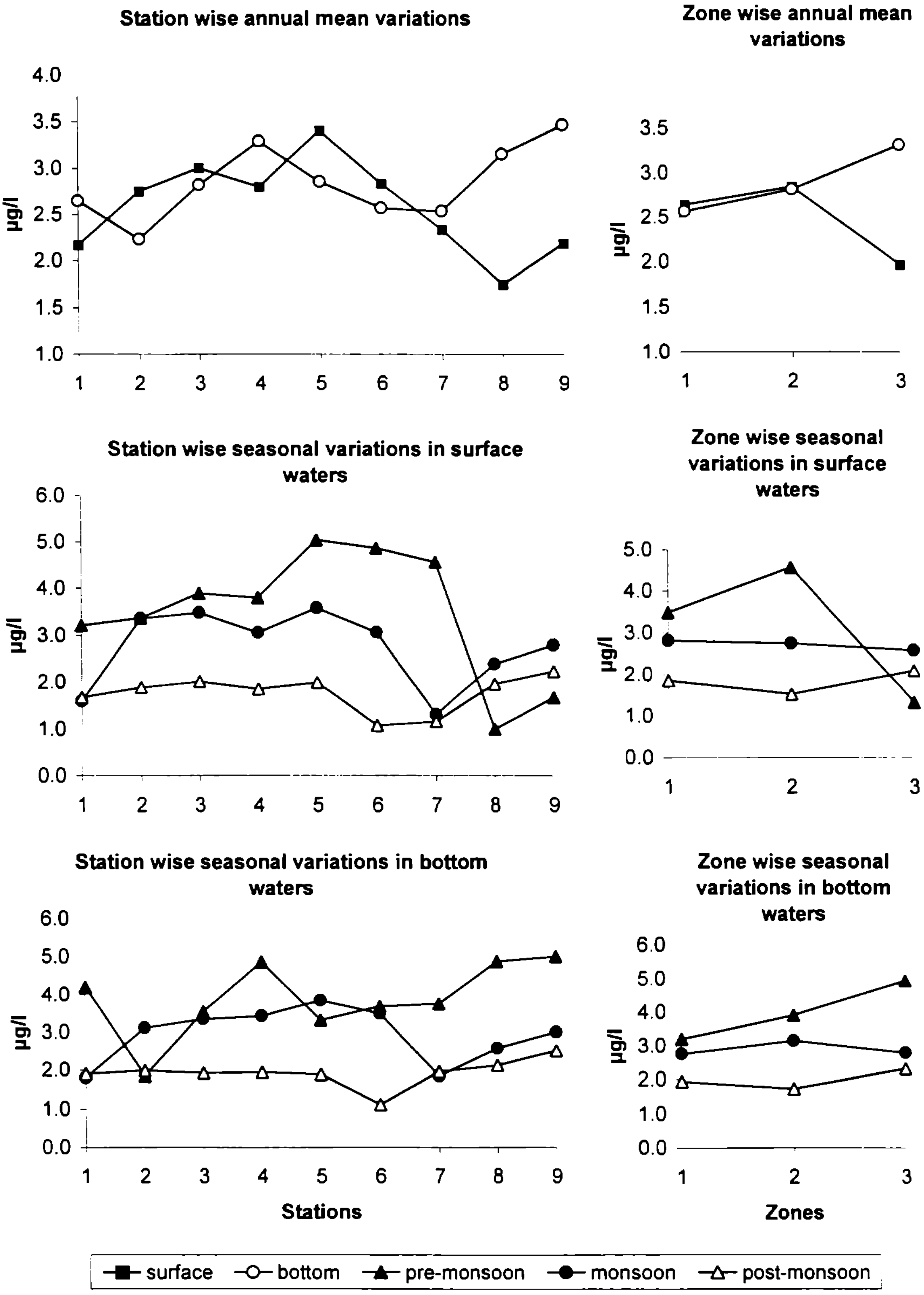


Figure 4.3 Seasonal and spatial variations of dissolved chromium.

highest at zone 2. No marked differences between surface and bottom values, as observed in the case of cadmium, were observed in the annual mean values of chromium except at stations 8 and 9. At zones 1 and 2, surface and bottom water concentrations did not differ much but there was distinct difference between surface and bottom water concentrations at zone 3, the bottom water showed a clear increase in concentration.

The pre-monsoon values were found to be the highest and the post-monsoon values were found to be the lowest from stations 1 to 7 in surface waters (Figure 4.3). At stations 8 and 9, the order was monsoon > post-monsoon > pre-monsoon. Bottom water also showed more or less similar trend. The pre-monsoon values of dissolved chromium in surface waters were found to increase from station 1 to station 5, then decreased to station 8 followed by a slight increase at station 9. This type of behaviour was not observed in bottom waters. In bottom waters, the values were found to increase rather than decrease from station 5 to station 9. In monsoon and post-monsoon periods also, the surface water showed more or less a similar trend as shown for surface water in the pre-monsoon period. Unlike in pre-monsoon period, the bottom water in monsoon period showed an increase in values towards the middle of the zone, then decreased followed by a slight increase. But in the post-monsoon, the values remained almost steady up to the middle of the estuary. In short, the seasonal variations observed at zones 1 and 2 in surface and bottom waters was similar with a pre-monsoonal hike and post-monsoonal depletion in concentration of dissolved chromium (Figure 4.3). Zone 3 also showed increased concentration in pre-monsoon season and decreased concentration in post-monsoon season in bottom water, but in surface water, the highest value was observed in monsoon and the lowest in pre-monsoon season.

The average concentration of Cr in sea water is 0.08 µg/l (Cranston and Murray, 1978) and in fresh water is 0.5 µg/l (Trefrey and Presley, 1976). Chromium and manganese form oxidised and reduced species, which have contrasting chemistry. During reduction reactions, chromium becomes more insoluble and manganese becomes more soluble. This type of an inverse relationship is not observed in the present study. This may be due to the effect of other more influencing factors like pH and salinity. Higher concentration of dissolved chromium in the pre-monsoon season suggests that salinity induced desorption may be occurring. This is supported by the fact that dissolved Cr in bottom waters showed good positive correlation with salinity ($r = 0.356$, $n = 108$, $p < 0.001$). Dissolution of chromium at lower pH observed in pre-monsoon period can be another reason for the increased concentration of dissolved Cr in this season.

4.3.4 Dissolved copper

The primary sources of copper in the aquatic environment include domestic waste water from both central and non-central sources, manufacturing processes involving metals, industrial effluent discharges, the dumping of sewage sludge and application of fertilizers, algicides, fungicides and molluscicides. Atmospheric deposition, of which approximately 56 % comes from anthropogenic emissions (Nriagu, 1989), is another major source to water.

Copper shows a pronounced tendency to form complexes with inorganic and organic ligands. In fresh water at circumneutral pH as well as in sea water, most of the inorganic copper in solution is present as complexes with carbonate, nitrate, sulphate and chloride, rather than as the hydrated divalent cupric ion (Luther et al., 1986). Neutral ligands such as ammonia, ethylenediamine, pyridine etc., form strong 4-coordinated complexes. Copper forms relatively insoluble complexes with sulphides. In some fresh waters, more than 90% of total Cu may be bound to humic acids (Mantoura et al., 1978). These complexes are often quite stable, more so than those humic acid complexes formed with zinc and manganese (Campanella et al., 1987a & b). In sea water, no more than 10 % of total Cu may be bound to humic acids (Mantoura et al., 1978). Dissolved Cu in surface waters is very strongly complexed by dissolved organic molecules, keeping the free ionic Cu concentration 3-4 orders of magnitude below its total dissolved concentration (Turner et al., 1981).

The world mean concentration of Cu in the aquatic environment is reported to be 3 µg/l in the range, 0.2 to 30 µg/l in uncontaminated fresh water systems; 0.03 to 0.23 µg/l in surface sea water and 0.2 to 0.69 µg/l in deep sea water (Bowen, 1985). Concentrations of dissolved Cu in this survey were found to vary from 0.30 to 8.85 µg/l in surface waters and 0.61 to 7.85 in bottom waters (Table 4.1). The mean value in surface water was found to be 2.08 µg/l and 2.30 µg/l in bottom water (Table 4.1). Copper showed lowest variability of concentrations in dissolved phase after cadmium (coefficient of variation 63 and 52 for surface and bottom waters respectively). Station wise, the highest annual mean concentration (2.65 µg/l) was observed at station 2 and the lowest annual mean concentration (1.73 µg/l) was observed at station 8 (Table 4.4) in surface waters. In bottom waters, the lowest (1.82 µg/l) and highest (2.52 µg/l) annual mean concentrations were observed at stations 3 and 9 respectively. The annual mean concentrations of dissolved Cu showed a decreasing trend from station 2 to station 8 in surface waters (Figure 4.4). At zone 1, slightly higher value was observed in surface water than in bottom water. But zones 2 and 3 showed higher values in bottom water (Figure 4.4).

The general trend observed in the seasonal variations of dissolved Cu in surface and bottom waters was such that highest and lowest

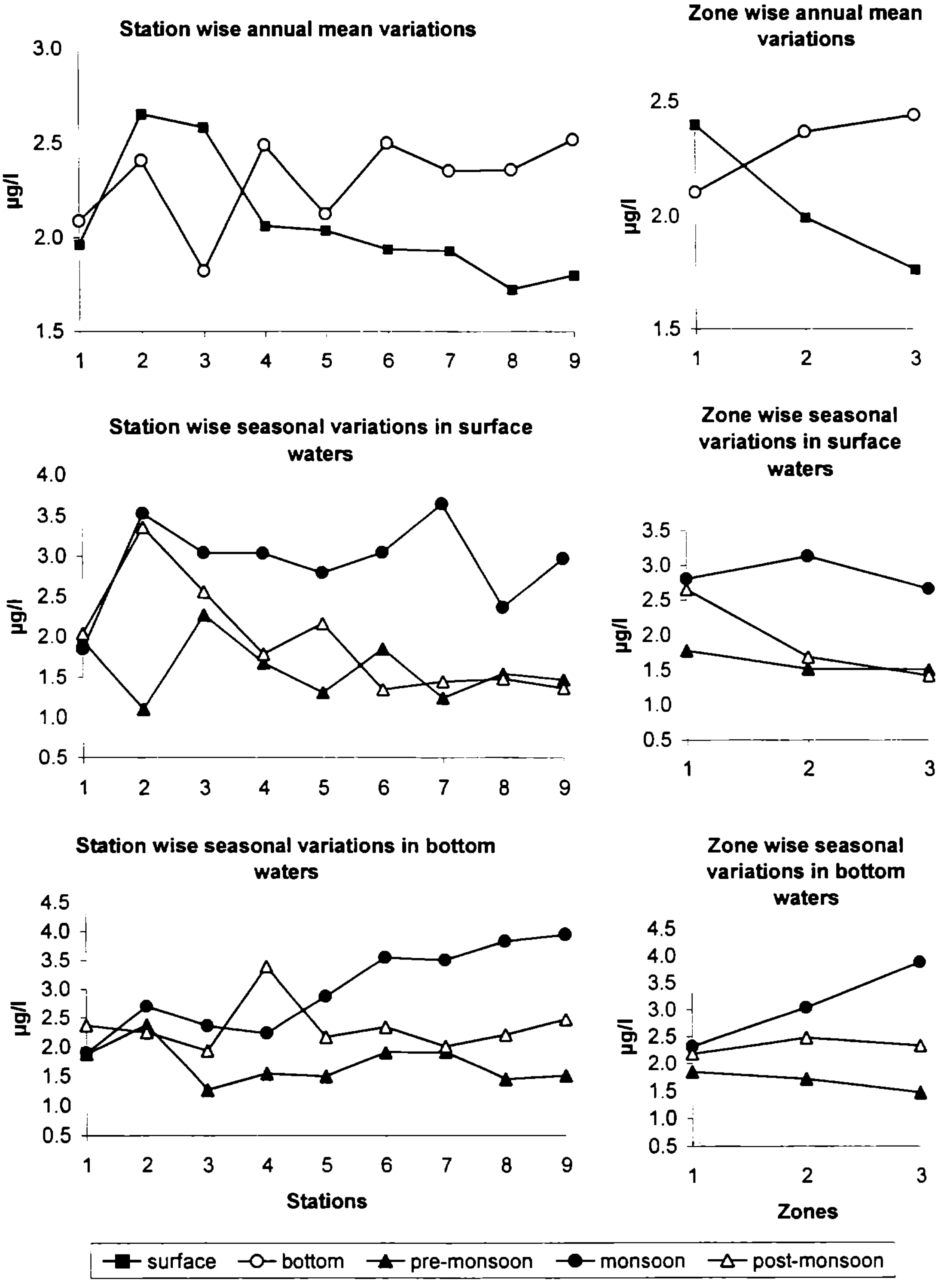


Figure 4.4 Seasonal and spatial variations of dissolved copper.

concentrations were in the monsoon and pre-monsoon seasons respectively (Figure 4.4). In the pre-monsoon season, when the land runoff is minimum, zone 1 recorded highest value but zones 2 and 3 recorded almost equal concentrations in surface water (Figure 4.4). In bottom water, there was a gradual decreasing trend from zone 1 to zone 3 in this season. In monsoon season, zonal average value increased from zone 1 to zone 2 and then decreased at zone 3 in surface water, whereas there was an increasing tendency from zone 1 to zone 3 in bottom water. The generally observed higher concentration of dissolved copper in the monsoon season indicates that the land and river drainages during monsoon season are the major sources of dissolved copper into the estuarine water. The pre-monsoon season during which generally lower concentrations of dissolved copper were observed is characterised by low flow condition and higher residence time. The low discharges and high residence time of water in the pre-monsoon season help to attain sorptive equilibrium between dissolved and particulate phase at a faster rate (Ackroyd et al. 1986). This will lead to removal of copper from the dissolved phase to living and non-living particulate matter and finally to the sediment phase (Flemming and Trevors, 1989).

Total copper is detected at low concentrations, generally at < 20 µg/l, in most fresh waters. Whitehead et al. (1988) working on a north Mediterranean River, found that copper in filtered water samples, ranged from 100 to 280 ng/l; however, much higher levels, 100-6600 µg/l, were found in suspended solids. DeLeon et al. (1986) reported that residues in the Mississippi River ranged from 2 to 39 µg/l; these residues were based on acidified and filtered samples. Dissolved levels in fresh waters rarely exceed 5 µg/l in the absence of an anthropogenic source of copper (Canadian Water Quality Guidelines, 1987). Dissolved Cu in the fresh water/sea water mixing zones of estuaries is often greater than those levels in the inflowing rivers. This is generally due to the desorption caused by competition with the chloride ion and, to a lesser degree, bacteria-mediated decomposition of organic material.

Patel et al. (1985) reported that dissolved Cu in Bombay Harbour, which receives large amounts of industrial and municipal wastes, averaged 630 µg/l with a range of 20 to 1300 µg/l. Although these values are obviously high, dissolved Cu residues, upto 16 µg/l, were found in the Mindhola Estuary (India), which also receives waste water (Zingde et al., 1988). The range of values in the southern part of the estuarine system as observed in the present study (0.30 to 8.85 µg/l) is comparable to the range of dissolved copper concentrations reported by Babukutty (1991) (1.49 to 9.42 µg/l) and Shibu et al. (1990) (in the range 1.3 to 6.4 µg/l) with a mean value of 3.6 µg/l from the northern part of the Cochin estuarine system. Shibu et al. (1990) have also reported extensive organic association of copper from the northern side of Cochin estuarine system. Higher values of dissolved copper concentrations observed in the present study during the monsoon season are associated with large amount of land and river drainage during this season. Such seasonal variations of dissolved copper concentrations were also observed from Vellar Estuary (Senthilnathan and Balasubramanian, 1997). The behaviour of dissolved copper in different estuaries showed contrasting behaviour. Duinker (1983) observed an initial removal of copper in the low salinity region of the Rhine Estuary, whereas an addition of dissolved copper was reported in the Cochin Estuary (Paul and Pillai, 1983a), in the Savannah and Ogeechee estuaries (Windom et al., 1983) as well as in the Mandovi and Zuari Estuaries (George, 1989). On the other hand, Windom et al. (1988) noticed a conservative behaviour of copper during estuarine mixing from the Bang Pakong Estuary. Conservative behaviour for dissolved copper was also observed in a laboratory study by Loic L'Her Roux et al. (1998). The observed increase in dissolved concentration of copper in bottom waters would be due to the remobilisation of copper from the sedimentary phase due to microbial degradation of organic matter. Flemming and Trevors (1989) have noticed this process, helping to add significant amounts of copper to the dissolved phase. Windom et al. (1983) also observed such remobilisation of copper from the sedimentary phase in the Savannah and Ogeechee estuaries at higher salinities.

4.3.5 Dissolved iron

Although iron is the second most abundant metallic element in the earth's crust, concentration of iron dissolved in water is generally low. The chemical behaviour of iron and its solubility in water depend strongly on the oxidation intensity in the system in which it occurs; pH has a strong influence as well. The availability of iron in aqueous solution is strikingly affected by environmental conditions, especially changes in degree or intensity of oxidation or reduction. High concentrations of dissolved ferrous iron can occur in solution at the sites of either reduction of ferric oxyhydroxides or oxidation of ferrous sulphides. In the latter process, the sulphur is attacked first and altered to sulphate, releasing the ferrous iron. Iron is present in organic wastes and in plant debris in soils, and the activities in the biosphere may also have a strong influence on the occurrence of iron in water. Micro - organisms are commonly involved in processes of oxidation and reduction of iron, since some species may use these reactions as energy sources.

It has been assumed that iron in oxic-sea water is present predominantly in the insoluble and thermodynamically stable 3+ oxidation state (Morel and Hering, 1993; Stumm and Morgan, 1996). Dissolved inorganic species of Fe (III) in sea water are predominantly the hydrolysis products, $Fe(OH)_2^+$ and/or $Fe(OH)_4^-$ (Hudson et al., 1992; Kuma et al., 1996). Recent reports (van den Berg 1995; Wu and Luther 1995; Kuma et al., 1996 & 1998) pointed out that iron complexation with organic ligands is possible in oceanic water. In general, dissolved iron concentrations in sea water are defined with an operational distinction made between particulate (>0.45 μm) and dissolved (<0.45 μm) fractions. In the dissolved fraction, the fraction between 0.25 to 0.45 μm is called the colloidal fraction and the fraction <0.25 μm is called the true dissolved fraction. Wu and Luther (1994 &

1996) have reported the colloidal fraction of iron in sea water, and Kuma et al. (1998) have reported the colloidal fraction of iron in estuarine /coastal waters.

Iron occurs to a large extent as colloidal hydrous iron oxides in river water (Murray and Gill, 1978; Hong and Kester, 1985). The hydroxides tend to be complexed with organic compounds, which give the colloids a negative surface charge (Tipping, 1986; Tipping and Cooke, 1982). Destabilisation of river-borne colloids by sea water cations is accepted as a primary cause for aggregation (Mayer, 1982; Tipping and Cooke, 1982). pH, suspended particle's concentration, velocity gradients, organic matter and organisms are also important in the aggregation process (Eisma, 1986; Tsai et al., 1987). The sedimentation of aggregates formed during estuarine mixing is determined by the physical properties controlling their aggregate stability and density (Hawley, 1982; Mayer, 1982; Burban et al., 1990). Aston and Chester (1973) concluded that suspended particles affected both the rate and extent of iron precipitation, while Boyle et al. (1977) noted that river-borne particulate material had a minor effect on iron precipitation.

Iron has an extensive ability to form soluble complexes with naturally occurring organic compounds. Iron occurs at higher concentrations in river water than in sea water. This fact coupled with the tendency of dissolved iron to form insoluble hydroxide polymers, has led to the suggestion that changes in pH, pE and ionic strength encountered from river-borne dissolved iron in estuaries may lead to its removal from solution (Aston and Chester, 1973).

Dissolved iron concentrations in the survey area were found to vary from 9.80 to 394.00 µg/l in surface waters and from 23.80 to 346.00 µg/l in bottom waters (Table 4.1). Station 9 recorded the highest values in surface and bottom waters (Table 4.5). While station 6 recorded the lowest value in

Table 4.5 Station wise summary statistics on dissolved iron and manganese (µg/l)

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Iron	1	29.80	28.20	128.00	131.00	67.53	58.89	39.73	35.71	58.84	60.63
	2	15.10	30.20	127.00	191.00	62.61	75.83	39.83	50.22	63.62	66.22
	3	29.20	28.60	149.80	137.00	77.07	58.20	44.61	36.09	57.89	62.01
	4	24.10	27.40	238.00	108.00	86.53	53.12	60.80	27.32	70.27	51.43
	5	31.00	26.90	123.00	222.00	59.51	63.68	34.78	55.83	58.45	87.67
	6	9.80	25.00	121.00	136.00	55.94	57.86	34.76	33.33	62.14	57.60
	7	32.30	29.50	283.60	298.70	100.13	97.93	78.89	81.08	78.79	82.80
	8	27.50	23.80	172.40	199.00	78.56	70.63	46.13	49.16	58.72	69.60
	9	30.90	26.80	394.00	346.00	90.20	101.61	100.54	90.71	111.46	89.27
Manganese	1	0.18	0.18	2.70	0.90	0.51	0.35	0.70	0.21	136.32	59.50
	2	0.16	0.16	0.56	0.54	0.32	0.35	0.14	0.13	42.83	36.47
	3	0.15	0.16	0.81	0.79	0.38	0.36	0.21	0.19	54.20	52.71
	4	0.05	0.25	1.61	0.88	0.42	0.44	0.40	0.19	95.66	43.64
	5	0.14	0.13	0.82	5.25	0.39	0.83	0.22	1.42	56.51	170.49
	6	0.19	0.20	4.45	5.05	0.82	0.85	1.20	1.35	145.57	159.45
	7	0.14	0.20	117.50	67.00	11.67	8.44	33.46	18.76	286.69	222.24
	8	0.21	0.24	1.10	22.35	0.52	2.31	0.30	6.31	57.93	272.93
	9	0.17	0.20	46.60	64.00	4.52	9.91	13.27	22.04	293.50	222.37

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

surface waters, the lowest in bottom waters was observed at station 8. In the present study, iron was found to be the most abundant trace metal in dissolved phase and the mean values recorded in surface and bottom waters were 75.34 µg/l and 70.86 µg/l respectively (Table 4.1). The station wise annual mean concentrations were found to be within the range 55.94 to 100.13 µg/l in surface waters and 53.12 to 101.61 µg/l in bottom waters (Table 4.5). The highest station wise annual mean concentrations were recorded at stations 7 and 9 in surface and bottom waters respectively. The lowest annual mean concentration was found at station 6 in surface water and at station 4 in bottom water. A slightly increasing trend was observed in the annual mean concentrations from station 1 to station 9 (Figure 4.5). Surface water concentrations were higher than bottom water concentrations at zones 1 and 2 but zone 3 recorded almost equal annual mean concentrations (Figure 4.5). The fresh water zone (zone 1) recorded the lowest zonal average and the zone 3 recorded the highest value of annual mean concentrations.

Seasonal variations were observed in the distribution of dissolved iron concentrations (Figure 4.5). Generally, the pre-monsoon average was found to be the highest in surface and bottom waters with very few insignificant exceptions. The average values in pre-monsoon season recorded at stations 7, 8 and 9 were comparatively higher. Both surface and bottom waters clearly showed seasonal minima in the post monsoon season, and monsoon season generally showed intermediate values. In the pre-monsoon and post-monsoon seasons, there was an increasing trend in dissolved iron concentrations from zone 1 to zone 3 and this trend was more predominant in pre-monsoon season (Figure 4.5). Contrary to this, the seasonal average values showed a decreasing trend from zone 1 to zone 3 in monsoon season.

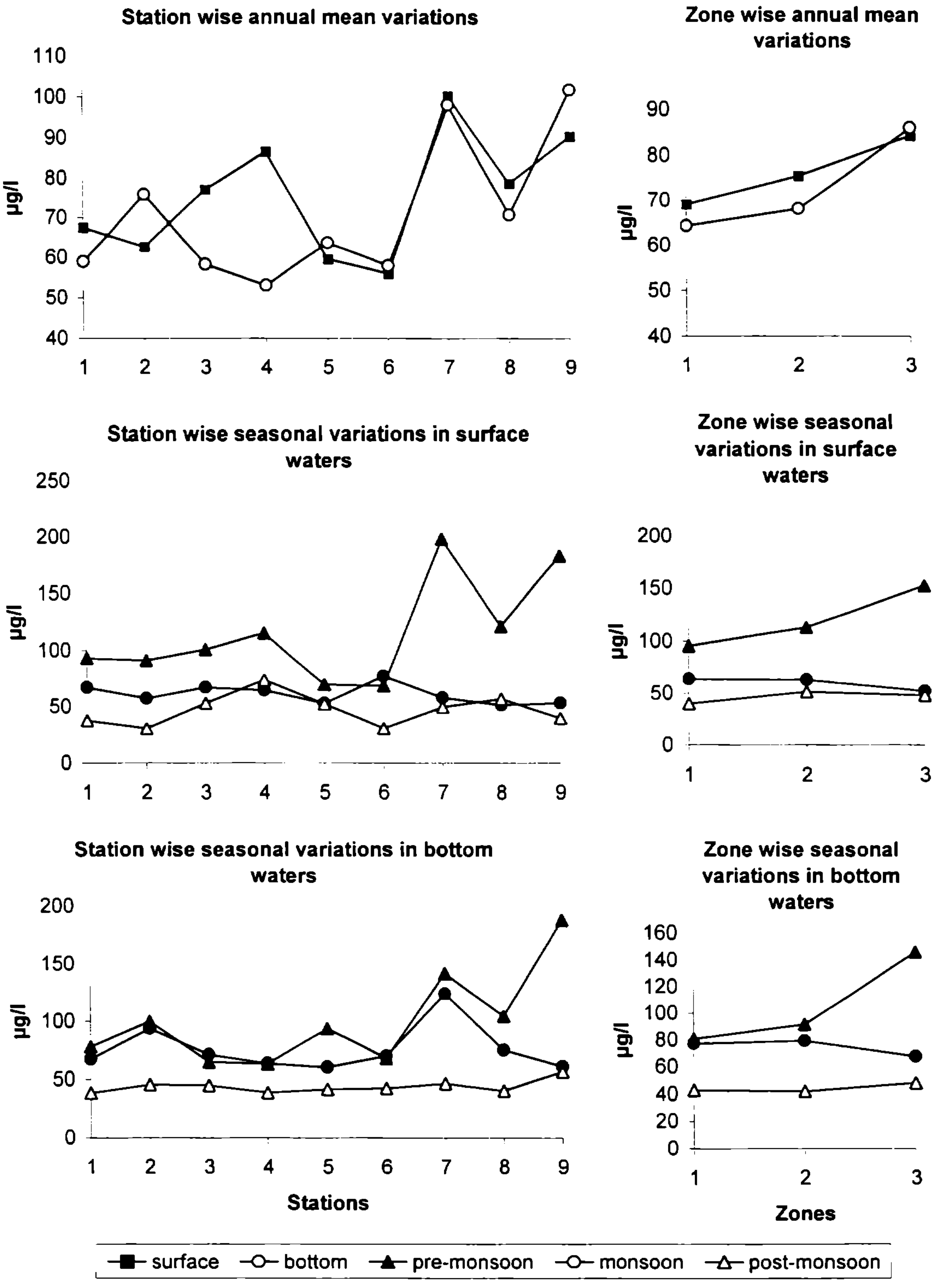


Figure 4.5 Seasonal and spatial variations of dissolved iron.

The estimations of the average concentrations of dissolved iron in river water are more difficult to arrive at because of its greater variability. The available data show wide differences in the values. Livingstone (1963) reported global average dissolved iron content in river waters as 700 µg/l, compared to the corresponding amount of 10 µg/l in sea water. Burton and Liss (1974) also reported world average concentration of dissolved iron in river water as 670 µg/l, whereas Martin and Meybeck (1979) reported only 40 µg/l as the world average of dissolved iron.

Non-conservative behaviour of iron has been observed in the low saline region (0-5) of a number of estuaries around the world (Bale and Morris, 1981; Crerar et al., 1981; Mayer, 1982; Fox, 1983; Hong and Kester, 1985). The results of studies on the 4 estuaries namely Satilla Estuary (Windom et al., 1971), Mullica River (Coonley et al., 1971), Merrimack Estuary (Boyle et al., 1974) and Beaulieu Estuary (Holliday and Liss, 1976) also indicated non-conservative behaviour of dissolved iron during estuarine mixing. This was interpreted as large scale removal of iron from solution during mixing process, such removal being essentially complete by the time the estuarine water has reached salinity of 15%, if not before. Contradictory to the above observations, it was found in the present study that dissolved iron concentration has high degree of positive correlation with salinity ($r = 0.462$ and 0.470 respectively for surface and bottom waters, $p < 0.001$). The soils in Kuttanad are generally acidic especially in pre-monsoon season when the soil is poorly flushed (KWBS, 1989). This increased soil acidity and the reductive solubilization of iron due to a partial reducing environment prevalent in this higher salinity period are the reasons for the observed positive correlation of dissolved iron with salinity and the higher concentrations of iron observed during the pre-monsoon season of higher salinity, especially at zones 2 and 3. It is also assumed that Fe^{2+} formed under reducing conditions, which is more soluble than Fe^{3+}, fluxes out of the sediment and leads to an increase in dissolved iron concentration during the pre-monsoon season (Pohl et al., 1998). Kremling et al. (1997) also observed such summer time increase in dissolved iron concentration due to diffusion of the metal from the sediments under low oxygen or anaerobic conditions. Due to the high flow conditions in the monsoon season, the estuarine water, which is almost stagnant in the pre-monsoon season due to the closing of the shutters of salinity barrier, gets flushed and diluted with river water. This may be the reason for the reduction in the dissolved iron concentration during the monsoon season. This observation is supported by the fact that in the present study the fresh water zone (zone 1) recorded the lowest annual mean concentrations and the estuarine zone (zone 3) recorded the highest annual mean concentrations (Figure 4.5).

4.3.6 Dissolved manganese

The chemistry of manganese resembles to that of iron in that both metals are redox sensitive and are relatively mobile in the aquatic environment. Manganese may exist in oxidation states ranging from –3 to +7 However, the Mn^{2+} and the Mn^{4+} states are most important in aqueous systems. The +3 species is unstable in that they may disproportionate, i.e., two Mn^{3+} ions may interact spontaneously to produce one Mn^{2+} ion and one Mn^{4+} ion, and these products are thermodynamically more stable than the original Mn^{3+} species. The Mn^{7+} is not persistent because of its rapid reduction, which is mediated through oxidation with organic complexes. The thermodynamically stable form of Mn in oxygenated sea water is the insoluble Mn (IV) ion. The nitrate, chloride and sulphate salts of manganese are soluble in water, whereas the corresponding hydroxides, sulphides, carbonates, oxides, and phosphates are only sparingly soluble and are found in the particulate fraction (>0.45 µm) of the water column (Luther et al., 1986).

The dominant factor influencing the aquatic geochemistry of manganese is the change of oxidation state of the element between reducing and oxidising environments, coupled with the marked difference between the oxidation states in terms of their forms and reactivity.

$$MnO_2\,(s) + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$$

(Reduction)

$$Mn^{2+} + O_2 + 2e^- \longrightarrow MnO_2\,(s)$$

(Oxidation)

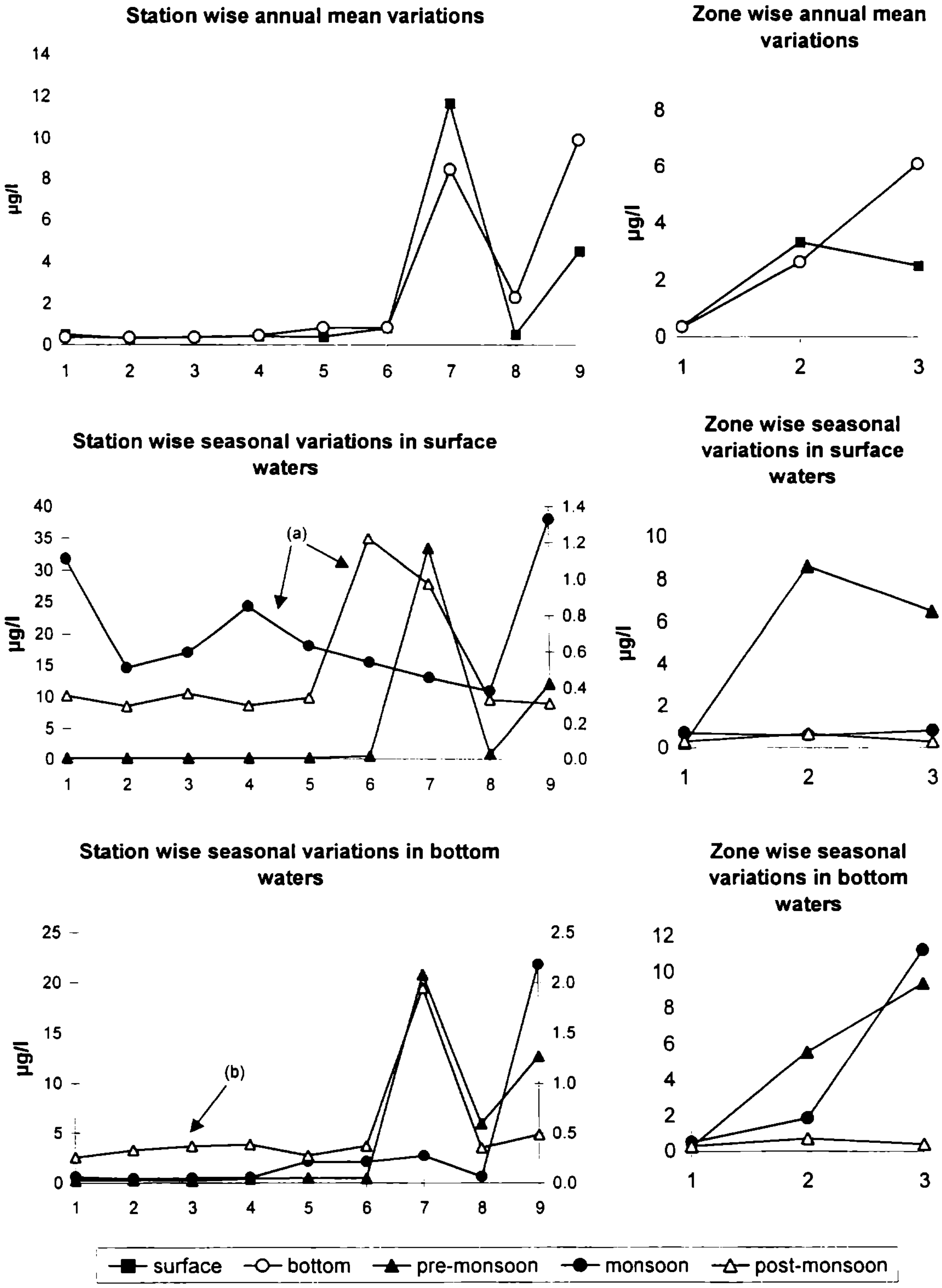
The oxidation-reduction cycle is important in controlling the fate of manganese in most surface waters (Forstner and Wittmann, 1983). The cycle varies seasonally, particularly in water bodies that develop an anoxic hypolimnion during the summer (Forstner and Wittmann, 1983). Oxygen concentrations at the water-sediment interface often approach zero. This causes the reduction of Mn^{4+} to soluble Mn^{2+} which is then transported upward in the water column, where it gets oxidised and settles to the bottom to repeat the cycle.

Total manganese in fresh water is extremely variable, ranging from 2 to 4000 µg/l (Moore, 1991). Similarly, varying concentrations are found in estuaries and harbours, but concentrations are uniformly lower in offshore marine areas (Nolting, 1986). Zingde et al. (1988) reported values in the range 900 to 1360 µg/l from the Mindhola Estuary (India). The average concentration of manganese in sea water is 0.2 µg/l (Brewer, 1975). Turekian

(1969 & 1971) compiled data on dissolved manganese concentrations from rivers and oceans and found that the global average in river water is 7 µg/l as against the average of 0.4 µg/l in sea water.

Dissolved concentrations of Mn in the surveyed area varied from 0.05 µg/l (at station 4) to 117.50 µg/l (at station 7) in surface waters and 0.13 µg/l (at station 5) to 67.00 µg/l (at station 7) in bottom waters. The mean values were 2.17 µg/l and 2.65 µg/l in surface and bottom waters respectively (Table 4.1). Among the ten dissolved metals studied, Mn recorded maximum variability in concentrations with a coefficient of variance 556 for surface waters and 383 for bottom waters. The station wise annual mean concentrations ranged from 0.32 µg/l to 11.67 µg/l in surface waters and 0.35 µg/l to 9.91 µg/l in bottom waters (Table 4.5). Lowest annual mean concentration was observed at station 2 for both surface and bottom waters. The spatial distribution trend of dissolved manganese showed almost equitable annual mean concentrations in surface and bottom waters from stations 1 to 4 (Figure 4.6). The values from stations 5 to 9 were found higher, especially at stations 7 and 9.

Seasonal variations were also observed for dissolved Mn concentrations (Figure 4.6). Stations 1 to 5 recorded slightly higher values in surface and bottom waters in the monsoon season. Station 6 also recorded highest value in the monsoon season but only in the bottom water, but in surface water, highest value was recorded in the post-monsoon season. Stations 7, 8 and 9 behaved in a little different way such that the pre-monsoon season recorded the highest value, except at station 9 where the bottom water showed highest value in the monsoon season. Another conspicuous difference between stations 1 to 6 and stations 7 to 9 was in the magnitude of the highest seasonal average values. Zone wise, zones 2 and 3 recorded considerably higher values in pre-monsoon season in surface



Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 4.6 Seasonal and spatial variations of dissolved manganese.
(compare graphs 'a' and 'b' with secondary Y- axis)

waters (Figure 4.6). In bottom water also, zones 2 and 3 recorded much higher values; in addition to this, a monsoonal hike in the concentration of dissolved Mn was also observed at zone 3.

The main sources of manganese pollution in the environment are fertilizers and pesticides. Since, the surveyed area is surrounded by vast area of agricultural land, inputs of dissolved manganese in the estuary can be partially attributed to the excessive use of pesticides and fertilizers in the area, which contains manganese. Input of dissolved manganese can also be attributed to desorption from suspended particles (Bewers and Yeats, 1978), reductive solubilization (Duinker et al., 1979; Laslett, 1995) and advective and diffusive fluxes of sediment pore waters (Morris and Bale, 1979; Knox et al., 1981; Laslett, 1995). A concentration minimum was usually evident in the low salinity region. This may be due to oxidative precipitation, which is catalysed by an initial sorptive uptake onto suspended particles as observed by Morris and Bale (1979), Morris et al. (1982) and Ackroyd et al. (1986). Owens and Balls (1997) observed a remarkable increase in the dissolved manganese concentrations in the middle of the estuary (mid estuarine maxima). Knox et al. (1981) and Laslett and Balls, (1995) also observed similar type of mid estuarine maximum for manganese. In a survey of Beaulieu Estuary, Holliday and Liss (1976) reported that concentrations of dissolved Mn showed decreasing trend with increase in salinity. They found that the plot of Mn versus salinity showed reasonably linear relationships. In the present study, higher concentrations of dissolved manganese observed at zones 2 and 3, especially in the pre-monsoon season, are comparable to the above observations. This type of feature has been attributed to the inputs of reduced Mn(II) from sediments (Knox et al., 1981; Laslett and Balls, 1995; Owens and Balls, 1997). Seasonal summer-time increases in dissolved Mn concentrations have been observed in the Western Baltic (Balzer et al., 1987), the North Sea (Burton et al., 1993; Hydes and Kremling, 1993), the

English Channel (Tappin et al., 1993) and in British Coastal waters (Laslett, 1995). According to Laslett (1995), the newly formed organic matter from primary productivity reaches the sediments in early summer. This undergoes rapid microbial degradation and causes the development of suitably sub-oxic or anoxic conditions. Solid manganese oxides in the sediment are then reduced to soluble Mn (II), and this enters the water column by diffusion or mixing. Another possible reason for the increased concentration of dissolved Mn during pre-monsoon season is the increased soil acidity (KWBS, 1989) during this season. Benthic fluxes as observed in the Tamar (Knox et al., 1981), which are enhanced in the warmer pre-monsoon season, when biological activity is increased and oxygen concentrations are generally lower (Dehairs et al., 1989) may also be playing a role in increasing the concentrations of dissolved Mn during the pre-monsoon season at zones 2 and 3.

4.3.7 Dissolved molybdenum

Molybdenum is an essential nutrient for all nitrogen-fixing organisms since nitrogen fixation is coupled to a molybdenum process and occurs regularly in all plant tissues (Forstner and Wittmann, 1983). But high dietary concentrations of molybdenum are harmful to several animal species; all cattle are susceptible to molybdenosis, a scouring disease known as tearts, which arises from ingestion of excessive amounts of this element from the herbage of affected areas. Acute or chronic toxic effects have not been reported for humans.

Geochemically, molybdenum is relatively less reactive in the ocean, with long oceanic residence time. The mean oceanic residence time (MORT) of Mo is 7.3 x 10^5 year (Martin and Whitfield, 1983), which is the highest among the ten trace metals studied. Molybdenum has pronounced enhancement of concentration in sea water compared with average river water concentration. Molybdenum is a minor dissolved constituent of sea water with a concentration of approximately 11 µg/l (Head and Burton, 1970; Jones, 1974). The average concentration in river water is less than in the marine environment, being less than 1µg/l (Martin and Whitfield, 1983). Near molybdenum mining areas, the surface water concentration may rise upto 0.2 – 0.4 mg/l.

In the present study, the values were found to be within the range 0.01 µg/l (at stations 3 and 4) to 9.65 µg/l (at station 5) in surface waters and 0.02 µg/l (at station 3) to 10.25 µg/l (at station 6) (Table 4.6) in bottom waters. The mean values of dissolved molybdenum in surface and bottom waters were 1.74 µg/l and 1.94 µg/l respectively (Table 4.1). Station wise, the lowest annual mean concentration was found at station 1 for surface and bottom waters, the values being 1.13 µg/l and 1.22 µg/l respectively. The highest annual mean concentration was observed at station 9, the values being 2.24 µg/l for surface water and 2.56 µg/l for bottom water. Unlike other metals, surface / bottom variations in annual mean concentrations of molybdenum were very much discrete, bottom values being always at a higher level than the surface water. Annual mean concentrations of surface and bottom waters showed an increasing trend from stations 1 to 9 (Figure 4.7). Zone wise, highest annual mean concentration was observed at the estuarine zone (zone 3) and the lowest at the fresh water zone (zone 1) (Figure 4.7).

Monsoon season recorded highest values in all the nine stations, the values being distinctly higher than the pre-monsoon and post-monsoon seasons (Figure 4.7). This is true for both surface and bottom waters. The pre-monsoon and post-monsoon averages of dissolved molybdenum in surface and bottom waters were almost in the same range except at stations 8 and 9 where, the pre-monsoon values showed a slight increase than the

Table 4.6 Station wise summary statistics on dissolved molybdenum and nickel (µg/l)

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Molybdenum	**1**	0.13	0.24	3.50	5.55	1.13	1.22	1.19	1.69	105.45	138.09
	2	0.06	0.09	6.55	6.95	1.57	1.63	2.29	2.32	145.45	142.05
	3	0.01	0.02	7.85	8.70	1.81	2.03	2.80	3.08	154.36	151.50
	4	0.01	0.09	8.65	9.10	1.51	1.86	2.59	2.85	171.57	153.47
	5	0.11	0.14	9.65	8.55	2.01	2.11	3.04	2.96	151.08	140.38
	6	0.04	0.05	9.15	10.25	1.68	1.74	2.63	2.90	156.24	166.85
	7	0.06	0.14	9.60	9.90	1.69	1.90	2.72	2.76	161.14	145.40
	8	0.20	0.21	9.10	9.50	2.03	2.38	2.59	2.86	127.55	119.85
	9	0.23	0.09	8.15	8.50	2.24	2.56	2.58	2.80	115.02	109.03
Nickel	**1**	0.90	0.47	4.37	9.10	2.08	3.62	1.29	3.37	61.92	93.12
	2	0.68	0.47	10.30	12.00	3.44	4.09	3.41	4.25	99.12	103.85
	3	0.55	0.68	11.50	12.25	3.93	3.96	3.66	4.05	93.07	102.16
	4	0.75	1.35	14.75	11.40	4.12	4.05	4.47	3.43	108.47	84.81
	5	0.99	1.12	12.95	12.70	4.13	4.35	4.12	4.23	99.93	97.24
	6	0.36	0.76	17.15	18.15	4.25	4.45	4.89	4.97	114.96	111.80
	7	0.68	0.86	12.50	13.40	4.30	4.38	3.15	3.30	73.28	75.47
	8	0.42	0.52	10.35	12.55	3.90	4.69	3.13	4.08	80.20	87.14
	9	0.29	0.62	11.50	12.55	5.23	5.40	3.99	4.12	76.33	76.28

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

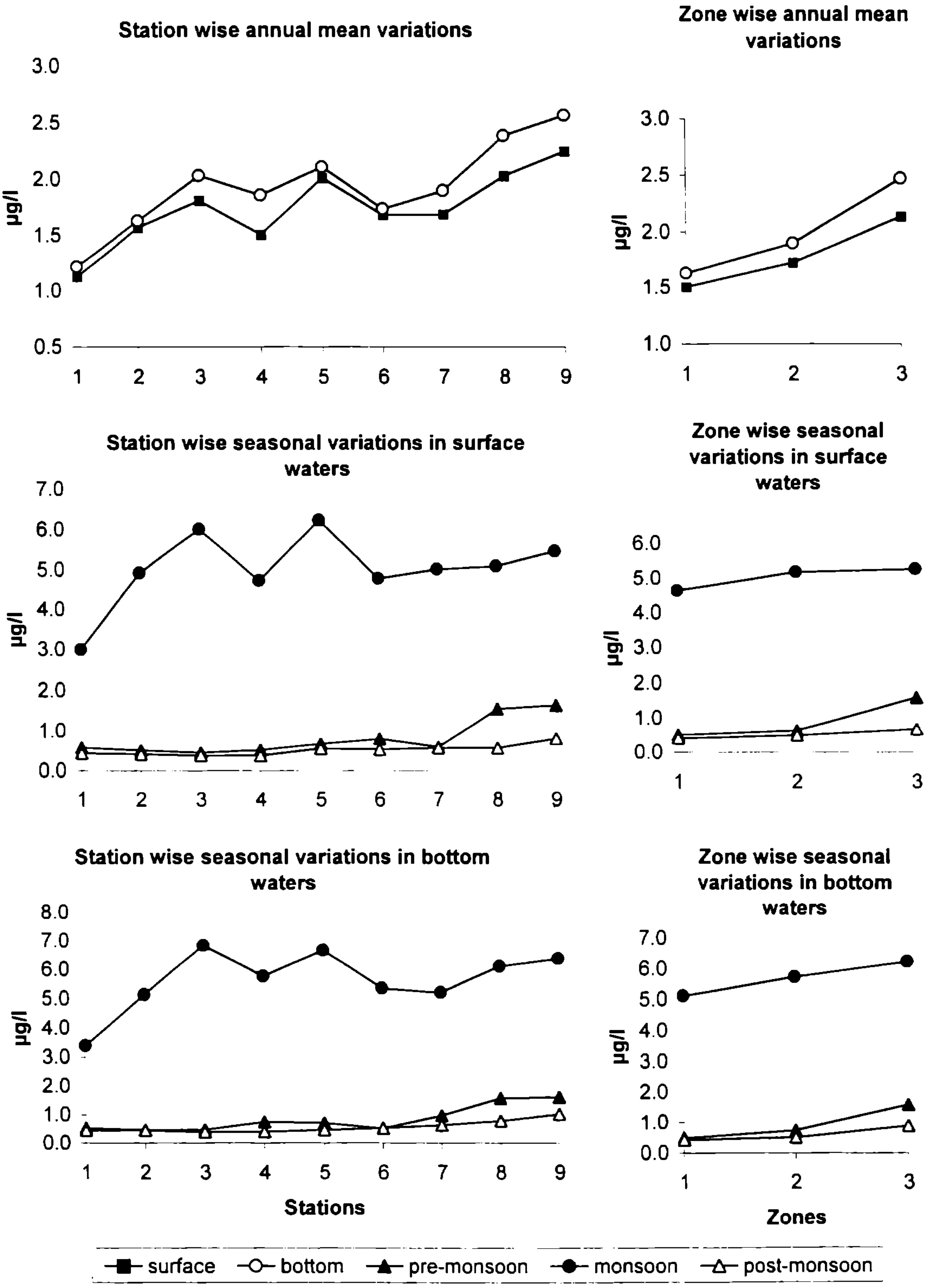


Figure 4.7 Seasonal and spatial variations of dissolved molybdenum.

post-monsoon values. Surface and bottom variations were also distinct in monsoon season since bottom water concentrations were higher than surface waters in all stations. But this trend was not followed in the pre-monsoon and post-monsoon seasons. The annual mean concentrations were found to be slightly higher in the estuarine region of stations 8 and 9 than from the riverine regions of stations 1 and 2.

Kharkar et al (1968) had reported an average of 1.8 µg/l of molybdenum from U.S. streams. The average dissolved concentration of molybdenum reported from some of the fresh water streams of the world is 0.5 µg/l (Martin and Whitfield, 1983; Martin and Meybeck, 1979) and the average dissolved concentration in sea water is 10 µg/l (Martin and Whitfield, 1983). Though the average (of surface and bottom waters) dissolved concentration of molybdenum recorded in the present study (1.84 µg/l) was slightly higher than the fresh water average reported by Martin and Whitfield (1983), it is much lower than the average sea water concentration. The comparatively higher values of dissolved molybdenum concentrations recorded during the monsoon season in all the stations can be attributed to the input of dissolved Mo in the backwaters along with the runoff water during the heavy rains in monsoon season. The observed hike in dissolved molybdenum concentrations at zone 3 during pre-monsoon may be related to the increased salinity at this zone during these periods. Head and Burton (1970) had investigated the variation of dissolved molybdenum with salinity in Southampton water and found that there is a close linear relationship between dissolved molybdenum and salinity. Further, a hike in the dissolved molybdenum concentrations at zone 3 during post-monsoon season may be due to the desorption of Mo from particulate matter at a lower salinity. A similar observation was made by Jones (1974) in a survey of the Conway Estuary. According to Jones, although dilution of molybdenum rich sea water by river water is the major factor controlling the molybdenum concentrations in the estuarine water, some desorption of molybdenum from particulate material probably also occurs. This mechanism is proposed to explain higher molybdenum values found at some intermediate salinity, which were above that expected on the basis of a linear relationship between molybdenum and salinity.

4.3.8 Dissolved nickel

The total amount of nickel discharged from anthropogenic sources to fresh waters amounts to 33 - 194 x 10^3 M.T./year (Nriagu and Pacyna, 1988). The major source of discharge is municipal waste water followed by smelting and refining of non-ferrous metals (Nriagu and Pacyna, 1988). Mining and smelting of nickel-bearing ores contribute substantially to the anthropogenic cycling of nickel in surface waters. The use of fossil fuels, particularly coal, is widely implicated in the release of nickel to the atmosphere and surface waters (Wilson et al., 1986). Another major source of Ni input into the aquatic system is crude oil and its products. Though, Ni occurs in a number of oxidation states, Ni (II) is the most common due to its stability over a wide range of pH. The toxic action of Ni is due to its ability to replace essential metals in the metallo-enzymes resulting in the disruption of metabolic pathways (McGroth and Smith, 1990).

Dissolved nickel levels in unpolluted fresh waters typically range from 1 to 3 µg/l (Scoullos and Hatzianestis, 1989), but may range upto 20 µg/l in areas where nickel-bearing ores reach the surface. The input of anthropogenic material may increase surface concentrations by 10-50 µg/l. Although dissolved nickel residues in uncontaminated coastal waters generally range from 1 to 5 µg/l (Seng et al., 1987), residues of about 15 µg/l can be found in contaminated areas (Moore, 1991). Nolting (1986) noted that dissolved nickel in the Ditch Wadden Sea averaged approximately 3 µg/l, decreasing to <1 µg/l in the open waters of the North Sea.

Nickel occurs principally as Ni^{2+} in surface waters, but oxidation states ranging from Ni^{1-} to Ni^{4+} have been reported from time to time (Moore, 1991). 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 estuaries (Luther et al., 1986). Above pH 9 (rarely found in surface waters), the hydroxide and carbonate complexes precipitate.

Dissolved nickel concentrations in the surveyed area varied from 0.29 µg/l (at station 9) to 17 15 µg/l (at station 6) in surface waters. The range of values in bottom waters was 0.47 µg/l (at stations 1 and 2) to 18.15 µg/l (at station 6) (Table 4.6). The overall mean values in surface and bottom waters were 3.93 µg/l and 4.33 µg/l (Table 4.1) respectively. Station wise, the annual mean concentrations of dissolved nickel varied from 2.08 to 5.23 µg/l in surface waters and in bottom waters, the range was 3.62 to 5.40 µg/l (Table 4.6). The lowest and the highest annual mean concentrations were observed at station 1 and station 9 respectively for surface and bottom waters. The spatial distribution pattern of dissolved nickel was such that stations at zone 1 recorded lowest annual mean concentrations and stations at zone 3 recorded the highest annual mean concentrations in surface and bottom waters (Figure 4.8). Generally, bottom water recorded higher annual mean values.

Seasonal variations in dissolved nickel concentrations were clearly distinguishable (Figure 4.8). In the entire stations, monsoon season recorded

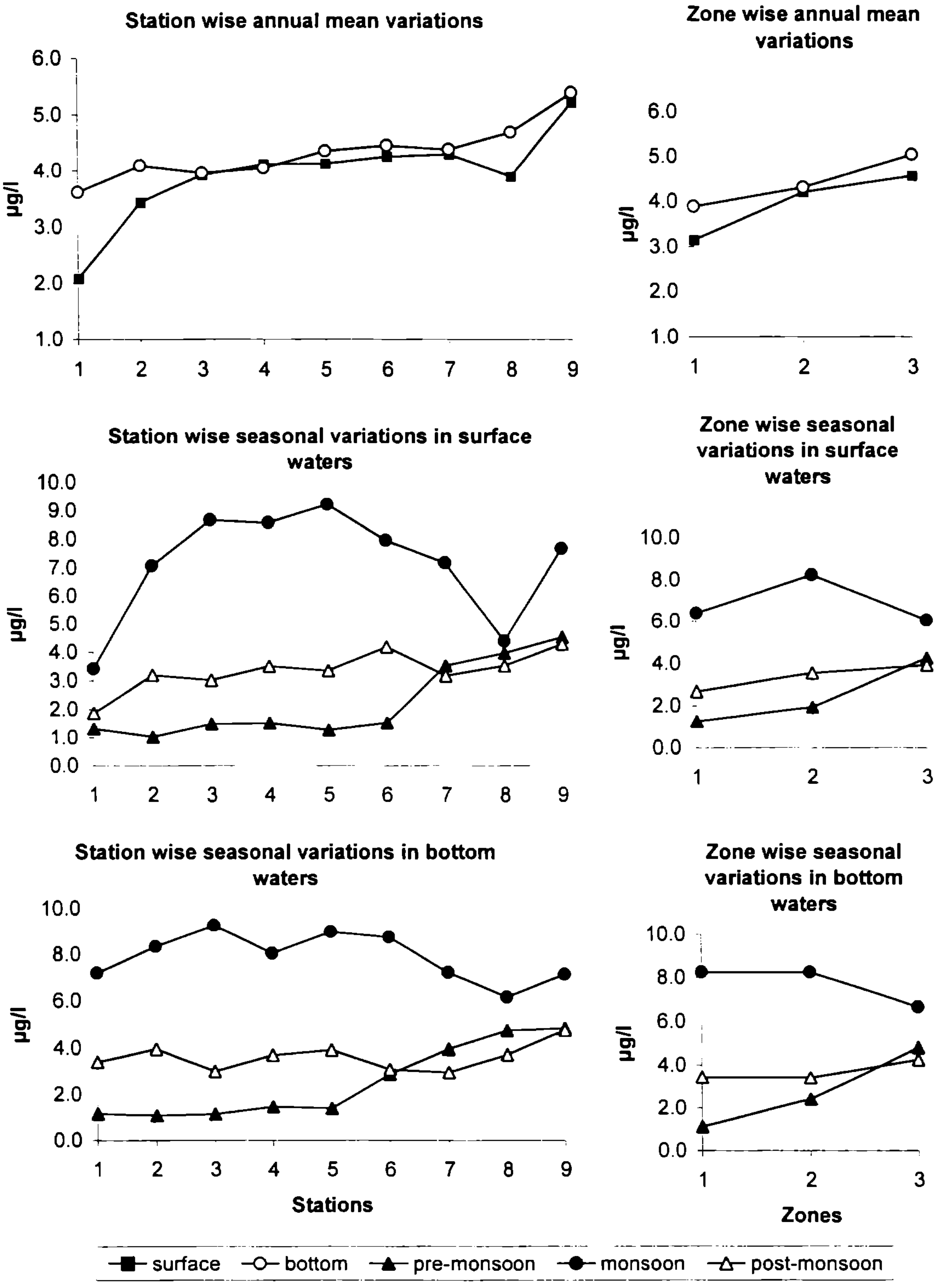


Figure 4.8 Seasonal and spatial variations of dissolved nickel.

the highest values in surface and bottom waters, as observed for cobalt, copper and molybdenum. The lowest values were recorded in pre-monsoon but only from stations 1 to 6. From stations 7 to 9, the lowest values were recorded in post-monsoon season. As in the case of chromium, the variation of nickel in the monsoon period showed an increase from station 1 to station 5, and then decreased to station 8 and slightly increased to station 9. This trend can be seen both in surface and bottom waters. These types of variations were not visible in pre-monsoon and post-monsoon seasons. During the pre-monsoon season, there was a study increase in the zonal average concentration from zone 1 to zone 3. A similar trend was observed in the post – monsoon seaon, but only in surface waters.

The average concentrations of dissolved nickel in river and sea waters are 0.5 and 0.2 µg/l respectively (Martin and Whitfield, 1983). Babukutty (1991) had reported dissolved nickel concentrations in the northern part of the Cochin estuarine system in the range 1.08 to 5.27 µg/l and a station wise annual mean concentration in the range 1.66 to 2.67 µg/l. Compared to this, the present study observed a wider range of values, 0.29 to 18.15 µg/l, but the range of station wise annual mean concentrations (2.08 to 5.40 µg/l) was comparable. As observed in the case of iron and manganese, higher concentrations of dissolved nickel were observed at zones 2 and 3. Similarities in the distribution of nickel with those of iron and manganese can be attributed to Ni being released upon the dissolution of iron-manganese oxyhydroxide phases in sub-oxic sediments from zones 2 and 3 especially, in pre-monsoon season and to a certain extent in post-monsoon season. Laslett (1995) also observed such an association of Ni with Mn from the Tweed Estuary. But the increasing trend of dissolved nickel from zone 1 to zone 3 in the pre-monsoon and post-monsoon seasons shows that salinity also plays an important role in the distribution of dissolved nickel in the pre-monsoon and post-monsoon periods in addition to the reductive solubilization of iron-manganese hydroxides as these seasons are characterised by high salinities in zone 3 and to a certain extent in zone 2. The higher nickel concentrations in the monsoon period can be attributed to the large amount of land and river drainage contaminated with nickel during this period. Thus, land and river runoff during the monsoon season acts as a major source of dissolved Ni into the estuary. During the pre-monsoon season, fresh water flow from the rivers becomes considerably reduced. The low flow condition together with the closing of shutters at the Thanneermukkom salinity barrier makes the water body to a stagnant condition in the pre-monsoon season. This stagnant condition is in favour of the adsorption of dissolved nickel onto particulate phases, eventually reducing the dissolved Ni concentrations especially from stations 1 to 6 in the pre-monsoon period.

4.3.9. Dissolved lead

In the earth's crust, lead mainly exists in the carbonate, sulphide and oxide forms, and the average concentration is approximately 13 µg/g. The average concentrations of lead in river and ocean waters are 0.1 and 0.003 µg/l respectively (Martin and Whitfield, 1983). Polluted rivers and estuaries may contain levels upto approximately 100 µg/l.

Sources of lead contamination to the environment include fairly localised impacts such as disposal of lead-acid batteries, lead-based paint wastes in landfills, fillings from the processing of Pb 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. The soil environment has been able to immobilise the lead in most cases. However, the immobility of lead has resulted in its accumulation in the soil. Because of the toxicity of lead, shallow contaminated soil can pose an ingestion risk.

The total amount of lead discharged to fresh waters from anthropogenic sources amounts to 97 180 x 10^3 M.T./year (Nriagu and Pacyna, 1988). Primary sources include manufacturing processes (particularly metals), atmospheric deposition, and domestic waste water. Approximately 96 % of the total lead emissions originate from anthropogenic sources (Nriagu, 1989), particularly combustion of leaded fuels, pyrometallurgical non-ferrous metal production, and coal combustion. Lead is emitted in large amounts from municipalities, both from the incineration of waste products and the discharge of waste water.

Since lead continues to be used as an antiknocking agent in gasoline in many nations, residues are correspondingly elevated in urban air. Lead generally occurs in high concentrations in urban snow, a reflection of the combustion of leaded gasoline. 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 (Urban et al., 1987). A major pathway of lead is the organo-metallic form, whereas many other metals are released in the inorganic form (e.g., Zn, Cd etc).

Lead is a non-essential and potentially toxic element. So an accurate assessment of the lead concentration and its physico-chemical partitioning in the aquatic environment would be of great concern. Lead resembles the divalent alkaline earth group metals in chemical behaviour more than its own Group IV metals. It differs from the Group IIA metals in the poor solubility of lead salts such as hydroxides, sulphates, halides, 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, and (less commonly) sulphates. Lead also partitions favourably with humic and fulvic acids, forming moderately strong chelates (Moore, 1991). At pH 10, $Pb(OH)^+$ dominates all other species (Moore, 1991). Speciation shifts to favour chloride and hydroxide complexes in salt water. Approximately 75% of lead in rivers is in suspension and 25% in solution, but in salt water, the corresponding ratio is approximately 50:50 (Moore, 1991).

Dissolved concentrations of lead in the backwaters of Kuttanad were found in the range 0.59 to 39.15 µg/l and 1.49 to 40.95 µg/l in surface and bottom waters respectively, with a mean value of 10.40 µg/l in surface water and 10.86 µg/l in bottom water (Table 4.1). Both surface and bottom waters recorded highest values at station 9, whereas the lowest value in surface water was at station 9, while in bottom water it was observed at station 5 (Table 4.7). Station wise, the annual mean concentrations were minimum at station 1 and maximum at station 4 for surface water, whereas for bottom water, lowest and highest annual mean values were observed at stations 1 and 9 respectively. The annual mean concentrations of dissolved lead showed spatial variations in such a way that there was a regular increase from stations 1 to 4 (Figure 4.9) followed by a slight decrease towards station 7 and a further increase towards station 9. This trend was common for both surface and bottom waters. Thus, the general distribution trends pointed out to an increase of this dissolved metal longitudinally from upper fresh water reaches to the estuarine region. A similar trend in the variation of station wise annual mean concentrations was also observed in

Table 4.7 Station wise summary statistics on dissolved lead and zinc (µg/l)

Parameter	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Lead	1	2.48	2.27	13.00	12.75	5.71	6.41	3.08	3.40	53.92	53.14
	2	2.82	2.15	25.95	26.55	8.37	8.66	7.58	8.15	90.55	94.08
	3	0.65	1.94	30.70	26.50	10.98	10.54	8.76	8.52	79.76	80.78
	4	4.66	4.26	29.70	29.35	12.75	12.54	7.32	7.80	57.44	62.17
	5	3.54	1.49	31.20	34.50	11.35	11.79	7.90	10.99	69.54	93.18
	6	2.90	3.31	32.60	37.55	10.81	11.85	10.36	9.92	95.89	83.68
	7	1.68	2.58	23.30	28.55	9.59	10.61	6.91	7.48	72.07	70.50
	8	2.31	2.68	27.30	30.15	11.49	11.93	7.23	8.11	62.88	67.98
	9	0.59	1.94	39.15	40.95	12.55	13.38	10.79	10.39	86.02	77.69
Zinc	1	2.94	3.70	75.00	13.85	13.93	6.66	19.69	3.37	141.31	50.56
	2	1.93	2.81	387.50	15.70	37.44	6.14	110.26	3.73	294.53	60.68
	3	2.82	2.26	36.20	11.65	10.00	6.20	8.92	3.28	89.17	52.82
	4	4.76	4.55	17.97	97.00	9.60	22.44	4.59	30.60	47.81	136.37
	5	1.73	2.53	24.40	14.75	7.92	6.80	6.39	3.17	80.64	46.70
	6	2.36	2.54	11.65	19.10	6.17	8.61	3.04	5.76	49.28	66.87
	7	3.92	4.44	17.00	13.00	8.69	8.68	3.91	3.12	45.02	35.93
	8	3.14	4.83	25.45	23.05	7.37	10.00	5.95	6.34	80.79	63.38
	9	3.92	4.62	17.05	35.55	7.77	11.29	3.86	8.78	49.67	77.76

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

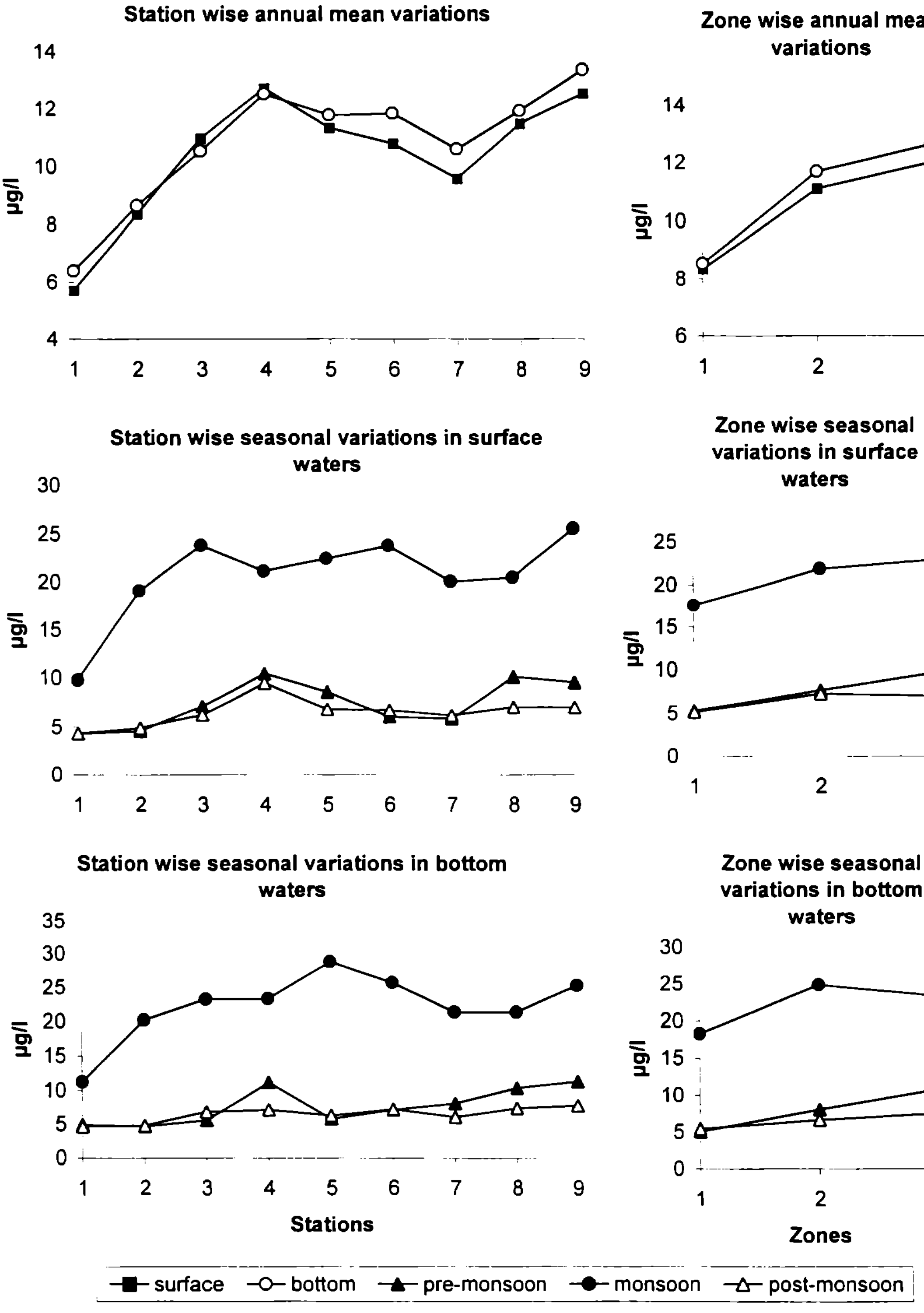


Figure 4.9 Seasonal and spatial variations of dissolved lead.

the case of cobalt and to a certain extent in chromium. The similarity with cobalt was also observed in the zone wise variation of annual mean concentrations (Figure 4.9). Except at stations 3 and 4, the annual mean values showed slightly higher values in bottom waters, and this difference was more pronounced in the estuarine region.

The seasonal variations observed in the case of dissolved lead concentrations were characterised by a predominant hike during monsoon season (Figure 4.9). Such a pronounced increase in dissolved concentration was also observed in the case of cobalt, copper, molybdenum and nickel. During the pre-monsoon and post-monsoon seasons, stations at zone 1 and zone 2 recorded almost equitable concentrations but at zone 3, pre-monsoon values were found slightly higher than the post-monsoon values (Figure 4.9). More or less similar distribution patterns were observed in the case of cobalt and molybdenum. During the entire seasons, the seasonal average values were found in the increasing order from zone 1 to zone 3 except a small decrease observed at zone 3 than that of zone 2 during the monsoon season in bottom waters.

Some of the available data on dissolved lead concentrations in estuarine waters include those of Danielsson et al. (1983), Elbaz-Poulichet et al. (1984 & 1991), Windom et al. (1985 & 1988), George (1989) and Harper (1991). The data available for Cochin Estuary are those of Ouseph (1987) and Nair et al. (1990). In a study of the northern part of the Cochin estuarine system, Babukutty (1991) had reported the dissolved concentrations of lead in the range 1.2 to 16.8 µg/l and station wise annual mean concentrations in the range 2.10 to 11.23 µg/l. In the present study, the values were found to vary in a wider range (0.59 to 40.95 µg/l) but the range of station wise annual mean concentrations were comparable (5.71 to 13.38 µg/l). The generally observed increasing trend from the upper fresh water region to the lower estuarine zone may be attributed to factors like desorption from particulate phase, remobilisation from sediments, dredging activities in the lake and runoff from the agricultural lands. Remobilization is the (diffusive) flux of a dissolved substance from the sediment pore water into the water column. It has been observed that increase in the dissolved phase has been accounted more by the remobilisation from the sedimentary phase, than the dissolution of the metal from the particulate phase. The benthic lead fluxes have been established in the field studies (Duarte and Flegal, 1994; Puls et al., 1997). This together with the dredging activities in the lagoon gives rise to a situation of lower dissolved concentration in the upper fresh water regime than in the lower estuarine region. de Groot et al. (1976) and Luther et al. (1986) had observed the release of lead from the sediments during dredging activities. The higher concentration of dissolved lead in the monsoon season, as observed in the case of copper and nickel indicates that the river and land runoff in the monsoon season is a major source of lead input into the estuary. The slight increase in dissolved fraction at zones 2 and 3 during the pre-monsoon season may be attributed to the salinity induced desorption from particulates and sediments (Elbaz-Poulichet et al., 1984 & 1986; Shibu, 1992). Lead initially adsorbed onto particles in the upper estuary can subsequently be released back to the dissolved phase at higher salinities (Elbaz-Poulichet et al., 1984 & 1986). The above two observations were also noticed from the northern part of Cochin Estuary by Shibu (1992).

4.3.10 Dissolved zinc

Zinc is one of the most abundant of the essential elements required by the human body and approximately 100 times as abundant as copper (Vahrenkamp, 1973). As with cobalt (II), zinc (II) has the ability to occupy low symmetry sites in enzymes, and can therefore, function as an essential constituent of several of them. The total amount of zinc discharged to fresh waters from anthropogenic sources comes to 77 373 x 10^3 M.T./year (Nriagu and Pacyna, 1988). There are several major sources including the discharge of domestic waste water, coal-burning power plants, manufacturing processes involving metals, and atmospheric fallout. Approximately 34 % of the total emissions of zinc to the atmosphere come from natural sources, the remainder originating from metal production, burning of coal and oil, and fertiliser and cement production (Nriagu and Pacyna, 1988; Nriagu, 1989).

Under aerobic conditions, Zn^{2+} is the predominant species at acidic pH, but is replaced by $Zn(OH)_2$ at pH 8-11, and $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ at pH >11 (Vymazal, 1985). Anaerobic conditions lead to the formation of ZnS, regardless of pH. Zinc binds readily with many organic ligands, particularly in the presence of nitrogen or sulphur donor atoms (Moore, 1991). Stability constants for zinc-humic acid complexes are variable, typically ranging from 2.3 to 5.9 (Moore, 1991). This means that the fate of zinc will vary among water ways, depending on the fate of humic material present in the system. Zinc also shows variable behaviour in binding to suspended particulates, depending on pH and Eh conditions, and the input of anthropogenically derived zinc.

Dissolved Zn concentrations varied from 1.73 to 387.50 µg/l in surface waters and from 2.26 to 97 µg/l in bottom waters (Table 4.1). Babukutty (1991) had reported values similar to this range (7.89 to 214 µg/l) from the northern part of the Cochin estuarine system. The lowest value was recorded at station 5 in the pre-monsoon period, and the highest concentration was recorded at station 2 in the monsoon period (Table 4.7). The overall mean values were 12.10 µg/l and 9.65 µg/l in surface and bottom waters respectively (Table 4.1). After Mn, maximum variability in the concentrations of dissolved trace metals was found in the case of Zn (Table 4.1). Station wise annual mean concentration varied from 6.17 to 37.44 µg/l in surface waters and 6.14 to 22.44 µg/l in bottom waters which, is comparatively lower than the range of station wise annual mean concentrations (13.84 to 80.17 µg/l) observed by Babukutty (1991) from the northern part of Cochin Estuary. The highest annual mean concentrations were recorded at stations 2 and 4 in surface and bottom waters respectively and the lowest at stations 6 and 2 respectively in surface and bottom waters. The difference between the annual mean concentrations of dissolved Zn in surface and bottom waters at zone 1 is higher than that observed at zones 2 and 3 (Figure 4.10). This may be due to the shallowness of the stations 4 to 9, compared to the stations 1 to 3, which were comparatively deeper.

Generally, dissolved concentrations of zinc were found to be lower in surface and bottom waters during pre-monsoon season (Figure 4.10). The highest seasonal average value in surface waters was observed at zone 1 during the monsoon season but zones 2 and 3 recorded highest concentrations during post monsoon season (Figure 4.10). In bottom waters, post-monsoon season recorded highest value at zones 1, whereas at zone 2 there was not much seasonal difference in dissolved Zn concentrations during monsoon and post-monsoon seasons but, they were higher than pre-monsoon values. At zone 3 pre-monsoon and post–monsoon seasons recorded almost equal values.

The concentration of dissolved zinc in fresh waters usually ranges from < 1 µg/l to approximately 50 µg/l with an average concentration of approximately 10 µg/l (Moore, 1991). The average Zn level in sea water varies between 0.1 µg/l in the surface and 0.62 µg/l in the deep waters (Bruland et al., 1978). Martin and Whitfield (1983) reported the average zinc concentration in river water and in sea water to be 30 and 0.1 µg/l

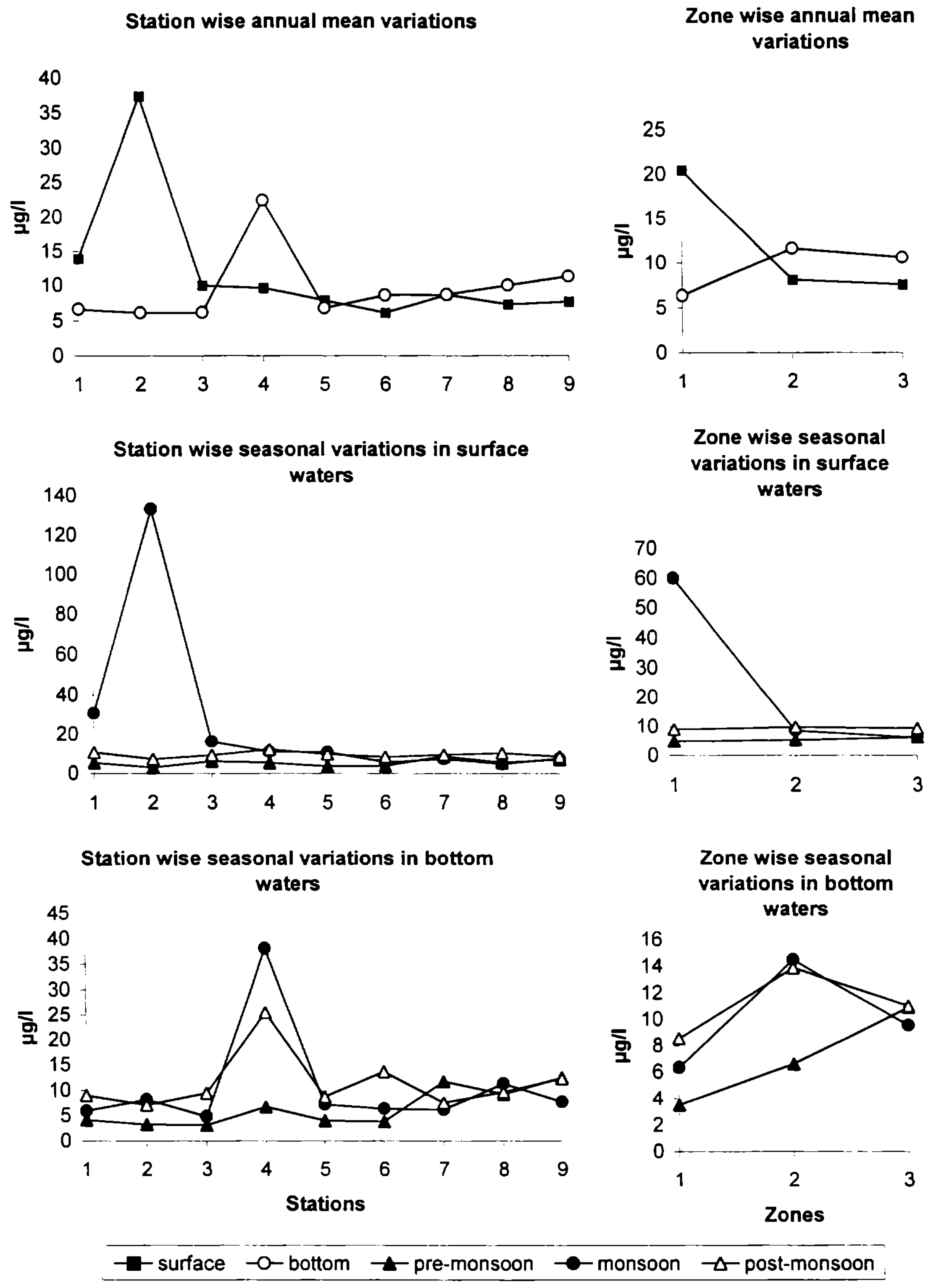


Figure 4.10 Seasonal and spatial variations of dissolved zinc.

respectively. Higher concentrations of dissolved Zn during monsoon and post-monsoon seasons at zone 1 and zone 2 can be attributed to Zn carried into the backwater system along with land runoff. The higher concentration of dissolved Zn at zone 2 than that of the riverine zone (zone 1) during monsoon and post-monsoon seasons indicate that the major source of dissolved zinc in this zone is not river water, but the runoff from the nearby paddy fields where fertilizers and pesticides (Mancozeb) containing zinc are extensively used during these seasons. Slightly higher concentrations of dissolved Zn in the surface water at zone 3 during the post-monsoon season and in bottom water during pre-monsoon and post-monsoon seasons show the dependence of salinity on the distribution of dissolved Zn at this zone. The desorption of Zn from sediment particles at higher salinity (Ackroyd et al., 1986) during pre-monsoon and post-monsoon seasons may be one of the reasons for the increased concentration of dissolved Zn at this zone during the above seasons. The pre-monsoonal increase in dissolved zinc concentrations can also be due to remobilisation processes of recently sedimented biogenic particulates (Kremling et al. 1997). The values of dissolved zinc observed in the present study revealed the anthropogenic input of zinc into the backwater system. In general, on comparing the dissolved trace metal concentrations measured in this study with world's other estuaries, it could be seen that the Kuttanad backwaters of the Cochin estuarine system is contaminated with respect to non-industrialized estuaries like the Amazon (Boyle et al., 1982), the Krka (Elbaz-Poulichet et al., 1991) or the Bang-Pokong (Windom et al., 1988). In addition to anthropogenic inputs, association of zinc with organic matter (Paul and Pillai, 1983b) and dissolution of zinc from the sedimentary to the dissolved phases with increasing salinity may also be responsible for the generally higher concentration of dissolved zinc in the waterway (Ackroyd et al., 1986). The tendency for dissolved zinc to resist removal during estuarine mixing has also been observed by Nair et al. (1990) and Shibu et al. (1990) from the northern part of Cochin estuarine system and has also been observed in other estuaries (Duinker, 1980). In a study of Vellar Estuary, Senthilnathan and Balasubramanian (1997) found high concentration of dissolved zinc (mean 25.51) in the estuarine waters and the same was attributed to zinc containing fertilizers, pesticides and rodenticide residues from the nearby agricultural fields. Many workers have investigated the behaviour of zinc during estuarine mixing in the past. Conservative behaviour was observed in the San Fransisco Bay (Eaton, 1979), the Gota River (Danielsson et al., 1983), the Bang Pakong Estuary (Windom et al., 1988) and a non-conservative behaviour was observed in the Fraser River Estuary (Grieve and Fletcher, 1977), the Tamar Estuary (Morris et al., 1978; Ackroyd et al., 1986), the Elbe Estuary (Duinker et al., 1982a) and for the Cochin Estuary (Shibu et al., 1990).

Correlation among variables

In order to find out the interrelationship between various dissolved trace metals and other environmental parameters like pH, dissolved oxygen, salinity, and dissolved major elements, the Pearson correlation coefficients among these parameters were determined and is given in Table 4.8. Except iron and manganese, no other dissolved trace metal showed any significant correlation with pH. High degree of negative correlation ($p < 0.001$) was observed between dissolved iron and dissolved manganese with pH. This inverse relationship of pH with dissolved iron and manganese is not unexpected, as decrease in the pH will cause dissolution of iron and manganese hydroxides from sediment and suspended particles. No significant correlation was observed between any of the dissolved trace metals and dissolved oxygen. No dissolved trace metal showed any significant correlation with suspended particulate matter. Excellent positive correlation was observed between Pb/Co, Pb/Cu, Pb/Mo, Pb/Ni, Ni/Co, Ni/Cu, Ni/Mo, Mo/Co, Mo/Cu, Mn/Fe and Cu/Co, indicating common source and

Table 4.8 Correlation values (r) between dissolved trace metals and other environmental parameters (n = 108)

Metal		pH	DO	Salinity	SPM	Zn	Pb	Ni	Mo	Mn	Fe	Cu	Cr	Co
Cd	S	-0.060	0.129	0.312	0.182	-0.130	-0.219	-0.379	-0.368	0.149	0.080	-0.373	-0.107	-0.367
	B	-0.119	0.051	0.521	-0.022	0.108	-0.200	-0.361	-0.285	0.146	0.390	-0.439	0.200	-0.300
Co	S	-0.106	-0.018	-0.209	-0.123	0.223	0.889	0.764	0.855	-0.068	-0.156	0.440	0.202	
	B	0.004	0.140	-0.209	-0.014	0.170	0.879	0.685	0.848	-0.034	-0.054	0.394	0.099	
Cr	S	-0.076	0.045	-0.019	-0.204	0.026	0.209	0.168	0.178	0.150	0.144	0.061		
	B	-0.225	-0.064	0.356	-0.072	0.009	0.193	0.112	0.168	0.210	0.235	-0.096		
Cu	S	-0.023	-0.171	-0.199	-0.071	-0.003	0.418	0.384	0.344	-0.104	-0.103			
	B	0.113	0.169	-0.275	0.030	0.076	0.423	0.541	0.380	-0.038	-0.099			
Fe	S	-0.358	-0.005	0.462	0.022	-0.067	-0.028	-0.184	-0.099	0.547				
	B	-0.335	0.040	0.470	-0.045	-0.008	0.019	-0.112	-0.050	0.498				
Mn	S	-0.565	-0.037	0.206	-0.024	-0.002	-0.059	0.037	-0.041					
	B	-0.361	0.131	0.235	0.067	0.031	0.023	0.049	-0.008					
Mo	S	-0.141	-0.030	-0.092	-0.021	0.213	0.818	0.784						
	B	-0.015	0.137	-0.114	-0.066	0.122	0.838	0.725						
Ni	S	-0.230	-0.079	-0.044	0.075	0.142	0.708							
	B	-0.146	0.155	-0.052	0.057	0.151	0.676							
Pb	S	-0.110	-0.032	-0.110	-0.025	0.208								
	B	-0.052	0.137	-0.091	-0.043	0.152								
Zn	S	-0.039	-0.079	-0.073	-0.052									
	B	0.003	0.157	0.019	-0.028									

(S = surface, B = bottom, SPM = suspended particulate matter) similar cycling for the pairs of metals considered in the Kuttanad backwaters. The high degree of correlation between metals indicates that they are coming from similar sources and behave similarly. Significant negative correlation was found between Ni/Cd, Mo/Cd, Cu/Cd and Co/Cd. The significant positive correlation of iron, and to a certain extent Mn, with salinity requires special attention. It is well established that dissolved iron in river water gets precipitated when fresh water comes into contact with saline water. A behaviour contrary to this means that factors other than salinity play an important role in the behaviour of iron in the Kuttanad backwaters. One possible reason for the contradictory behaviour of iron and the observed behaviour of Mn is the increased soil acidity and the corresponding decrease in the pH of water during the pre-monsoon season, which is also characterised by increase in salinity. Highly significant negative correlation of dissolved iron and manganese with pH supports this view. Another possible reason for this behaviour is, as explained before, the reductive solubilization of iron and manganese from the sediment and subsequent diffusion into the water column during the pre-monsoon season of increasing salinity during which a partial reducing atmosphere prevails in the sedimentary atmosphere. A similar increase in dissolved chromium with salinity was observed in the bottom water. This again may be due to the increased soil acidity in the pre-monsoon season of increasing salinity. This is further established by the good negative correlation of dissolved chromium with pH in the bottom water. Runnels et al. (1977) observed that elevated pH increases solubility and leachability of molybdenum in water. Acidic conditions decrease the transfer of molybdenum from soil to water. But the correlation values of molybdenum with pH observed in the present study do not allow making any such generalisation.

Studies in six relatively unpolluted Texas estuaries using clean room techniques (Benoit et al., 1994) found that the behaviour of copper varied widely in each estuary and that no simple variation of copper with salinity could be established. In the present study, the correlation graphs (Figures 4.11 & 4.12) shows that in the Kuttanad backwaters removal of copper takes place as river water mix with saline water.

From laboratory experiments using ^{59}Fe, Aston and Chester (1973) showed that both increase in salinity and presence of pre-existing particles increased the rate and magnitude of the removal of iron from sea water. They found that in the absence of sediment particles, the rate of removal was dramatically decreased. The implication of this laboratory result for processes in the field is that iron removal is more likely to be by heterogeneous nucleation on natural suspended sediment particles than by formation of a homogeneous floc of iron hydroxide. The field results of Holliday and Liss (1976) for the Beaulieu Estuary indicate that removal of iron from solution can occur even in the absence of sea salt. In the present study, such an observation could be made for neither iron nor any of the dissolved trace metals. One of the reasons may be the comparatively higher background dissolved trace metals found in the study area which makes it impossible for differentiating any slight variations in dissolved trace metals associated with the slight variations in comparatively lower suspended load.

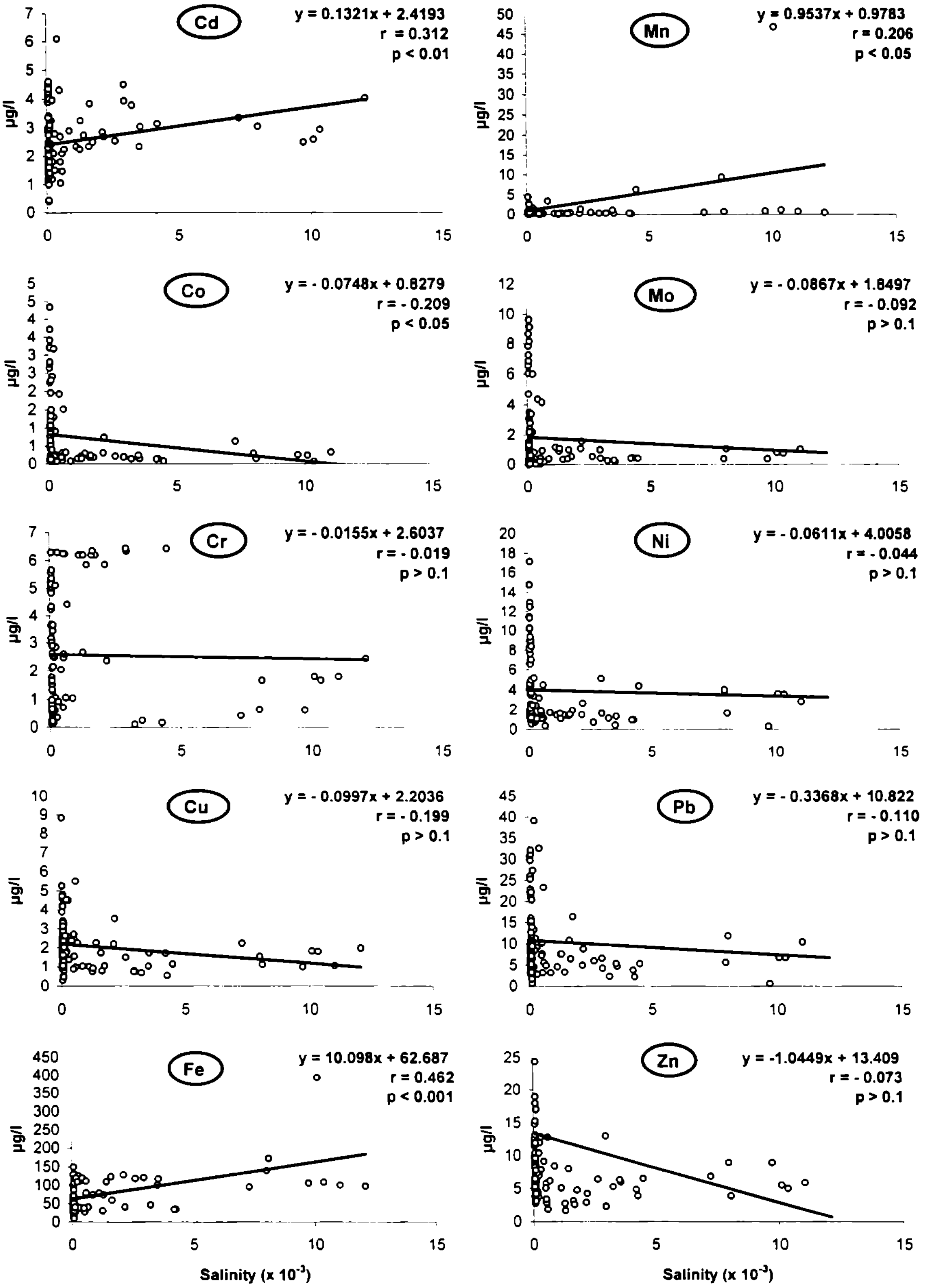


Figure 4.11 Variation of dissolved trace metal concentration with salinity (surface water, n = 108)

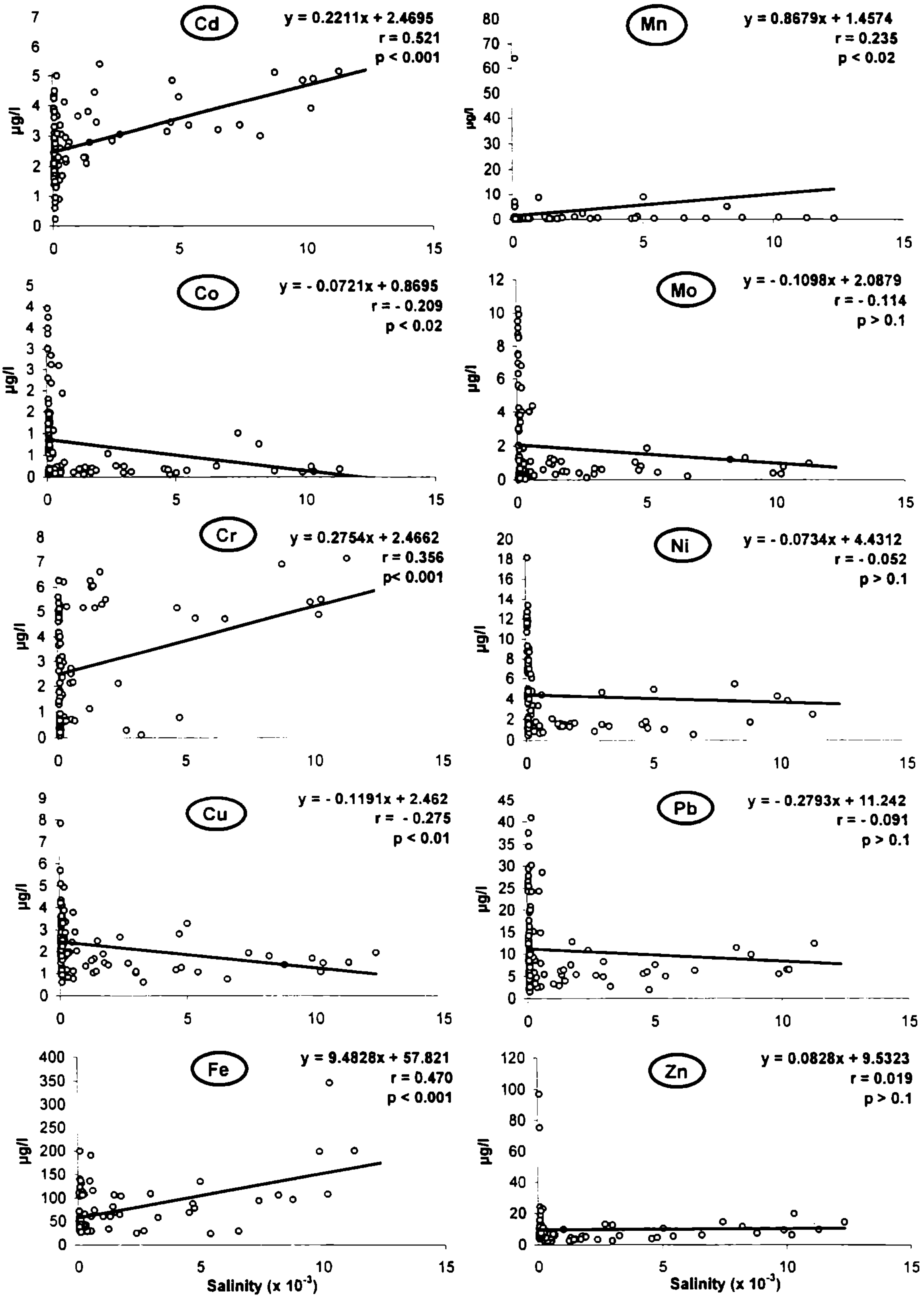


Figure 4.12 Variation of dissolved trace metal concentration with salinity (bottom water, n = 108)

CHAPTER 5

PARTICULATE TRACE METALS

5.1 INTRODUCTION

In aquatic systems, most contaminants, especially trace metals show a high affinity for particulate matter. Thus, for a realistic and complete assessment of river fluxes and potential pollution, the composition of suspended matter is an obligatory parameter in addition to the concentration of dissolved elements (Wollast, 1982; Church, 1986). Particulate trace metal distributions can also be used to examine and quantify chemical reactivity and pollution sources in less dynamic estuaries, specifically, where suspended particle concentrations are sufficiently low (approx. 10 mg/l), and there is little interaction of suspended particles with the bed sediment (Turner, 1999). 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.

Estuaries act as a transition zone in which continental weathering material is trapped and through which some of the material is transported to the open sea. The composition and variability of suspended particulate matter (SPM) in this river-ocean boundary are affected by many complex geochemical processes (precipitation and flocculation, desorption-adsorption, etc) and by physical processes (river flow, tidal energy, currents) and are, therefore, often difficult to interpret (Morris et al., 1978; Turner et al., 1991 & 1994).

Some important prerequisites for developing an understanding of the physical, chemical, and biological processes that control the distribution of major and trace elements in particulate matter of coastal waters include:

- determination of the spatial and temporal variations of particulate matter and associated elements.
- identification of the most abundant solid phases within the particulate matter and their sources.
- determination of the chemical forms and concentrations of trace elements within the major solid phases.
- determination of the physico-chemical processes affecting the distribution and composition of the solid phases.

Heavy metals are generally particle-reactive so that as they enter riverine or estuarine waters, many are quickly adsorbed onto suspended matter and will be ultimately removed to coastal bottom sediments (de Groot et al., 1976; Santschi et al., 1984). Studies of water column concentrations of heavy metals for the purpose of environmental quality assessments are difficult because of the possibility of sample contamination during collection and handling, and requirements for ultra-trace analyses. Water column assessments provide only brief glimpses of metal contamination conditions. Measurements of suspended particulate material, on the other hand, do not usually involve such difficult ultra trace analysis and sample contamination can be less pronounced. Also, metals on suspended sediments represent temporally and spatially a more integrated picture of metal contamination (Niencheski et al., 1994). From the above, it is evident that dissolved trace metal concentrations in rivers and estuaries provide inadequate bases for the evaluation of anthropogenic inputs. Variability in concentrations may be due as much to river and estuarine chemistry as to anthropogenic input. Analysis of suspended sediments may provide a better basis for estimating anthropogenic contributions to rivers and estuaries (Windom and Smith, 1991; Niencheski et al., 1994). The mechanisms involved in trace metal transport in rivers vary widely but there appears to be a significant trend for many metals to be found in the particulate phase (Delfino and Otto, 1986). Hydrologic conditions can contribute to this trend since periods of high discharge maintain high total suspended matter levels in the rivers (Delfino and Byrnes, 1975; Delfino, 1977). Jenne (1968 & 1977) suggested that hydrous oxides of Fe and Mn might exert a controlling influence on the distribution of other trace metals in aquatic systems through processes such as adsorption, since metal oxide surfaces provide attractive sites for metal ion binding.

Metals associated with suspended particles are unavailable for uptake by bacteria and phytoplankton and are transported with suspension to deposition areas (eg. estuaries). However, the majority of these metals are mobilized in the interstitial water of the sediments under reducing conditions caused by decomposition of organic material, forming free metal ions which are known to be extremely toxic to marine organisms (Muller, 1996).

The concentrations of suspended material in rivers are in contrast with the average value of about 100 µg/l (Chester and Stoner, 1972) for the open surface ocean. In a study of Atlantic Ocean surface waters, Eckard Helmers (1996) recorded an overall average of 27 µg/l of suspended particulate matter, within the range 1 µg/l to 115 µg/l. In estuaries, variable amounts of the suspended material can enter with the inshore sea water and resuspension of settled sediments within the estuary may occur.

Some of the recent works on particulate trace metals are reported by Sfriso et al. (1995) from the Lagoon of Venice, El-Nady (1996) from Mediterranean coast of Egypt, Moran and Woods (1997) from Ob-Irtysh Rivers (Russia), Zhulidov et al. (1997) from the wetlands of the Russian Arctic, Pohl et al. (1998) from Oder and Peene Rivers and the southern Pomeranian Bight and Turner and Millward (2000) from the estuarine plume regions of the Humber.

Particulate trace metal data from Indian waters are relatively scarce. The available literature include data on particulate Cd, Cu, Fe, Mn, Zn, Pb, Co and Ni by Sanzgiry and Braganca (1981) from Andaman Sea, particulate Mn, Fe, Co, Ni Cu, Zn, Cd and Pb from harbour and coastal environment of Visakhapatnam (Bay of Bengal) by Satyanarayana et al. (1985a) and particulate Cu, Mn, Fe, Zn, Co, Ni and Pb from the Western Bay of Bengal by Rajendran et al. (1982). Ouseph (1992) have reported particulate Cu, Zn, Cd, Pb, Ni and Fe from the northern part of Cochin estuarine system. Sankaranarayanan and Rosamma Stephen (1978) also reported particulate Fe, Mn, Cu and Zn in the waters of the northern part of Cochin estuarine system.

This Chapter focuses on the spatial and temporal variations of trace elements (Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn) associated with suspended matter and the seasonal variability in the transport modes of the above trace metals from the southern upstream part of Cochin estuarine system over an annual cycle with a view to understand their relation to major sources as well as biogeochemical reactions affecting trace element distributions in suspended matter.

5.2 MATERIALS AND METHODS

Details are given in Chapter 2.

5.3 RESULTS AND DISCUSSION

Trace metal concentrations in suspended particulate matter are expressed in two units; (1) for comparison with dissolved metal concentrations, they are expressed as volumetric concentrations in µg/l and (2) for comparison with the metal contents of the sediment, they are expressed in gravimetric form with µg/g. Table 5.1 gives the overall summary statistics of particulate trace

Table 5.1 Overall summary statistics on the distribution of particulate trace metals (µg/g)

Trace Metal	Min.		Max.		Mean		Mean of	SD		CV	
	S	B	S	B	S	B	S & B	S	B	S	B
Cd	0.56	0.53	191.51	165.91	33.84	16.50	25.17	36.26	21.61	107.15	131.02
Co	5.84	7.39	1051.05	768.11	184.95	127.99	156.47	263.84	95.49	131.51	74.61
Cr	6.59	9.98	925.00	728.51	264.04	191.49	227.77	177.16	124.06	67.09	64.79
Cu	7.62	7.90	1559.88	1138.87	244.16	188.81	216.49	242.28	224.68	99.23	119.00
***Fe**	2.50	4.15	432.79	408.49	126.26	106.28	116.27	85.31	54.01	67.57	50.82
***Mn**	0.21	0.55	272.64	152.23	32.41	17.04	24.73	51.05	23.78	157.50	139.55
Mo	3.02	2.43	830.77	674.52	173.91	135.52	154.72	145.39	106.19	83.60	78.36
Ni	8.96	1.54	860.38	847.11	284.08	147.30	215.69	205.07	141.02	72.19	95.74
Pb	8.82	16.61	2556.89	2130.79	561.76	320.14	440.95	548.91	348.47	97.71	108.85
Zn	54.00	75.25	4602.59	3840.09	1106.68	730.03	918.35	856.68	666.49	77.41	91.30

(*Fe and *Mn in mg/g, S = surface, B = bottom, SD = standard deviation, CV = coefficient of variation)

metals in µg/g and Table 5.2 gives the values in µg/l for comparison with some values found in literature in the same units. The overall summary statistics on the percentages of the particulate fractions of trace metals in water are given in Table 5.3 and the values of trace metals in the particulate phase reported from different parts of the world are given in Table 5.4. In the present survey, the concentrations of metals in the particulate phase (µg/g) followed the trend: Fe > Mn > Zn > Pb > Cr > Cu > Ni > Co > Mo > Cd. The monthly data of particulate trace metals in surface and bottom waters are given as Annexure 3.

PARTICULATE CADMIUM (Cd_p)

Particulate cadmium is often highly variable, largely reflecting the mobilization of contaminated bottom sediments under high flow conditions. In the present study, Cd was found to be the least abundant metal in the particulate phase. For the area surveyed, the concentration of particulate cadmium was found in the range 0.56 to 191.51 µg/g (0.01 to 0.40 µg/l) in surface waters and 0.53 to 165.91 µg/g (0.03 to 0.39 µg/l) in bottom waters (Tables 5.2 and 5.5). The mean surface concentration (33.84 µg/g) was almost double that of bottom concentration (16.50 µg/g). The values were found to be highly variable both in surface as well as in bottom waters, which are evident from the comparatively high coefficient of variation (Table 5.1). Figure 5.1 gives the trend in the variation of station wise annual mean concentrations of Cd in surface and bottom waters. The surface water concentrations clearly showed higher values than the bottom water concentrations. Stations 3 to 7 showed an increasing trend, whereas stations 7 to 9 showed a decreasing trend. For surface waters, the station wise annual mean concentrations were in the range 20.04 to 45.33 µg/g, with the lowest average at station 9 and the highest at station 2. For bottom waters, the same was in the range 8.58 to 24.19 µg/g, obviously wider range of values was observed in surface waters than in bottom waters. In general, zone 2 recorded the highest annual mean concentration, which was 1.7 times higher than that observed at zone 3 in

Table 5.2 Overall summary statistics on distribution of particulate trace metals (µg/l)

Trace Metal	Min.		Max.		Mean		Mean of	SD		CV	
	S	B	S	B	S	B	S & B	S	B	S	B
Cd	0.01	0.03	0.40	0.39	0.12	0.14	0.13	0.06	0.07	48.94	50.69
Co	0.08	0.02	4.62	8.13	0.93	1.87	1.40	0.74	1.50	79.84	80.20
Cr	0.01	0.29	50.69	16.66	2.04	2.72	2.38	6.63	2.65	325.28	97.27
Cu	0.31	0.42	5.88	9.74	1.11	1.89	1.50	0.81	1.46	73.21	77.10
***Fe**	0.02	0.02	2.42	7.96	0.65	1.64	1.15	0.43	1.41	65.89	85.78
***Mn**	0.00	0.00	1.15	1.22	0.15	0.22	0.19	0.19	0.26	121.45	116.81
Mo	0.01	0.01	3.04	9.74	0.90	2.01	1.45	0.63	1.97	70.48	98.29
Ni	0.46	0.03	4.13	5.87	1.23	1.52	1.38	0.50	0.89	40.28	58.54
Pb	0.33	0.26	9.92	15.01	2.37	3.31	2.84	1.73	2.39	73.02	72.13
Zn	1.95	2.00	19.39	28.10	5.48	7.94	6.71	3.61	4.56	65.77	57.43

(*Fe and *Mn in mg/l, S = surface, B = bottom, SD = standard deviation, CV = coefficient of variation)

Table 5.3 Overall summary statistics on percentage fractions of particulate trace metals in water

Trace Metal	Min.		Max.		Mean		Mean of S & B
	S	B	S	B	S	B	
Cd	0.2	0.8	33.5	45.9	5.9	6.3	6.1
Co	5.0	1.7	96.8	98.8	62.5	70.9	66.7
Cr	9.0	10.9	92.6	96.1	42.3	50.8	46.6
Cu	6.2	11.6	84.6	79.4	36.3	43.7	40.0
Fe	99.4	99.4	99.9	99.9	99.9	99.9	99.9
Mn	99.9	99.8	99.9	99.9	99.9	99.9	99.9
Mo	0.8	0.3	97.9	96.9	49.2	59.4	54.3
Ni	4.3	5.7	86.5	77.2	33.6	34.1	33.8
Pb	3.5	3.7	80.2	72.3	22.5	27.4	25.0
Zn	1.4	6.2	78.4	85.3	41.1	49.2	45.1

(S = surface, B = bottom)

Table 5.4 Values of some particulate trace metals reported from other parts of the world (µg/g)

Location	Cd		Co		Cr		Cu		Fe*		Reference
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Coastal Gulf of Mexico, U.S.A.	1.10 - 3.00						43.2 - 81 1				Trefrey and Presley (1976).
St. Lawrence Estuary	0.20 - 1.60										Cossa and Poulet (1978)
Hudson River Estuary, USA	ND - 0.04						0.60 - 1.30				Klinkhammer and Bender (1981)
Andaman Sea	ND - 95						ND - 521		0.247 - 44.182		Sanzgiry and Braganca (1981)
Periyar River and Cochin Estuary	4.00 - 95.0						39.00 - 107				Paul and Pillai (1983a)
Outer Harbour region of Visakhapatnam Bay		6.6		39.05				476		14.38	Satyanarayana et al. (1985a)
Inner Harbour region of Visakhapatnam Bay		12.3		135.8				666.5		11 136	Satyanarayana et al. (1985a)
Scheldt Estuary	0.01 - 60.0										Duinker (1986)
Wadge Bank region (Arabian Sea)	4.8 - 17.9						9.50 - 130				George (1986)
Western Scheldt	3.8 - 13.9						26 -137				Valenta et al. (1986).
Eastern Scheldt	0.4 - 2.2						14 - 56				Valenta et al. (1986).
Ganges Estuary				53		98		44		42.111	Subramanian et al. (1988)
Meuse River		33				398		292			Nolting et al. (1989)
Rhine River		56				1413		521			Nolting et al. (1989)
Rhine - Meuse Estuary		22.5				546.5		254.5			Nolting et al. (1989)
Periyar and Muvattupuzha River and Cochin estuary	8.00 - 60.0						20.0 - 300				Shibu et al. (1990)
U.S. East Coast Rivers	0.6 - 1.9						25 - 150				Windom (1990)
Rhine/Meuse Estuary	5.0 - 50										Nolting et al. (1990)
Changjiang (Yangtze River)		0.32						149.5			Zhang et al. 1990
Clyde Estuary	1.1 - 2.7						130 - 280				Balls (1990)
Dogger Bank, Central North Sea	0.13 - 1.4	0.38			38 - 67	46.4	1.3 - 5.3	3.2			Fileman et al. (1991)
world average		1.2		20				100		48	Martin and Windom (1991)
Rhine/Meuse Estuary	2.0 - 17.0						20 - 140				Paalman & Van Der Weijden (1992)
Huanghe (Yellow River)	0.05 - 0.39						14.4 - 41 1				Zhang et al. 1994
Central and Souther North Sea	0.16 - 8.89						1.56 - 143				Tappin et al. (1995)
Humber Estuary	0.11 - 0.40										Laslett (1995)
Tees Estuary	0.64 - 5.4						61 - 140				Laslett (1995)
Wear Estuary	0.15 - 1.3						23 - 82				Laslett (1995)
Tyne Estuary	0.27 - 6.1						27 - 200				Laslett (1995)
Tweed Estuary	0.49 - 0.78						37 - 110				Laslett (1995)
Mersey Estuary	0.49 - 1.2						24 - 56				Laslett (1995)
Morecambe Bay	0.32 - 0.53										Laslett (1995)
Ob - Irtysh Rivers, Russia.	0.17 - 1.26	0.58			9 54 - 89.2	49.8	3.7 - 50.5	25.8			Moran and Woods (1997)
Wetlands of Russian Arctic	1.2 - 5.4						80 - 116				Zhulidov et al. (1997a)
Wetlands of Russian Arctic	0.04 - 0.46						0.7 - 63				Zhulidov et al. (1997b)
Tay Estuary	0.02 - 3.99						12 -133				Owens et al. (1997)
Forth Estuary	0.02 - 7.67						9 - 267				Owens et al. (1997)
Danube River		1 14		25.6				115		36	Guieu et al. (1998)
Baltic Sea off Poland	0.89 - 8.91						20.2 - 214				Pempkowiak et al. (2000)

Table 5.4 (Contd.) Values of some particulate trace metals reported from other parts of the world (µg/g)

Location	Mn[a]		Ni		Pb		Zn		Reference
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Coastal Gulf of Mexico, U.S.A.							169 - 297		Trefrey and Presley, (1976)
St. Lawrence Estuary							161 - 319		Cossa and Poulet, (1978)
Hudson River Estuary, USA							1 10 - 4.20		Klinkhammer and Bender, (1981)
Andaman Sea					60 - 1899		86 - 6160		Sanzgiry and Braganca, (1981)
Periyar River and Cochin Estuary							205 - 1131		Paul and Pillai, (1983a)
World river average									Martin and Whitfield (1983)
Outer Harbour region of Visakhapatnam Bay		0.919		44.5		315		2835	Satyanarayana et al. (1985a)
Inner Harbour region of Visakhapatnam Bay		1.312		50.15		510.5		3544	Satyanarayana et al. (1985a)
Scheldt Estuary							150 - 1600		Duinker, (1986)
Wadge Bank region (Arabian Sea)					11.3 - 81.8				George, (1986)
Western Scheldt					61 - 205				Valenta et al. (1986)
Eastern Scheldt			32 - 145						Valenta et al. (1986)
Ganges Estuary		0.732		49		32		151	Subramanian et al. (1988)
Meuse River						762			Nolting et al (1989)
Rhine River						1017			Nolting et al. (1989)
Rhine - Meuse Estuary						542.5			Nolting et al. (1989)
Periyar and Muvattupuzha River and Cochin Estuary							60.0 - 1550		Shibu et al. (1990)
U.S. East Coast Rivers			70 - 240		7.0 - 44				Windom, (1990)
Rhine/Meuse Estuary					200 - 1000		500 - 2300		Nolting et al. (1990)
Changjiang (Yangtze River)				124		50			Zhang et al. 1990
Clyde Estuary					250 -370		260 - 590		Balls (1990)
Dogger Bank, Central North Sea			1.0 - 33	8.3			3.2 - 31	11.8	Fileman et al. (1991)
World average		1.05		90		35		250	Martin and Windom (1991)
Rhine/Meuse Estuary	0.500 - 1.600		30 - 90		50 - 175		150 - 1100		Paalman & Van Der Weijden (1992)
Huanghe (Yellow River)			31.9 - 52.2		8.6 - 35				Zhang et al. 1994
Central and Southern North Sea	0.013 - 2.800				2 - 844		7 - 350		Tappin et al. (1995)
Humber Estuary	0.820 - 1.400								Laslett (1995)
Tees Estuary	0.270 - 0.680		19 - 28		110 - 320		190 - 1100		Laslett (1995)
Wear Estuary	0.800 - 2.100		24 - 49		43 - 510		140 - 860		Laslett (1995)
Tyne Estuary	0.230 - 0.900		27 - 50		44 - 650		80 - 1400		Laslett (1995)
Tweed Estuary	6.000 - 6.600		45 - 69		51 - 120		470 - 820		Laslett (1995)
Mersey Estuary	0.280 - 0.970		19 - 55		33 - 140		310 - 450		Laslett (1995)
Morecambe Bay	0.500 - 1.200		31 - 62		85 - 130		300 - 350		Laslett (1995)
Ob - Irtysh Rivers, Russia			7.7 - 52.	28.8	1.1 - 27.5	14.9			Moran and Woods (1997)
Wetlands of Russian Arctic			6.4 - 17		24 - 37		120 - 320		Zhulidov et al. (1997a)
Wetlands of Russian Arctic					1.3 - 41		8.6 - 190		Zhulidov et al. (1997b)
Tay Estuary	0.240 -3.739		9.0 - 63.0		18 -191		53 - 470		Owens et al. (1997)
Forth Estuary	0.054 - 1.370		11.0 - 71.0		3.0 -162		52 - 290		Owens et al. (1997)
Danube River		1.704		106		84		248	Guieu et al. (1998)
Baltic Sea off Poland	0.053 - 7.590		27 - 71		10.2 - 114		124 - 3460		Pempkowiak et al. (2000)

Table 5.5 Station wise summary statistics on particulate cadmium and cobalt (μg/g)

Trace metal	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Cadmium	1	0.79	0.53	88.48	66.78	27.32	21.99	26.14	21.87	95.66	99.43
	2	1.55	2.13	130.49	89.97	45.33	20.16	45.00	23.80	99.27	118.04
	3	5.71	2.40	95.62	21.41	30.29	8.63	26.72	5.79	88.21	67.13
	4	1.24	2.67	86.18	53.32	34.08	16.65	27.90	17.35	81.86	104.22
	5	2.89	2.64	185.30	20.22	41.12	8.58	57.37	5.09	139.54	59.28
	6	4.69	2.37	136.02	42.13	37.38	13.83	35.02	13.79	93.68	99.70
	7	1.64	1.01	191.51	165.91	43.45	24.19	52.69	45.96	121.27	190.02
	8	2.58	0.69	66.37	55.70	25.56	14.54	17.98	15.78	70.35	108.58
	9	0.56	2.23	64.34	62.75	20.04	19.66	17.72	17.97	88.45	91.45
Cobalt	1	30.61	27.70	654.77	768.11	221.72	156.90	190.38	212.66	85.86	135.54
	2	35.87	44.13	772.46	397.00	201.45	144.33	212.25	118.75	105.36	82.27
	3	27.29	18.58	832.89	218.67	194.90	104.59	219.08	48.37	112.41	46.25
	4	67.52	72.49	708.97	346.40	181.36	162.33	175.78	94.18	96.92	58.02
	5	55.32	61.73	370.53	237.57	144.06	115.53	111.41	59.96	77.34	51.90
	6	91.47	65.94	965.44	285.29	252.75	139.73	244.29	59.80	96.65	42.80
	7	48.64	18.47	1051.05	198.61	241.40	99.90	614.35	58.17	160.63	58.23
	8	5.84	7.39	238.66	178.52	116.88	108.51	61.03	42.38	52.21	39.06
	9	9.16	75.74	237.35	175.59	110.04	120.08	60.37	32.65	54.86	27.19

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

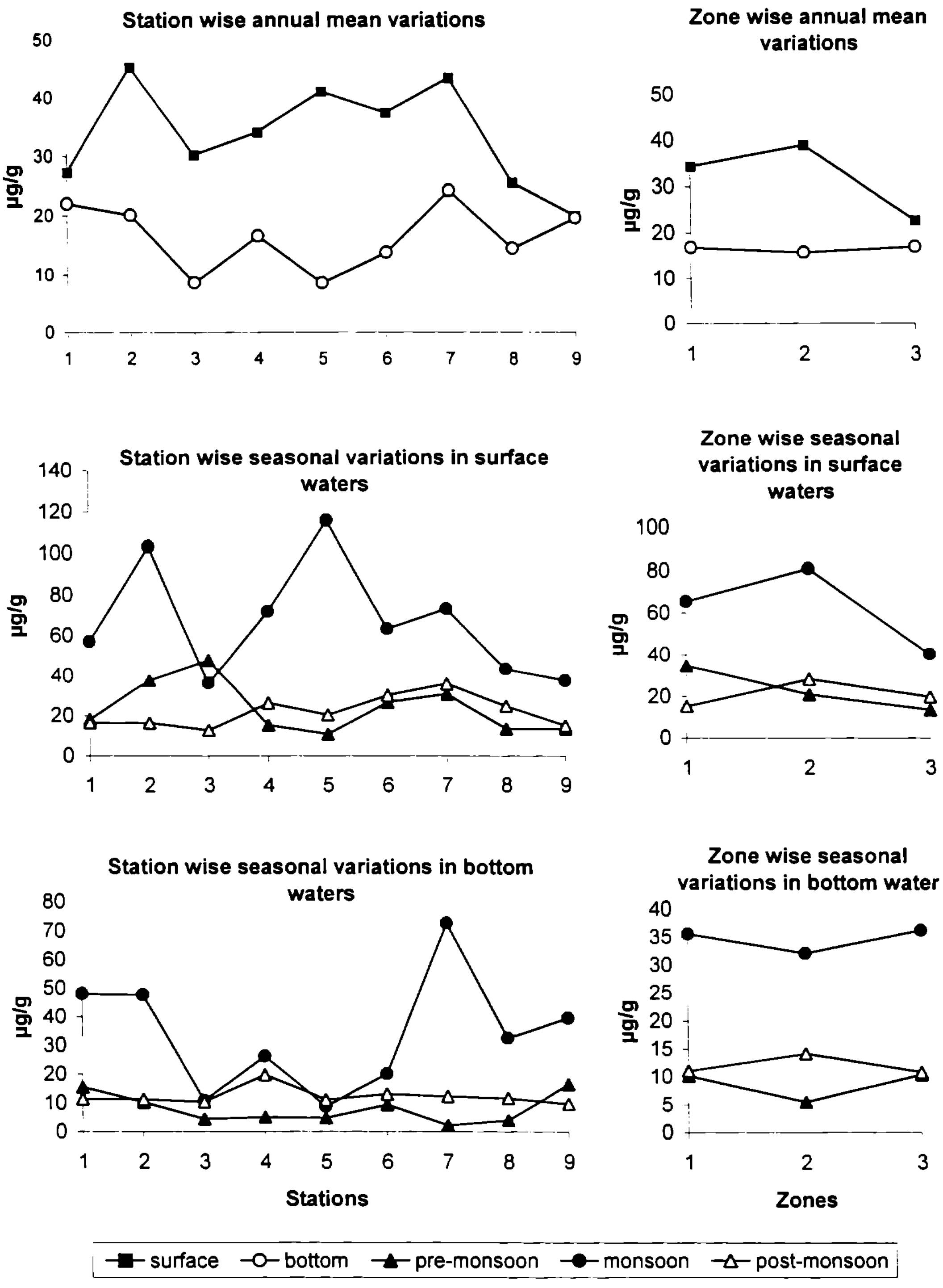


Figure 5.1 Seasonal and spatial variations of particulate cadmium.

surface waters. Zone wise variations in annual mean concentrations of Cd in bottom waters were not much pronounced (Figure 5.1).

Seasonal variations in particulate Cd concentrations were observed, with monsoon season showing the highest seasonal average in almost all stations (Figure 5.1). This is true for both surface and bottom waters. The seasonal average values during this season were found to vary from 36.17 to 115.90 µg/g in surface waters and 8.91 to 72.90 µg/g in bottom waters. The pre-monsoon and post-monsoon average values were more or less similar. Pre-monsoon season is characterised by a decrease in the concentration of particulate Cd, especially at stations of zones 2 and 3 in surface waters and almost at all stations in bottom waters. The lowest values in the surface waters of zone 1 were observed in post-monsoon season. Particulate cadmium concentrations were characterised by variations in zone wise distribution during different seasons (Figure 5.1). In pre-monsoon, the concentrations of particulate cadmium were found to be decreasing from zone 1 to zone 3 for surface waters; for bottom waters no appreciable differences were observed among the three zones. In the monsoon season, the highest values were found in zone 2 and the lowest in zone 3 of surface waters, whereas for bottom waters, zone 2 recorded the lowest value, while the other two zones recorded nearly equal concentrations.

Tappin et al. (1995) had reported concentrations of cadmium in SPM (Cd_p) in the range 0.16 to 8.89 µg/g. Jean-Francois et al. (1994) observed cadmium concentrations in the range 2.14 to 6.18 µg/g in the SPM from areas of Seine River and Estuary (France). Nolting et al. (1996) reported particulate Cd in the range 0.14 to 6.17 µg/g from Lena River Estuary. Other examples of the cadmium content of suspended matter in rivers are as follows: 120-840 µg/g in the Van River, Europe (Whitehead et al., 1988); 0.02-11.3 µg/g in the Roya River, Europe (Whitehead et al., 1988); 0.01-60.0 µg/g in the Scheldt Estuary (Duinker, 1986), and 5.0-50 µg/g in the Rhine/Meuse Estuary (Nolting et al., 1990). Shephard et al. (1980) reported average Cd_p concentration of 30.3 (µg/l) from the Indiana Lake of Palestine. Compared to the above reported values, cadmium concentrations observed in the present study (mean 25.17 µg/g) were higher. The values of Cd_p observed in the Kuttanad backwaters are in fact comparable to the values reported (50-180 µg/g) from the polluted part of Cochin estuarine system (Ouseph, 1992). Distinct seasonal differences in particulate Cd concentration were observed by Helmers (1996) from a study of Atlantic Ocean surface waters and the same was attributed to biological productivity. Higher concentration of cadmium in suspended particulate matter observed in the monsoon season may be partly due to the input of cadmium rich suspended matter from land runoff during the heavy rain in monsoon season and also partly due to the resuspension of fine material enriched in cadmium from bottom sediments. Biological productivity may also be playing a role in the variations of particulate Cd in different seasons. Though the suspended solids are found enriched in cadmium, the amount of cadmium in particulate phase per unit volume of water was found less in the present study than that observed by Babukutty (1991) from northern part of the Cochin estuarine system (range 0.21 to 1.74 µg/l). This may be due to the comparatively less concentration of suspended matter in the study area. The phase association of cadmium showed that (Figure 5.2) the concentrations are dominated by the dissolved phase rather than in the particulate phase, as observed for many other metals. The percentage of cadmium in the particulate phase varied from 0.2 to 45.9 (Table 5.3). In the Humber Estuary, Millward and Glegg (1997) observed that Cd was transported preferentially in the dissolved phase, although in winter, upto 40 % of Cd was found to be held on particles. Cadmium is often reported as being predominantly partitioned into dissolved phase in estuaries due to relatively week adsorption and formation of strong chloro-complexes (Balistrieri and Murray, 1982; Benjamin and Leckie, 1982; Williamson et al., 1996). The formation of chloro-complexes with increasing salinity is attributed to the low concentration of particulate cadmium in the pre-monsoon season at zones 2 and 3 (Figure 5.1). It is generally accepted that

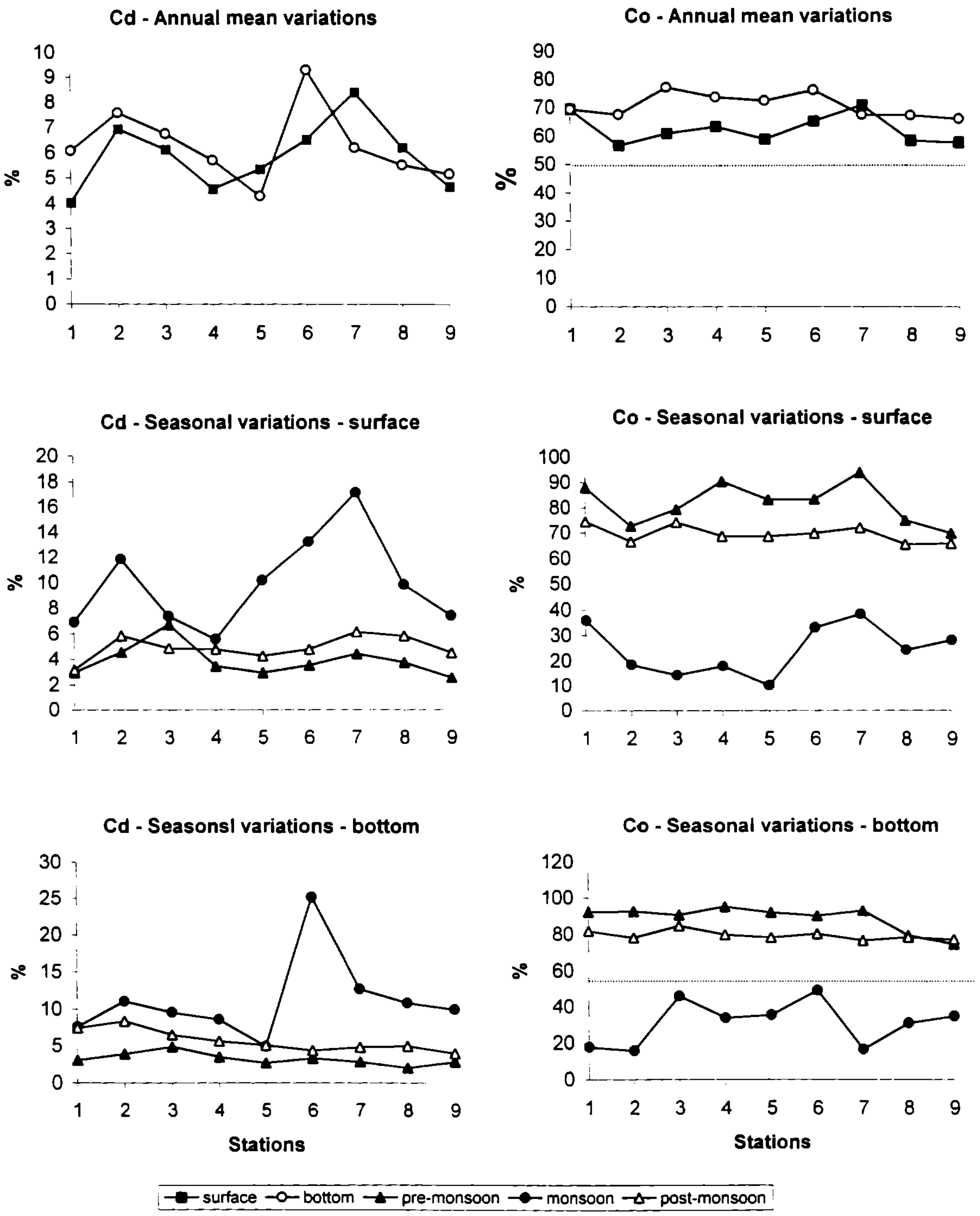


Figure 5.2 Percentage of particulate fractions of cadmium and cobalt in water.

mobilization processes, occurring when river water mixes with sea water, lead to the release of Cd from particles owing to the formation of soluble Cd-chloro complexes. This has also been observed in the lower part of the Scheldt Estuary (Duinker et al., 1982b; Salomons and Kerdijk, 1986), in the Amazon plume (Boyle et al., 1982), in the Changjiang and the Orinoco (Edmond et al., 1985), and in the Huanghe (Elbaz-Poulichet et al., 1987). It was estimated that the Cd input to the ocean might be increased by a factor of 2 to 30 owing to estuarine release from particles (Elbaz-Poulichet et al., 1987).

PARTICULATE COBALT (Co_p)

During the survey, the particulate cobalt concentrations were found in the range 5.84 to 1051.05 µg/g in the surface waters and 7.39 to 768.11 µg/g in the bottom waters (Table 5.1). Similar to that of Cd, the mean value in the surface waters was found to be higher (184.95 µg/g) than that in the bottom waters (127.99 µg/g). Spatial variations were observed with station 6 recording the highest station wise annual mean concentration for surface waters (252.75 µg/g) (Table 5.5). Generally, surface waters showed higher annual mean concentrations than that of bottom waters. The station wise annual mean concentrations for surface and bottom waters were in the range 110.04 to 252.75 µg/g and 99.90 to 162.33 µg/g respectively. The zone wise variation of annual mean concentration of Co was more or less similar to that of Cd (Figure 5.3). There was not much difference in the average values of zones 1 and 2 but a sharp decrease was observed at zone 3. In bottom waters, the zone wise annual mean concentrations did not differ much among the three zones (Figure 5.3).

Seasonal variations were not as clear as in the case of cadmium, but still many of the stations, especially in surface waters, showed higher seasonal average in pre-monsoon period (Figure 5.3). The station wise seasonal averages in this season were in the range 123.21 to 435.26 µg/g in surface

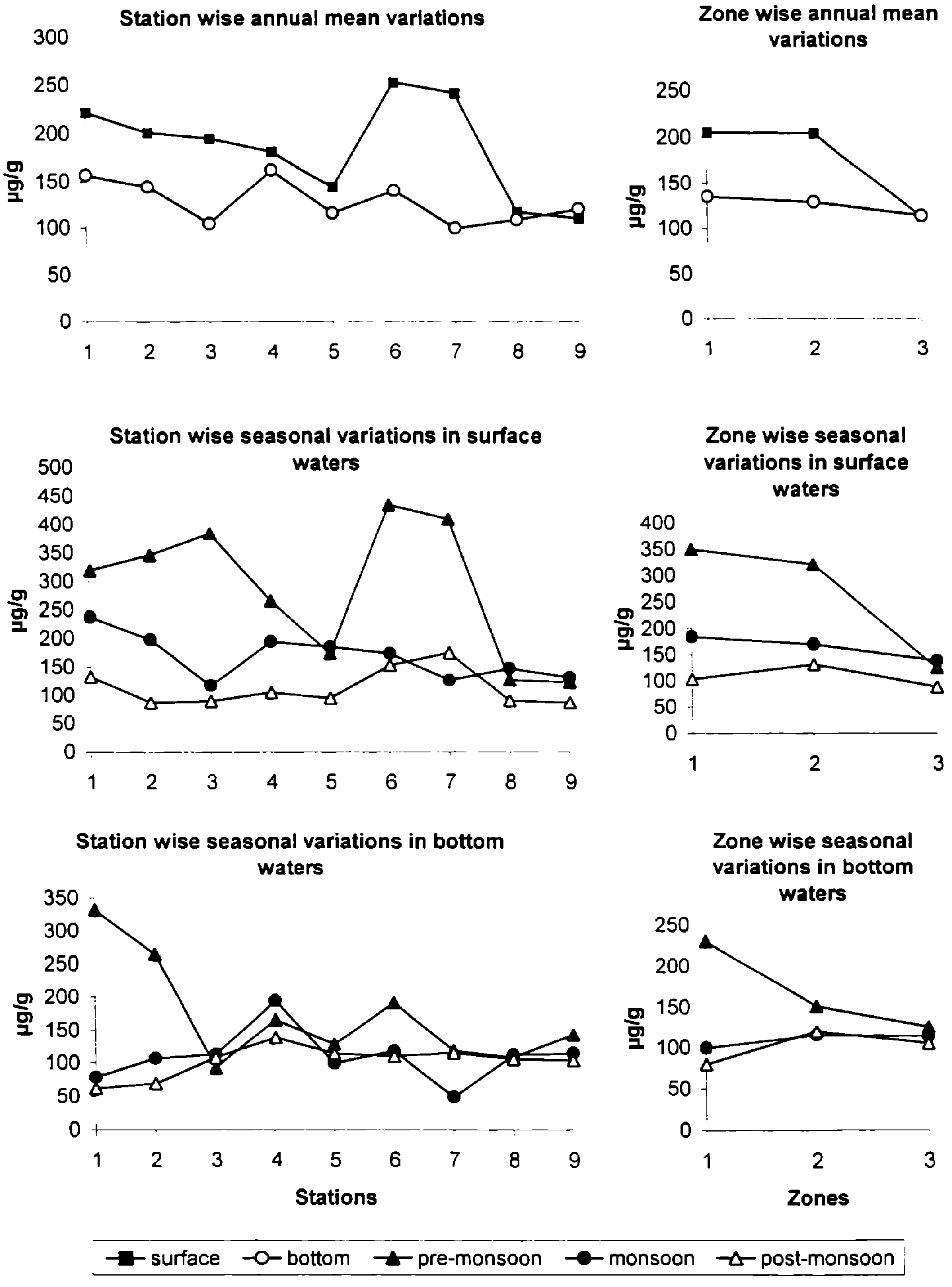


Figure 5.3. Seasonal and spatial variations of particulate cobalt.

waters and 108.38 to 333.22 µg/g in bottom waters. During the pre-monsoon period, concentrations of cobalt in the particulate phase were found highest in zone 1 and lowest in zone 3 (Figure 5.3). The highest seasonal average in this season was seen at stations 6 and 1 for surface and bottom waters respectively. In the monsoon period, the average values ranged from 117.59 to 238.07 µg/g and 49.14 to 194.72 µg/g respectively for surface and bottom waters, whereas for post-monsoon season the values varied from 86.86 to 175.24 µg/g and 62.54 to 139.43 µg/g respectively for surface and bottom waters. In zone 1, both surface and bottom waters recorded high value in pre-monsoon season. The values showed a decreasing trend in the monsoon season, which further decreased to the lowest during post-monsoon season. More or less similar seasonal variation was observed at zone 2 also, except that in bottom waters monsoon and post-monsoon season recorded equal values. The seasonal variations in the concentration of Co in bottom waters at zones 2 and 3 were identical. Unlike the trend of seasonal variations at zones 1 and 2, zone 3 recorded highest seasonal value in monsoon period in the surface water but the lowest value, as in the case of zones 1 and 2, was observed in the post-monsoon season.

Data on particulate cobalt from estuarine waters are relatively scarce. Many of the mean values of particulate cobalt reported from different parts of the world (Table 5.4) were found to be less than the mean value (156.47 µg/g) observed in the present study. Satyanarayana et al. (1985a) reported a mean value of 39.05 µg/g from the inner Harbour region of Visakhapatnam Bay, whereas Subramanian et al. (1988) recorded a slightly higher mean value (53 µg/g) from the Ganges Estuary. In a survey of different areas of Seine River and its Estuary, Jean-Francois et al. (1994) observed particulate cobalt concentrations in the range 7.07 to 14.14 µg/g and from Danube River, Guieu et al. (1998) reported an average of 25.6 µg/g of particulate cobalt. A more or less comparable value (135.8 µg/g) was observed by Satyanarayana et al. (1985a) from the outer Harbour region of

Visakhapatnam Bay (Bay of Bengal). The phase association characteristics of cobalt show that the extent of association is predominant in the particulate phase than in the dissolved phase (Figure 5.2). The phase association also showed clear seasonal trend such that in the pre-monsoon season, a predominant partitioning in the particulate phase was observed, whereas the monsoon season showed preference to the dissolved phase. This behaviour shows that when the estuary gets flushed with fresh water in the monsoon season, desorption of particulate cobalt takes place. During the pre-monsoon and post-monsoon seasons when the flow of fresh water in the estuary is considerably reduced, sorptive equilibrium between dissolved and particulate phases is attained in favour of the particulate phase. This partitioning behaviour of cobalt in monsoon and pre-monsoon seasons was quite opposite to that observed in the case of Cd (Figure 5.2).

PARTICULATE CHROMIUM (Cr_p)

Table 5.6 gives the station wise minimum, maximum, annual mean, standard deviation and coefficient of variation of the monthly data of particulate Cr. Particulate chromium concentrations were found to vary from 6.59 µg/g (at station 8) to 925 µg/g (at station 5) in the surface waters and 9.98 (station 8) to 728.51 µg/g (station 7) in the bottom waters. As in the case of Cd and Co, higher mean concentration (264.04 µg/g) was obtained in surface waters than in bottom waters (191.49 µg/g) (Table 5.1). Figure 5.4 gives the trend in the variation of station wise annual mean concentrations. The particulate concentrations of chromium in surface waters were clearly higher than that of bottom waters. In surface waters, the station wise annual mean concentrations of particulate chromium were in the range 216.16 to 310.99 µg/g and for bottom waters, it ranged from 145.33 to 239.95 µg/g. For surface waters, station 2 recorded highest annual mean concentration of particulate chromium and the lowest was at station 9, and in bottom waters, the same was at stations 7 and 3 respectively. The annual mean concentration of Cr in surface waters did not

Table 5.6 Station wise summary statistics on particulate chromium and copper (µg/g)

Trace metal	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Chromium	1	9.72	14.26	654.92	439.14	261.53	166.70	191.51	125.49	73.23	75.28
	2	45.80	51.62	778.78	359.49	310.99	159.35	207.60	92.89	66.76	58.29
	3	85.71	36.28	496.26	283.91	245.44	145.33	133.45	75.38	54.37	51.87
	4	86.80	108.42	592.07	534.40	255.19	226.01	160.23	122.27	62.79	54.10
	5	55.93	87.08	925.00	622.64	275.10	212.51	244.57	143.81	88.90	67.67
	6	70.08	91.66	690.04	360.87	284.07	166.46	203.29	81.13	71.56	48.74
	7	15.32	15.98	564.44	728.51	295.82	239.95	175.30	200.64	59.26	83.62
	8	6.59	9.98	479.44	418.91	232.11	203.60	143.62	129.39	61.87	63.55
	9	13.75	80.00	537.02	426.32	216.16	203.54	146.18	104.78	67.63	51.48
Copper	1	8.21	11.47	1398.81	299.76	285.66	151.00	370.22	87.22	129.60	57.76
	2	37.53	34.01	533.93	872.81	244.93	266.00	155.60	294.76	63.53	110.81
	3	112.47	22.03	580.25	238.51	231.35	113.51	137.73	60.56	59.53	53.35
	4	54.36	46.65	775.67	847.01	235.70	191.61	217.46	222.05	92.26	115.89
	5	50.65	38.48	942.33	802.04	269.36	164.79	243.84	206.83	90.52	125.52
	6	79.00	54.46	570.97	1014.87	209.16	169.56	123.57	268.67	59.08	158.45
	7	10.76	12.88	960.17	687.23	256.84	212.15	265.67	230.66	103.44	108.72
	8	7.62	7.90	1559.88	1138.87	291.56	282.43	411.81	369.35	141.24	130.78
	9	7.84	66.90	414.24	430.13	172.90	148.25	127.47	108.49	73.72	73.18

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

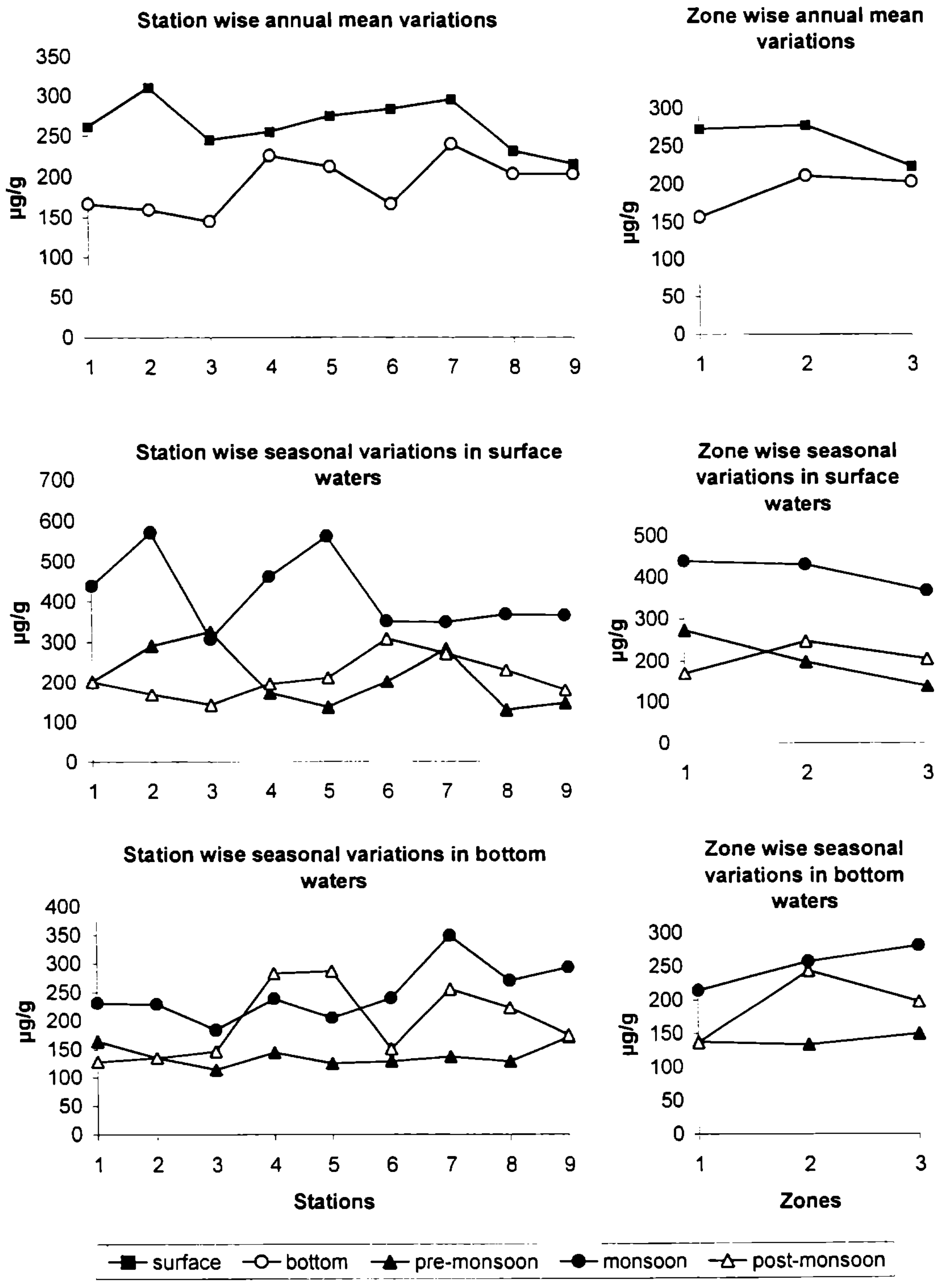


Figure 5.4. Seasonal and spatial variations of particulate chromium.

differ much at zones 1 and 2 but as in the case of Cd and Co, zone 3 recorded considerably lower values. Unlike that of Cd and Co, the annual mean concentrations at zones 2 and 3 were much higher than that observed at zone 1 (Figure 5.4).

Seasonal variations were observed and are represented in Figure 5.4. Monsoon season generally recorded higher seasonal average concentrations in surface and bottom waters. In this season, the concentrations in the surface waters showed a decreasing trend from zone 1 to zone 2 and then to zone 3 (Figure 5.4). But an increasing trend from zone 1 to zone 2 and then to zone 3 was found in bottom waters in the same season. The average particulate concentration in this season was in the range 307.66 to 572.02 µg/g and 183.38 to 349.35 µg/g in surface and bottom waters respectively. From stations 4 to 9, the post-monsoon values were slightly higher than the pre-monsoon values and at stations 4 and 5, the values were even higher than the values in monsoon season for bottom waters. In post-monsoon season, zone 2 recorded highest values, the lowest being in zone 1. The lowest seasonal average value was observed in pre-monsoon in the three zones except the surface water concentrations at zone 1. In this season, the concentration of cobalt in particulate phase showed a decreasing trend (as observed in monsoon season in surface water) from zone 1 to zone 2 and then to zone 3. The bottom water concentrations were found to decrease from zone 1 to zone 2 and then slightly increased at zone 3. It was found that cadmium and chromium showed some similarities in their seasonal variations. Seasonal variations in percentage fractions of particulate chromium are given in Figure 5.5.

The average value reported in the present study (228 µg/g) is higher than the average values reported by Turner et al. (1994) from Dee Estuary, Turner et al. (1991) from Humber and Thames Estuaries, Turner (1999) from the Clyde Estuary, Sfriso et al. (1995) from Lagoon of Venice, Moran and Woods (1997) from the Ob-Irtysh Rivers, Subramanian et al. (1988)

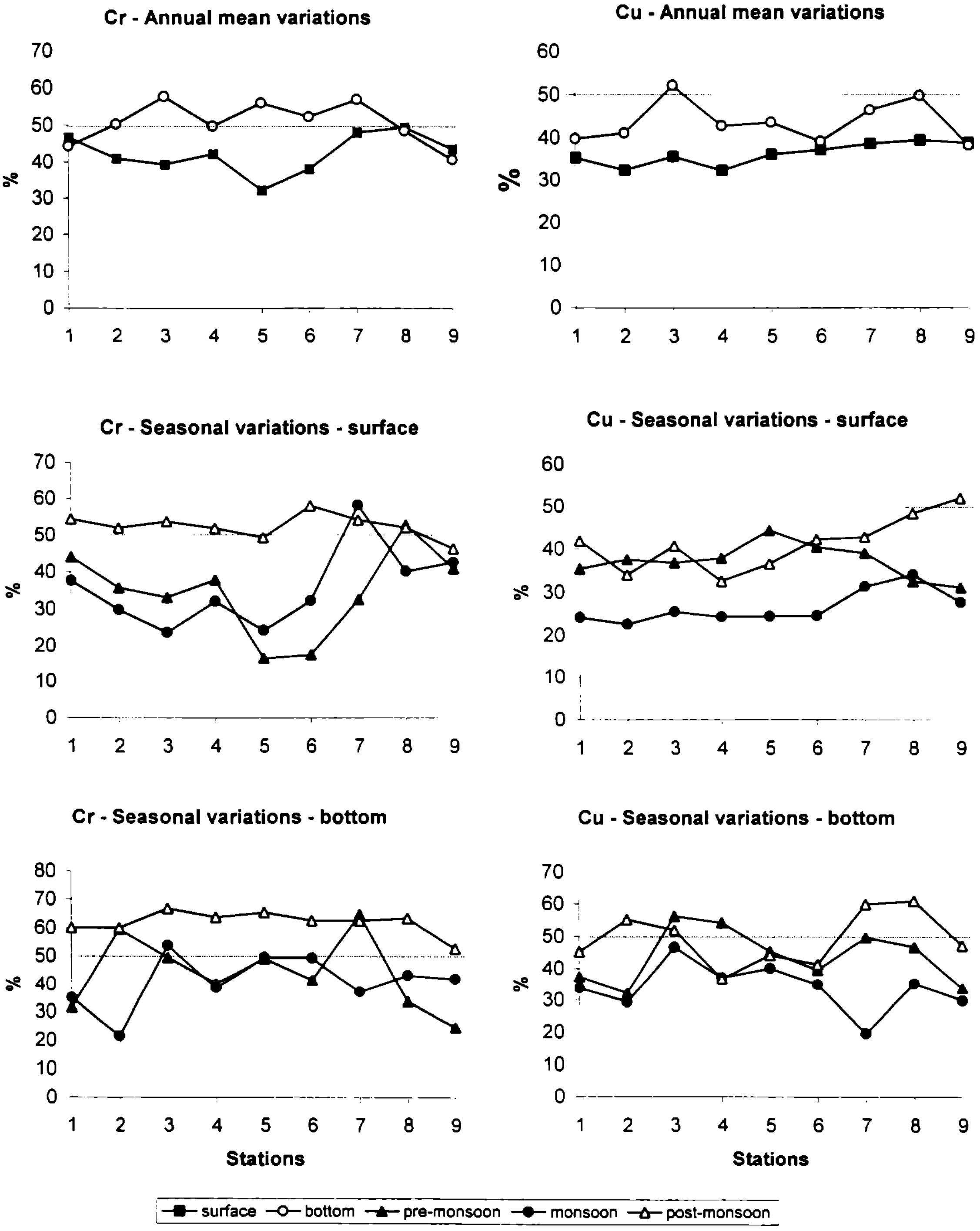


Figure 5.5 Percentage of particulate fractions of chromium and copper in water.

from the Ganges Estuary, Zhang et al. (1990) from the Yangtze River, Feely et al. (1981) from the Copper River and Fileman et al. (1991) from the Central North Sea (Table 5.4). Whereas, values higher than the one observed in the present study were also reported from Rhine and Meuse Rivers and Rhine-Meuse Estuary (Nolting et al., 1989) and from Mediterranean embayment (Scoullos and Dassenakis, 1983). The generally elevated concentrations of particulate chromium in the monsoon season indicated that riverine input and runoff from the land are the major sources of particulate chromium input into the backwater system. The relatively elevated concentrations of Cr in the suspended particulate matter of Kuttanad backwaters may be due to the combined effect of various natural processes like resuspension, weathering, in-situ reduction and anthropogenic perturbations. In a study of the suspended particulate chromium from the San Francisco Bay, Abu-Saba and Flegal (1995) suggested that processes which may contribute to the enrichment of Cr in suspended particulates are weathering, hydrolic mining and municipal and industrial discharges (Luoma and Philips, 1988). Weathering processes tend to enrich first row transition elements (to which chromium belongs) in suspended particulate matter and in sediments (Taylor and McClennan, 1985).

PARTICULATE COPPER (Cu_p)

The distribution of copper in the particulate phase during the period of survey was found to fall within the range 7.62 to 1559.88 µg/g (both at station 8) with a mean concentration of 244.16 µg/g in surface waters. Whereas, in bottom waters, the range was 7.90 to 1138.87 µg/g (both at station 8) with a mean value of 188.81 µg/g (Table 5.1 and Table 5.6). This corresponds to an overall range 0.31 to 9.74 µg/l (Table 5.2). Here also, the mean concentration recorded in the surface waters was higher than that of bottom waters. The distribution pattern of particulate Cu was also characterised by some definite seasonal and temporal variations. The station wise annual mean concentrations (Table 5.6) were in the range 172.90 µg/g (at station 9) to

291.56 µg/g (at station 8) in surface waters and 113.51 (at station 3) to 282.43 µg/g (at station 8) in bottom waters. Figure 5.6 gives the trends in the variations of station wise annual mean concentrations which shows that the concentrations of particulate copper in surface waters were higher than those of bottom waters, a behaviour similar to that of Cd, Co and Cr. The lowest station wise annual mean concentration was recorded at station 9 and the highest was observed at station 8 in surface waters. The variations in the annual mean concentrations of Cu in the three zones showed an entirely different trend with the surface waters exhibiting a decreasing trend from zone 1 to 3 and the bottom waters with a reverse pattern (Figure 5.6).

The variations of station wise seasonal average values are also represented in Figure 5.6. All stations recorded highest seasonal average either in the monsoon or in the post-monsoon season, except surface water at station 3. The highest seasonal average in the post monsoon season and the highest annual mean concentration at station 8 showed that there was a considerable anthropogenic input of Cu at this station during post-monsoon period. This may be due to the excessive use of fertilisers and copper containing pesticides in the agricultural lands near to this station. In the pre-monsoon season, both surface and bottom waters recorded highest value in zone 1 (Figure 5.6). In monsoon season, the concentrations of particulate copper were in the order, zone 2 > zone 1 > zone 3 for surface waters but for bottom waters the order was zone 3 > zone 1 > zone 2. In post-monsoon season, zone 3 recorded the highest values in surface and bottom waters. Zones 1 and 2 recorded highest seasonal average in monsoon season for surface as well as for bottom waters. The lowest value in zone 1 was in post-monsoon season but for zone 2 the lowest was observed in pre-monsoon season. In zone 3, the highest value was observed in post-monsoon and the lowest in pre-monsoon for both surface and bottom waters.

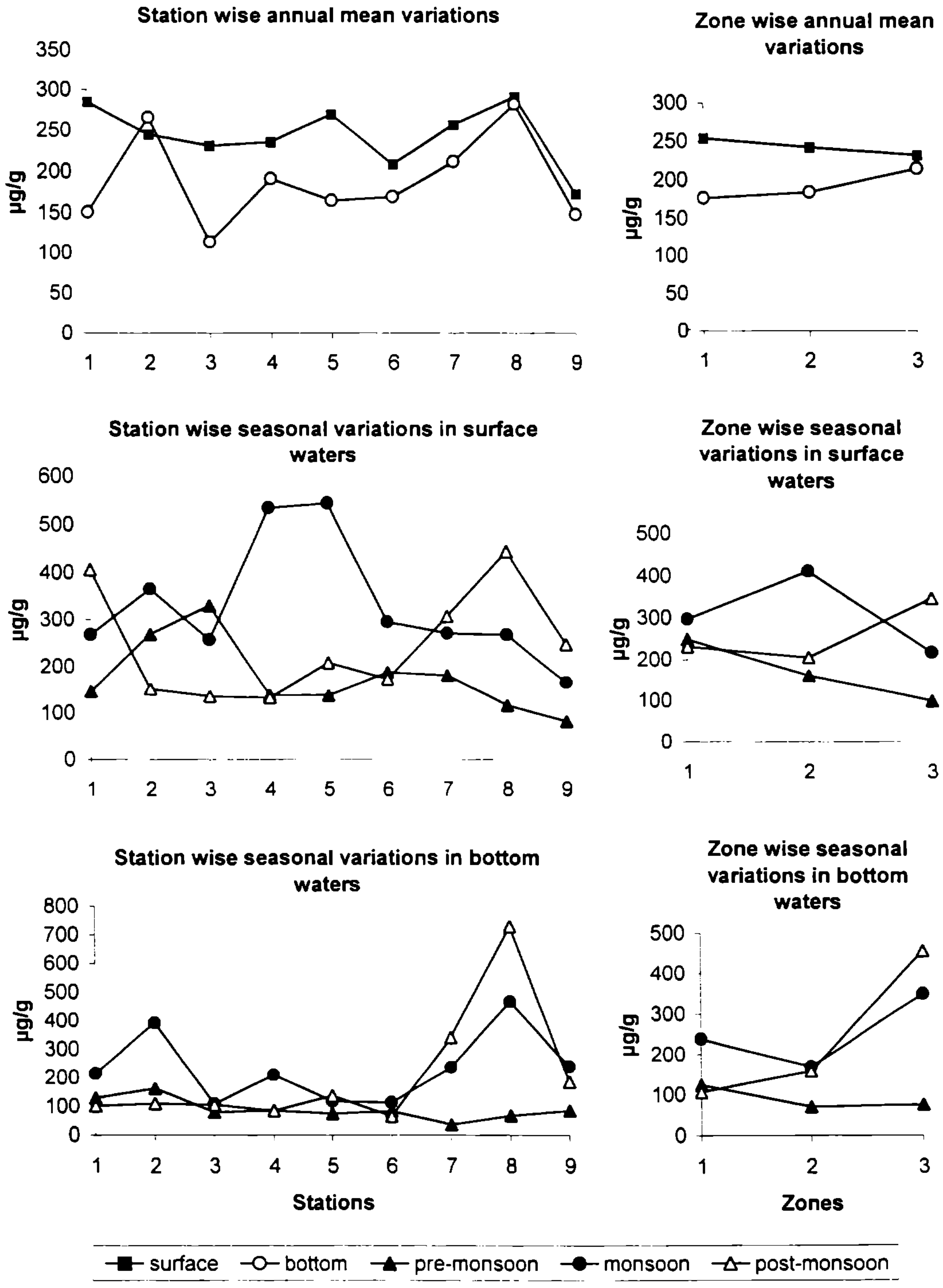


Figure 5.6. Seasonal and spatial variations of particulate copper.

Martin and Meybeck (1979) estimated average Cu concentration in suspended particulate matter to be 100 µg/g. Delfino and Otto (1986) observed that particulate Cu data ranged from 49 to 250 µg/g from Susquehanna and Bush Rivers. Martin and Meybeck (1979) suggested that 10 – 50 % of the total Cu would be in the dissolved phase and the variations in concentrations could be due to anthropogenic sources as well as natural occurrences. Among the 4 metals studied (Cu, Zn, Fe and Mn), Delfino and Otto (1986) found that Cu was the most soluble, ranging from 22 to 38 % of the total concentration in soluble phase. They ascribed this behaviour of Cu to the stabilization of Cu in soluble form by forming complexes with organic matter from the decay of vegetative matter. McDuffie et al. (1976) observed from the upper Susquehanna River that soluble Cu was approximately 80 % of the total Cu concentration, suggesting the possible presence of chelating agents that maintained Cu in the soluble phase. Their findings for Cu are in general agreement with the results of the present study in which the soluble fraction of Cu was found in the range 6 to 85 % of total copper (Table 5.3 and Figure 5.5). In a study of the northern part of Cochin estuarine system, Babukutty (1991) observed particulate copper concentrations in the range 1.49 to 9.42 µg/l with a station wise annual mean concentration in the range 3.34 to 4.36 µg/l. Per unit volume of water, these values are quite comparable to the overall mean values (1.11 µg/l and 1.89 µg/l respectively for surface and bottom waters (Table 5.2) obtained in the present study. But per unit mass of the suspended solids, the observed values in the present study are comparatively higher than many of the other reported values. From the fluvial estuarine region of Seine River (France), Jean-Francois et al. (1994) observed a mean concentration of 127.09 µg/g of Cu in particulate phase. Nolting et al. (1996) reported particulate Cu in the range 26 to 219 µg/g from Lena River Estuary. From the polluted zone of the Cochin estuarine system (northern part), Ouseph (1992) reported Cu_p values in the range 44-298 µg/g. Satyanarayana et al. (1985a) observed particulate Cu concentrations in the range 25.4 to 481 µg/g from the coastal waters of Visakhapatnam (Bay of Bengal). Resuspension of copper rich fine materials from bottom sediments during the high flow conditions of monsoon and post-monsoon seasons together with the land drainage from the paddy fields and rubber estates situated in the river basins, where fertilizers and copper containing pesticides are used extensively, partly explain the high concentration of copper in the suspended particulate matter, especially in these two seasons. Gibbs (1977) reported that 97 and 82 % of copper was transported in the particulate phase in Amazon and Yukon Rivers respectively and 65 % of Cu was transported in the particulate phase in the Elliot Bay (Paulson et al., 1989). Contrary to this, McDuffie et al. (1976) reported 40 % Cu in Susquehanna River and Hart and Davies (1981) reported 25 % in Yarra River system. Higher percentage of dissolved copper has been reported from Cochin Estuary by Paul and Pillai (1983a). Duinker (1983) observed an initial low salinity removal of copper, while a non-conservative behaviour during estuarine mixing was reported by Windom et al. (1988) and Paulson et al. (1989). The high value of particulate copper in monsoon season and also at zone 3 in post-monsoon season could be attributed to the copper carried into the estuary by runoff from the nearby paddy fields. The particulate phase of Cu in the present study was found in the range 6.2 to 79.8 % (Table 5.3). It was observed that in Kuttanad backwaters, copper shows preference to the dissolved phase. Matkar et al. (1981) observed 8.5 to 78.4 % of copper in the dissolved phase from the Bombay Harbour Bay. Dissolved copper in the estuarine waters is largely complexed with organics (Kramer and Duinker, 1984; Valenta et al., 1986; van den Berg et al., 1987). This strong association between dissolved Cu and organic ligands suggests that Cu is mainly bound to organic matter of riverine origin, which is progressively mineralised during its transport to the sea. The higher average values observed at zones 1 and 2 in surface waters during monsoon and the higher values found at zone 3 in bottom water during monsoon and post-monsoon seasons are attributed to the input of copper into the estuary by the rivers as well as from the runoff from the nearby paddy fields. The absence of a general trend in the spatial variations of particulate Cu concentrations suggests the combined influence of various natural processes and anthropogenic inputs.

PARTICULATE IRON (Fe_p)

The mean concentrations of iron in the particulate form were 126.26 and 106.28 mg/g in surface and bottom waters respectively (Table 5.1). As in the case of Cd, Co, Cr and Cu, high concentrations of particulate iron were observed in surface waters than in bottom waters. Iron is the metal, which recorded minimum variability in concentrations in the particulate phase, among the 10 metals studied. It also recorded the least ratio between surface and bottom water concentrations (1.19). The station wise minimum, maximum, annual mean, standard deviation and coefficient of variation are given in Table 5.7. The particulate iron concentrations varied from 2.50 to 432.79 mg/g in surface waters and from 4.15 to 408.49 mg/g in bottom waters. Station 8 recorded the lowest values of the surface as well as bottom waters, while the highest value in surface and bottom waters was recorded at stations 2 and 1 respectively. The station wise annual mean concentrations varied from 86.15 to 158.60 mg/g in surface waters and from 88.30 to 126.69 mg/g in bottom waters. The spatial variations in annual mean concentrations of iron in particulate form (Figure 5.7) in surface waters showed that the values increased considerably at stations 2 and 3 compared to that of station 1 and decreased towards station 5 followed by a further increase towards station 7 and a gradual decrease towards station 9. Thus, there were two peaks in the trend line, one at station 2 and the other at station 7 The trend in bottom water was slightly different. Instead of the initial increasing trend towards station 3, bottom water showed a decreasing trend from station 1 to station 3. Then, there was an increase at station 4 followed by a decrease towards station 7 and a further increase towards station 9. Except at stations 4 and 9, annual mean concentrations in the surface waters were found to be higher than those in bottom waters. The difference between the annual mean concentrations of surface and bottom waters was greater at stations 2, 3, 6 and 7 compared to the other stations. The behaviour of Fe was found to be entirely different from that of Cd, Co, Cr, and

Table 5.7 Station wise summary statistics on particulate iron and manganese (mg/g)

Trace metal	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Iron	1	3.34	11.06	295.47	408.49	124.76	121.74	81.89	104.73	65.64	86.03
	2	25.15	21.53	432.79	242.99	158.60	121.04	111.48	65.24	70.29	53.90
	3	6.93	23.41	349.62	158.93	158.33	110.39	98.76	38.67	62.37	35.03
	4	52.56	68.78	218.64	198.39	123.76	126.69	46.88	38.09	37.88	30.07
	5	23.75	55.55	419.02	187.19	119.15	105.40	112.02	39.29	94.01	37.27
	6	29.81	9.15	270.83	184.04	121.64	91.42	78.72	45.07	64.71	49.30
	7	7.37	8.54	366.28	151.68	142.13	88.30	101.37	47.69	71.32	54.00
	8	2.50	4.15	186.05	142.64	101.77	93.97	56.24	39.36	55.26	41.88
	9	5.43	56.55	166.99	172.43	86.15	97.54	49.99	31.42	58.03	32.22
Manganese	1	0.21	0.81	187.47	152.23	26.77	21.03	53.59	42.99	200.17	204.46
	2	3.77	1.90	121.36	99.82	28.38	20.25	41.86	28.30	147.49	139.75
	3	3.27	0.55	152.31	60.28	26.74	12.35	42.10	16.33	157.41	132.16
	4	5.86	2.51	96.81	41.83	28.26	15.81	31.98	13.43	113.16	84.92
	5	2.93	2.57	98.83	59.04	23.53	13.97	28.21	15.63	119.88	111.92
	6	4.54	2.16	271.88	80.01	58.28	23.25	81.11	27.32	139.16	117.53
	7	1.70	0.81	272.64	48.88	52.27	9.48	83.94	13.00	160.57	137.09
	8	2.66	2.34	120.90	86.59	24.51	23.44	33.91	29.91	138.31	127.61
	9	2.67	2.07	101.16	32.09	22.92	13.79	28.95	11.19	126.30	81.13

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

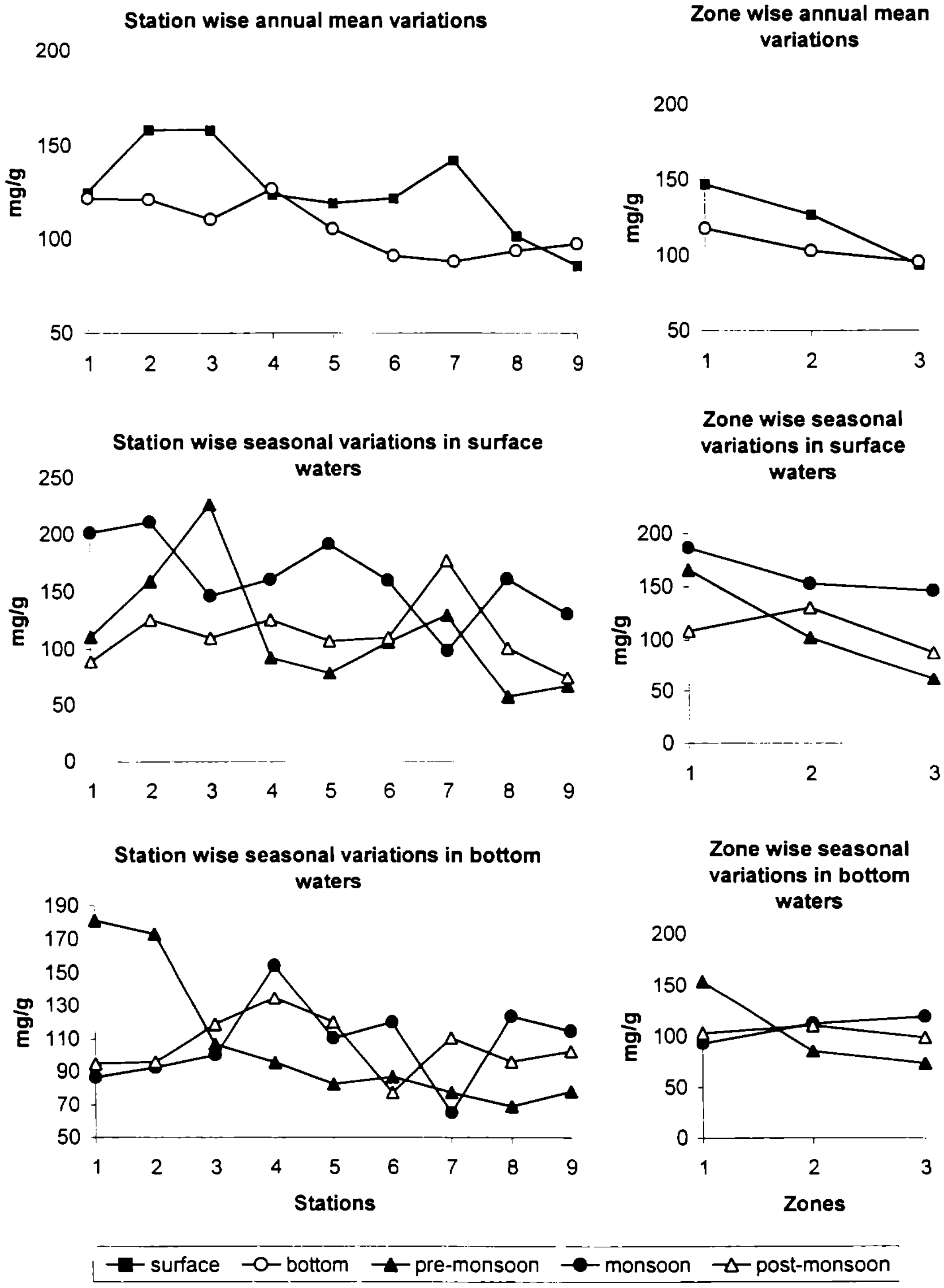


Figure 5.7. Seasonal and spatial variations of particulate iron.

Cu in that, the annual mean concentrations of particulate iron in surface and bottom waters showed highest value at zone 1 and it decreased at zone 2 and further at zone 3, and at zone 3 both surface and bottom waters recorded almost equal values (Figure 5.7).

In surface waters, all the stations recorded maximum seasonal average of particulate iron in the monsoon season (Figure 5.7) with exceptions at stations 3 and 7, which recorded maximum seasonal average in the pre-monsoon and post-monsoon seasons respectively. In bottom water, maximum seasonal average at stations 4, 6, 8 and 9 was in the monsoon season, while at stations 1 and 2, it was in the pre-monsoon season but at stations 3, 5 and 7, the maximum seasonal average was in the post-monsoon season. It can be seen that in monsoon season, the particulate iron concentration in surface water was higher than that of pre-monsoon and post-monsoon in all the three zones. But in bottom water, only zones 2 and 3 recorded higher values during monsoon period. Zones 2 and 3 recorded distinctly lower values during the pre-monsoon season for surface as well as bottom waters, which was the lowest among the three seasons. In the same season, the surface water at zone 1 recorded a value lower than that of monsoon season but higher than that of post-monsoon season, but bottom water recorded the highest value among the three seasons at zone 1. In general, the seasonal variations of particulate iron in zones 2 and 3 were found to be similar. The significant decrease in the particulate iron concentration during the pre-monsoon period at zones 2 and 3 may be largely due to the salinity dependence of particulate iron in the studied area. The higher salinity values observed at zones 2 and 3 during the pre-monsoon period may instigate the flocculation of particulate form of iron, which eventually settles down. Similar salinity induced flocculation of particulate iron was observed in the post-monsoon season, especially at zone 3.

As in the case of Cd and Cu, concentration of Fe in the suspended particulate matter was also higher in the study area when compared to the values (28.98 mg/g) reported from the northern part of the Cochin estuarine system by Ouseph (1992). Satyanarayana et al. (1985a) in a study of the coastal environment of Visakhapatnam (Bay of Bengal) observed particulate iron concentrations in the range 8.91 to 19.25 mg/g. Nolting et al. (1996) observed particulate Fe in the range 33 to 62 mg/g from Lena River Estuary. The higher particulate iron content could be partly due to the river water flow through laterite bed and also by sewage effluent. Higher iron values present at the river mouth may be due to the precipitation and flocculation in contact with saline waters and suspended particles. Elevated concentration of iron in suspended particulate matter can also be due to the resuspension of iron-rich lithogenous materials. Delfino and Otto (1986) in a survey of the two tributaries of the upper Chesapeake Bay (the Susquehanna and Bush Rivers) observed that particulate Fe phase contained 87 –100 % of total Fe. In the present study, the same was in the range 99.4 – 100 % (Table 5.3). The seasonal variations in the percentage fractions of particulate iron in water are depicted in Figure 5.8. Delfino and Otto (1986) observed a maximum value of 100 mg/g of particulate iron in winter season form Susquehenna and Bush Rivers. The trace metal transport studies by Gibbs (1973) who identified various mechanisms involving trace metals in Amazon and Yukon Rivers observed that Fe distribution was dominated by the particulate phase, which agrees with the findings of this study and substantiates the generally expected behaviour of Fe in rivers (Martin and Meybeck, 1979). It is found that iron in the Kuttanad backwaters is transported mainly in the particulate phase. Iron in the dissolved phase was found only less than 1% (Table 5.3). Similar to the observation made in the present study, Matkar et al. (1981) also observed less than 1 % of iron in the dissolved phase from the Bombay Harbour Bay. From a study of dissolved and particulate metals by Gibbs (1973) in the two Rivers Yukon and Amazon, it was found that for iron, transport in solution was negligible compared with the particulate flux. In Kuttanad backwaters also, it was found that transport in solution was negligible compared to the particulate flux.

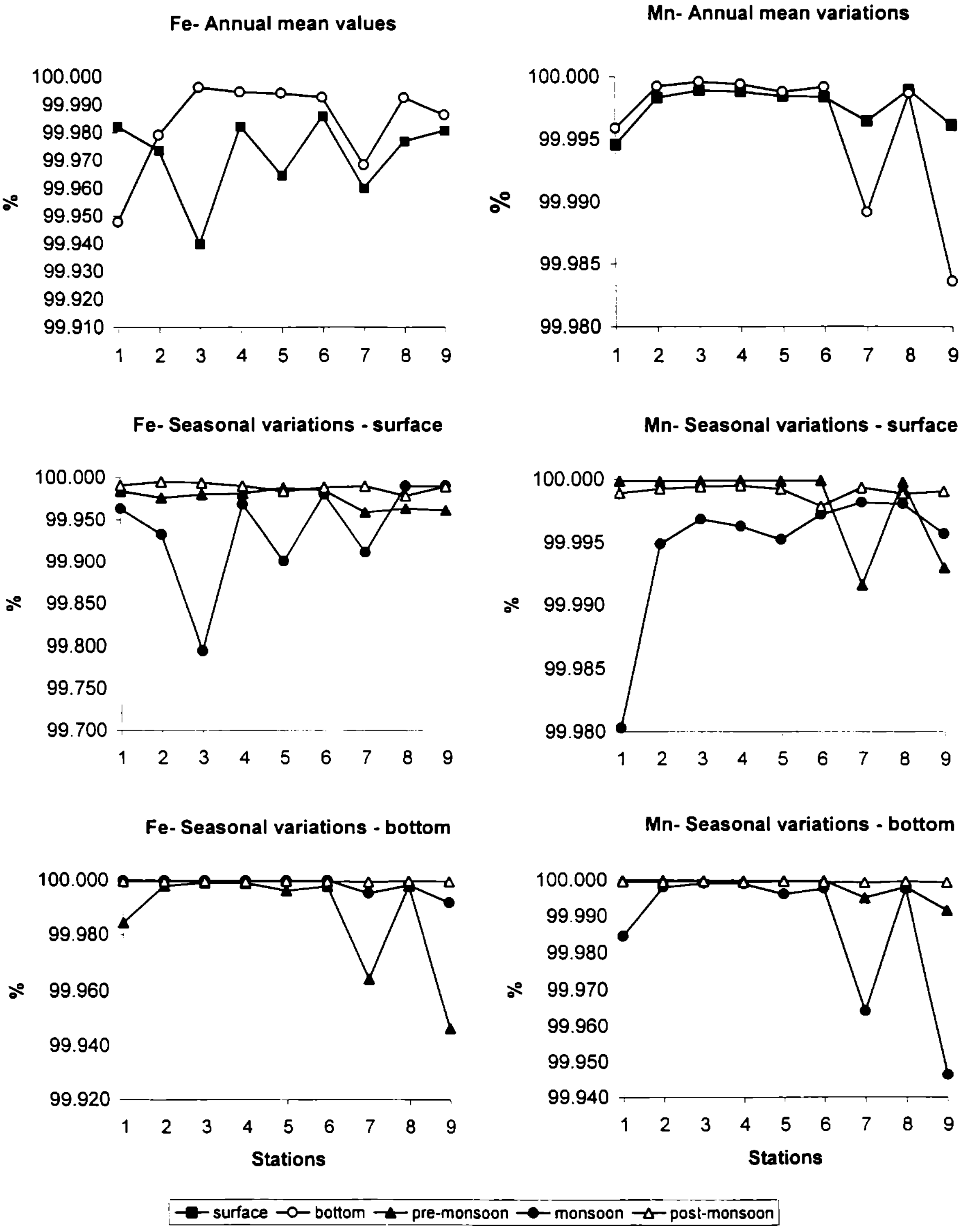
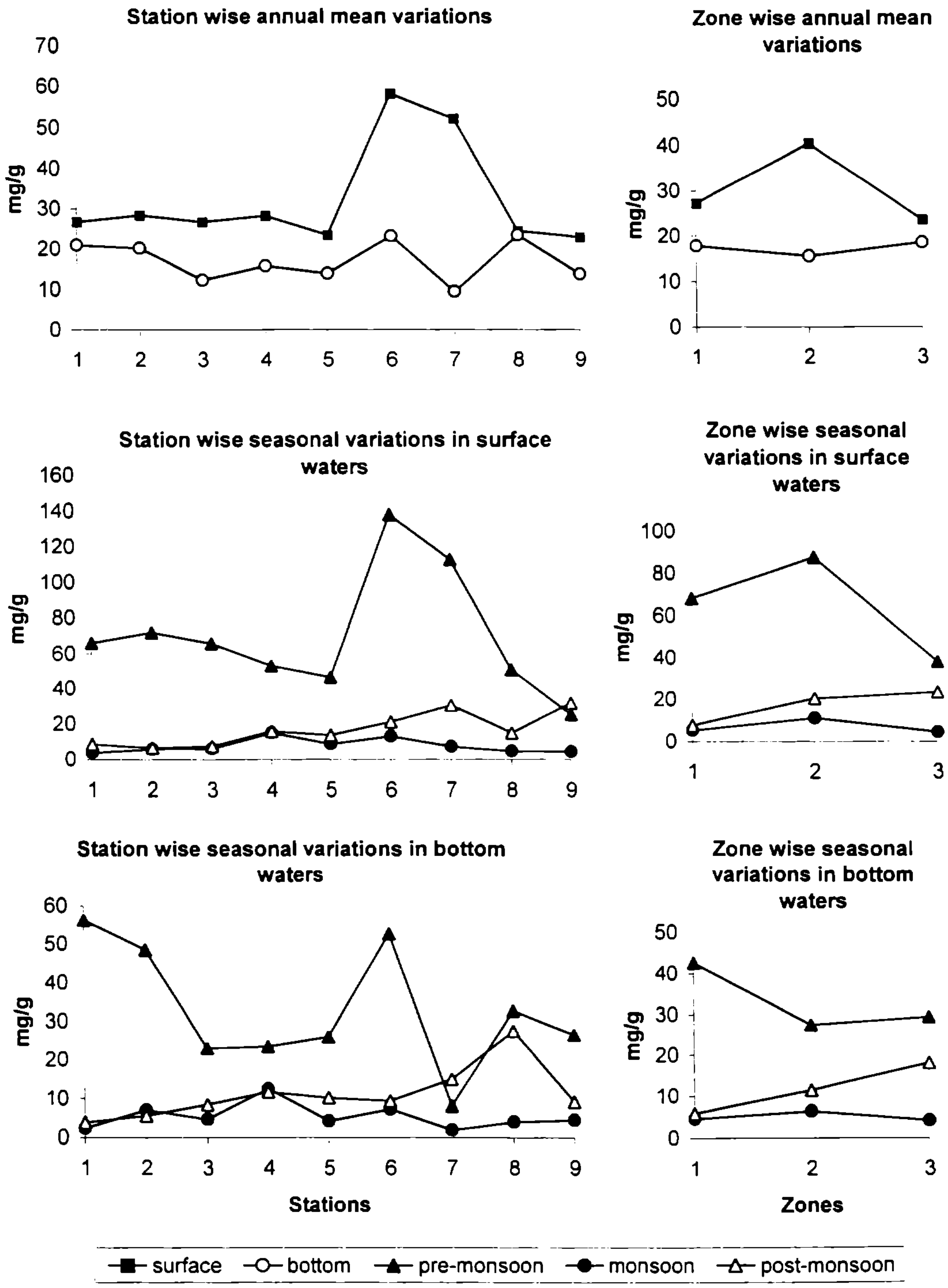


Figure 5.8 Percentage of particulate fractions of iron and manganese in water.

PARTICULATE MANGANESE (Mn_p)

Particulate manganese concentrations (Mn_p) varied by a factor of 1298 (from 0.21 to 272.64 mg/g) in surface waters and by a factor of 276 (from 0.55 to 152.23 mg/g) in bottom waters over the period of the survey (Table 5.1). The overall mean concentration in the surface water (32.41 mg/g) was almost double to that of bottom water concentration (17.04 mg/g). Among the ten metals studied, Mn showed the maximum coefficient of variation in concentrations both in surface and bottom waters. Clearly, the surface water showed a wider range than the bottom water. The station wise minimum, maximum, annual mean concentration, standard deviation and coefficient of variation of Mn_p are given in Table 5.7 The highest values in surface and bottom waters were reported from stations 7 and 1 respectively, while the lowest values were recorded at stations 1 and 3 respectively. The station wise annual mean concentrations of particulate manganese were in the range 22.92 to 58.28 mg/g and 9.48 to 23.44 mg/g in surface and bottom waters respectively. The highest annual mean concentrations in the surface and bottom waters were observed at stations 6 and 8 respectively. The lowest annual mean concentration for surface water was recorded at station 9, while that for bottom water was seen at station 7 Similar to that of Cd, Co, Cr, Cu and Fe, Mn also exhibited a hike in the annual mean concentrations in surface waters in all the stations (Figure 5.9). Similar to that of Cd, Co and Cr, Mn showed a considerable hike in annual mean concentration of surface water at zone 2 than that of zone 1 and a decrease at zone 3. In the case of bottom water, the particulate manganese values did not differ much in the three zones (Figure 5.9).

The variations in station wise seasonal averages are also depicted in Figure 5.9. It can be seen that the pre-monsoon season recorded the widest range and the monsoon season recorded the narrowest range. Figure 5.9 clearly shows that definite seasonal variations were recorded in the distribution


Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 5.9. Seasonal and spatial variations of particulate manganese.

of particulate manganese, the pre-monsoon season showing maximum value and the monsoon season recording the minimum for both surface as well as bottom waters. In the monsoon and post-monsoon seasons, the concentrations were more or less same for stations 1 to 6. In stations 7, 8 and 9, post-monsoon season showed slight increase in the values. Another observation made is that the concentrations of particulate Mn in zones 1 and 2 in the pre-monsoon season were comparatively much higher (Figure 5.9) than those in monsoon and post-monsoon seasons. In the monsoon season, zone 2 recorded the highest values and zone 3 recorded the lowest values. In post-monsoon season, zones 3 and 1 recorded the highest and the lowest values respectively. In the pre-monsoon season also, the surface water behaved in a similar way as that in monsoon season. A similar seasonal difference with increased concentration in the summer has been reported in the River and Estuary of the Rhine (van der Weijden and Middelburg, 1989; Paalman and van der Weijden, 1992), also in the Humber and Scheldt estuaries (Turner et al., 1991). This feature is attributed to increased concentrations of dissolved Mn (II) and its subsequent rapid oxidative precipitation to Mn (IV) at higher summer water temperatures. Laslett and Balls (1995) also confirmed a particulate manganese concentration peak in the summer. The pre-monsoon season is characterized by low flow conditions. This, together with the closing of Thanneermukkom salinity barrier during the pre-monsoon period makes the water body in the Kuttanad region into virtually static. Under these conditions, the probability of coarser particulates, which are impoverished in particulate Mn content, to settle at a faster rate is greater, leaving the finer particulates which are enriched in Mn content into the water column. This is ascribed as another reason for the higher particulate Mn content in the pre-monsoon period. A similar observation was made by Delfino and Otto (1986) from Susquehanna and Bush Rivers for particulate Mn.

Delfino and Otto (1986) recorded a maximum of 12 mg/g of particulate Mn. Jean-Francois et al. (1994) observed a concentration of 1.37

mg/g on Mn_p in the Seine River Estuary. Satyanarayana et al. (1985a) reported still lower values of Mn_p (34.3 – 336 µg/g) from the coastal waters of Visakhapatnam (Bay of Bengal). Owens et al. (1997) observed a highest concentration of 3.99 mg/g from the Tay Estuary. Nolting et al. (1996) observed particulate Mn in the range 0.07 to 3.18 mg/g from Lena River Estuary. As observed in the case of other elements, concentration of Mn in the suspended particulate matter was also higher (mean 24.73 mg/g) in the aquatic environment of Kuttanad. This indicates a substantial enrichment of the particulate Mn compared with an average world river water value of 1.05 mg/g calculated by Martin and Meybeck (1979) for their multi river data set. Manganese is a redox-sensitive element and is relatively mobile in the aquatic environment. The thermodynamically stable state of Mn in oxygenated sea water is the insoluble Mn (+4) oxidation state. In oxygenated water, the soluble Mn (+2) ions will get oxidized to insoluble Mn (+4). Farmers in Kuttanad use large quantity of pesticides, especially mancozeb for agricultural purposes. As a result, large quantity of Mn in soluble and particulate form reaches the backwater system. The soluble manganese may get oxidized to insoluble Mn (+4) when it comes into contact with oxygenated water. This is one of the most probable reasons for the high concentration of particulate manganese in the backwater system of Kuttanad. The resuspension of fine grade sediment particles, which are highly enriched in manganese, from the bottom sediments (Chapter 6) in the comparatively shallow water column is another major reason for the increased concentration of Mn in the particulate phase. The phase association of manganese shows that similar to that of iron, the transport of Mn in the Kuttanad waters is mainly in the particulate phase since particulate manganese was above 99.8 % (Table 5.3 and Figure 5.8). A similar observation was also made by Matkar et al. (1981) from the Bombay Harbour Bay.

PARTICULATE MOLYBDENUM (Mo_p)

Mo is the least abundant trace metal, next to cadmium, in the particulate phase, as observed in the present study (Table 5.1). Concentration of molybdenum in the particulate phase showed a range of values from 3.02 to 830.77 µg/g in surface waters and 2.43 to 674.52 µg/g in bottom waters (Table 5.1). This value is comparatively higher than the particulate Molybdenum concentration in river water (3 µg/g) reported by Martin and Whitfield (1983). Molybdenum showed the least difference between the mean surface water and bottom water concentrations (173.91 µg/g and 135.52 µg/g respectively) after iron. The highest and lowest values in surface waters were recorded at station 5, but in bottom waters, station 7 recorded the lowest and station 8 recorded the highest values (Table 5.8). Surface waters showed station wise annual mean concentrations in the range 106.12 to 214.66 µg/g, whereas in bottom waters the annual mean concentration was found in the range 97.96 to 225.45 µg/g (Table 5.8). The highest annual mean values were at stations 5 and 8 for surface and bottom waters respectively, whereas station 6 recorded the lowest annual mean concentration for both surface and bottom waters. Figure 5.10 gives the trend in the spatial variation of annual mean concentrations of particulate molybdenum. All stations showed higher concentrations in surface waters except at station 8. In general, the annual mean concentrations of molybdenum in surface waters at zones 2 and 3 were almost equal and were less than that of zone 1 but in bottom waters, the value increased slightly at zone 2 which further showed a sharp increase at zone 3 (Figure 5.10).

The season wise averages of particulate molybdenum concentrations are graphically represented in Figure 5.10. The surface waters showed widest range in monsoon season but the same was in post-monsoon season for bottom waters. Comparatively, higher values were observed at stations 1, 2 and 5 for surface waters in monsoon season. Similarly, in bottom waters, station 8 showed higher values in post-monsoon and monsoon periods.

Table 5.8 Station wise summary statistics on particulate molybdenum and nickel (µg/g)

Trace metal	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Molybdenum	1	12.45	6.32	713.51	390.21	204.65	112.38	242.84	117.14	118.66	104.24
	2	31.62	8.17	604.43	277.46	209.56	109.87	171.47	77.15	81.82	70.22
	3	41.18	31.65	357.71	266.78	170.59	129.46	88.92	78.87	52.13	60.93
	4	60.29	83.18	388.42	304.91	172.00	151.04	103.80	74.64	60.35	49.42
	5	3.02	52.08	830.77	228.61	214.66	129.93	225.64	61.19	105.12	47.09
	6	26.46	42.67	315.17	239.36	106.12	97.96	97.07	57.06	91.47	58.24
	7	18.16	2.43	319.07	398.71	162.55	131.16	90.44	103.82	55.64	79.15
	8	3.33	6.30	328.29	674.52	175.08	225.45	97.99	214.34	55.97	95.07
	9	9.30	63.06	333.18	199.30	150.00	132.44	102.12	49.76	68.08	37.57
Nickel	1	9.89	17.71	627.04	368.29	260.61	148.57	209.94	132.07	80.56	88.89
	2	54.02	1.54	629.94	365.15	313.47	126.84	208.73	96.83	66.59	76.35
	3	60.12	19.24	743.55	239.60	239.86	83.34	183.66	59.99	76.57	71.98
	4	86.28	40.32	664.02	784.62	288.71	180.92	192.33	208.34	66.62	115.16
	5	97.58	46.81	844.16	468.08	291.16	137.95	251.49	112.62	86.37	81.64
	6	155.82	30.27	860.38	318.08	392.52	158.01	212.47	87.87	54.13	55.61
	7	8.96	12.28	801.94	847.11	298.31	162.17	265.95	241.78	89.15	149.09
	8	17.39	19.51	731.81	564.56	266.10	188.53	186.56	167.06	70.11	88.61
	9	16.08	39.93	444.28	240.86	206.02	139.33	113.95	65.63	55.31	47.10

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

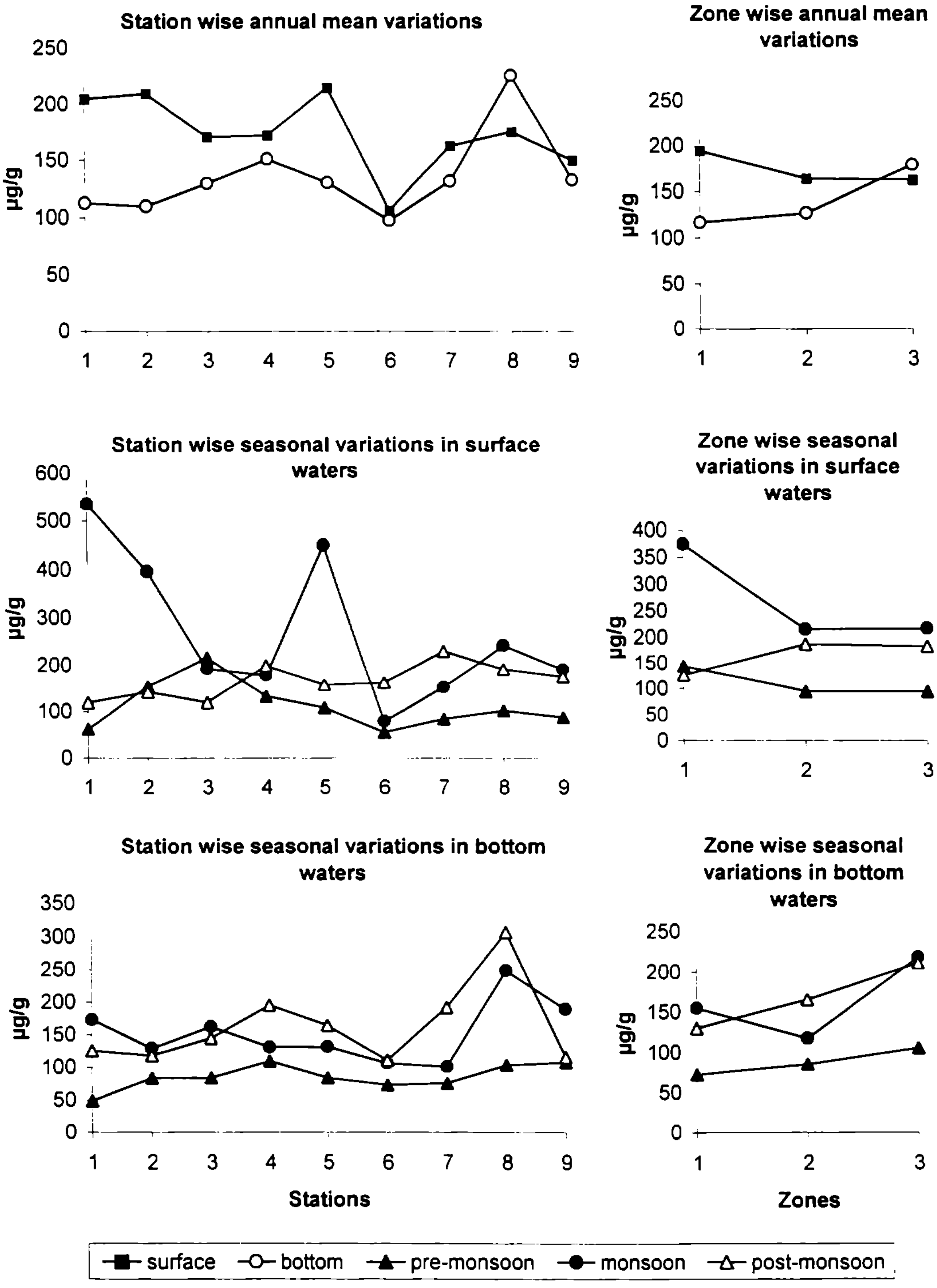


Figure 5.10. Seasonal and spatial variations of particulate molybdenum.

In general, pre-monsoon period showed lowest seasonal average concentrations of particulate molybdenum, especially in bottom waters and for most of the stations in surface waters. The surface water showed higher values in zone 1 than in zones 2 and 3, which were almost equal during pre-monsoon and monsoon seasons, whereas in post-monsoon season zones 2 and 3 recorded higher values than that in zone 1 (Figure 5.10). In bottom waters, zone 3 recorded the highest values in all the three seasons and there was an increasing trend from zone 1 to 3 in post-monsoon and pre-monsoon seasons.

On an average, molybdenum was found almost equally partitioned between dissolved and particulate phases (Table 5.3). From the Figure 5.11, it can be seen that generally, molybdenum shows preference to the particulate phase in the bottom water. This may be due to the higher concentration of suspended matter in the bottom water (Chapter 3), which is enriched in molybdenum. Seasonal diversity in the partitioning behaviour of molybdenum could be seen from (Figure 5.11). During the monsoon season, Mo showed preference to the dissolved phase in the surface and bottom waters.

PARTICULATE NICKEL (Ni_p)

This study showed that nickel in the particulate phase varied from 8.96 to 860.38 µg/g in surface waters and 1.54 to 847 11 µg/g in bottom waters (Table 5.1). The surface water mean concentration was 284.08 µg/g and in bottom water, it was 147.30 µg/g. The station wise annual mean concentrations were in the range 206.02 (at station 9) to 392.52 µg/g (at station 6) in surface waters and 83.34 (at station 3) to 188.53 µg/g (at station 8) in bottom waters (Table 5.8). All stations showed higher annual mean concentrations in surface waters (Figure 5.12). The zone wise variation in the annual mean concentration of Ni in surface water was almost similar to that of Cd, Co, Cr and Mn with the characteristic increase at zone 2 and a decrease at zone 3 than that in zone 1.

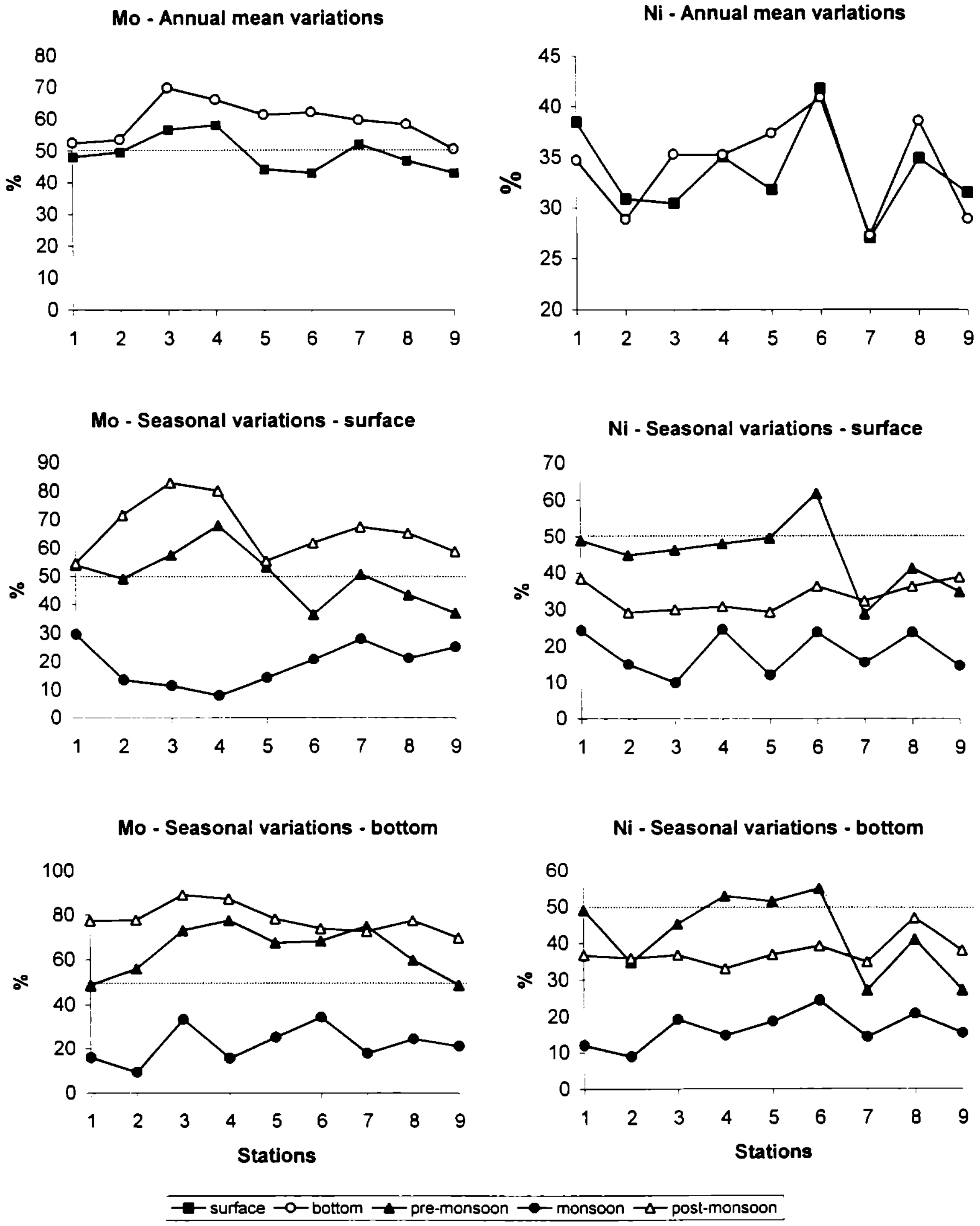
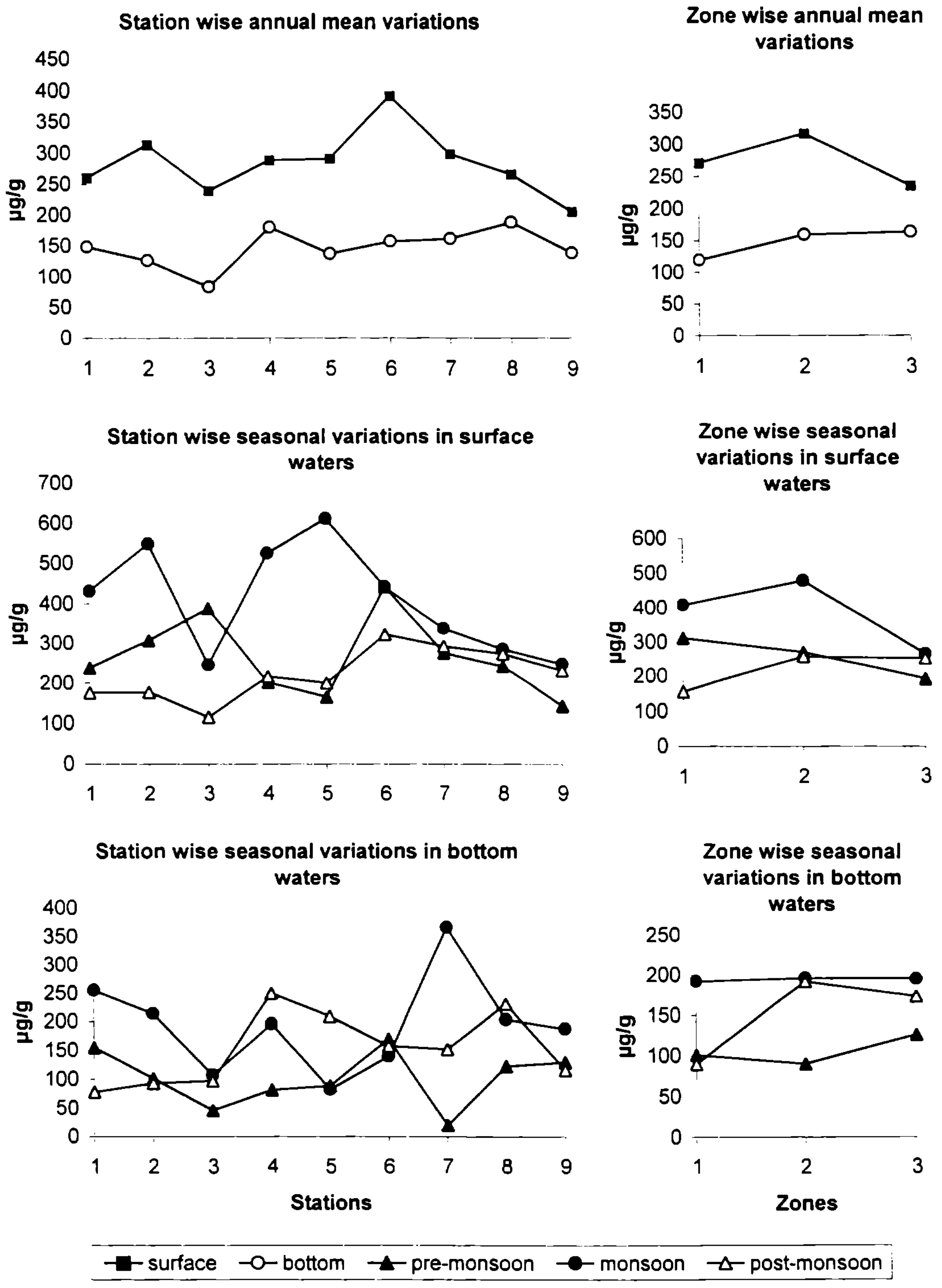


Figure 5.11 Percentage of particulate fractions of molybdenum and nickel in water.


Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations in surface waters

Zone wise seasonal variations in surface waters

Station wise seasonal variations in bottom waters

Zone wise seasonal variations in bottom waters

Figure 5.12. Seasonal and spatial variations of particulate nickel.

Whereas, in bottom waters, zones 2 and 3 recorded almost equal values and was higher than that of zone 1 (Figure 5.12).

Generally, the monsoon average was found to be the highest (Figure 5.12) and the post-monsoon average was the lowest in surface waters but in bottom waters, the trend varied with space. The seasonal variations of nickel in the particulate phase in the three zones are also represented in Figure 5.12. Monsoon season recorded highest values in all the three zones for surface and bottom waters. Lowest values in surface waters were observed in the post-monsoon season for zones 1 and 2 but at zone 3 pre-monsoon value was found to be the lowest. Whereas, in bottom waters, when zone 1 recorded lowest value in post-monsoon season, zones 2 and 3 recorded lowest values in pre-monsoon period. In the monsoon season, the bottom water concentrations of particulate nickel in the three zones did not differ appreciably. The behaviour of particulate nickel in the pre-monsoon season was found to be different from that in monsoon and post-monsoon seasons.

Total nickel (dissolved + particulate) levels are often relatively high, particularly in estuaries and flowing water. Zingde et al. (1988) reported that total nickel in the Mindhola Estuary (India) averaged 94 µg/l with a range of 78 to 131 µg/l. Similarly, average total nickel in the River Hindon (India) was 16 µg/l (range 10-21 µg/l) (Ajmal et al., 1987). For comparison, Nolting (1986) noted that particulate nickel in the Dutch Wadden Sea was lower to a value of 0.6 µg/l. Babukutty (1991) observed Ni concentrations in particulate phase (per unit volume) in the range 2.41 to 10.66 µg/l from the northern side of Cochin estuarine system. In the present study, a comparatively lower range (0.03 to 5.87 µg/l) was observed. This is due to the lower suspended matter concentrations in the water column (Table 3.6, Chapter 3). Jean-Francois et al. (1994) observed 39.91 µg/g of Ni_p from the outer Estuary of Seine River (France). Satyanarayana et al., (1985a) observed slightly higher values (31.8 to 90.6 µg/g) from the coastal waters of Visakhapatnam (Bay of Bengal). Nolting et al. (1996) observed particulate Ni in the range 17 to 80 µg/g from Lena River Estuary. Babukutty and Chacko (1995) reported a mean value of 295.27 µg/g of nickel in the suspended particulate matter from the northern part of the Cochin estuarine system. Ouseph (1992) in another study of Cochin Estuary reported Ni_p concentrations in the range 5 to 80 µg/g. Compared to the above values, higher concentration of Ni in the suspended particulate matter was observed in the present study (mean 215.69 µg/g). The elevated mean value of particulate Ni in the study area may be attributed to the increased percentage of small, probably authigenic particles that were observed in the area. Resuspension of Ni rich fine sedimentary particles (Salomons and Forstner, 1984) may also be contributing to the higher values of particulate Ni. The exchange of fine sedimentary particles between bottom sediments and the water column is highly probable in the shallow water body. In the Acheloos Estuary, Dassenakis et al. (1997) observed that particles having diameter < 8 µm, although consist of a small portion of the total SPM, contain significant percentage of total particulate metals. This study revealed that Ni is preferentially partitioned in dissolved phase (Figure 5.11). The partitioning behaviour of Ni is characterized by the preference of Ni to the dissolved phase at stations 7, 8, and 9 during the pre-monsoon season. These are the stations where maximum salinity intrusion takes place in the pre-monsoon season. This behaviour is attributed to the formation of chloride and sulphate complexes of Ni at higher salinities leading to a depletion of Ni in the particulate phase. Considerable portions of Ni ions were reported to exist in sea water as complexes with chloride and sulphate ions (Nriagu, 1980b).

PARTICULATE LEAD (Pb_p)

In terms of abundance, Pb is the second most abundant trace metal (first being Zn), excluding Fe and Mn, in the particulate phase observed in the present study. Concentrations of lead in SPM varied over a wide range, from 8.82 to 2556.89 µg/g in surface waters and from 16.61 to 2130.79 µg/g in bottom waters (Table 5.9). The mean concentration of particulate lead in surface water was 561.76 µg/g and in bottom water 320.14 µg/g (Table 5.1). The station wise annual mean concentrations (Figure 5.13) show that the concentrations of particulate lead in the bottom waters were lower than that in surface waters. The highest values in surface and bottom waters were recorded at stations 5 and 7 respectively and the lowest values were recorded at station 1. In surface waters, the annual mean concentrations showed a decreasing trend from stations 5 to 9, whereas in bottom waters, there was a decreasing trend from stations 1 to 3. After an increase at station 4, the values again decreased to station 6 followed by another increasing trend towards station 8. It can be seen that the differences between surface and bottom water concentrations of particulate lead in zones 1 and 2 were much higher than the difference observed at zone 3 (Figure 5.13).

Particulate lead concentrations showed seasonal variations, with a general pre-monsoonal depletion of concentration in surface and bottom waters and a monsoonal hike in surface waters (Figure 5. 13). The variations in concentrations of particulate lead among the three zones in different seasons are also represented in Figure 5.13. In the case of bottom waters, the lowest concentration of Pb was observed in pre-monsoon season in all the three zones. The highest concentrations in bottom waters were seen at zones 1 and 3 in monsoon season, but at zone 2, the highest value was recorded in the post-monsoon season. It can be concluded that no definite trend in the variation of particulate lead was observed in the zone wise variations in different seasons.

Tappin et al. (1995) had reported concentrations of Pb in SPM over a range 2 – 844 µg/g from the central and southern North Sea. Slightly higher range of values (223 – 1381 µg/g) was reported from the Visakhapatnam coastal waters (Bay of Bengal) by Satyanarayana et al. (1985a). Jean-Francois et al. (1994) observed a mean concentration of 159.54 µg/g of particulate Pb

Table 5.9 Station wise summary statistics on particulate lead and zinc (μg/g)

Trace metal	Stations	Min.		Max.		Mean		SD		CV	
		S	B	S	B	S	B	S	B	S	B
Lead	1	8.82	16.61	1996.07	1178.70	526.31	373.47	545.30	354.46	103.61	94.91
	2	57.74	39.21	1671.54	748.35	614.33	303.49	542.00	227.54	88.23	74.98
	3	118.02	25.36	977.25	467.09	492.77	185.20	304.61	129.34	61.82	69.84
	4	89.65	100.74	2116.04	1497.65	668.30	413.91	588.71	421.77	88.09	101.90
	5	96.67	28.79	2556.89	1419.03	770.28	284.73	925.01	368.56	120.09	129.44
	6	96.14	93.50	1955.30	749.84	567.32	268.31	598.53	223.31	105.50	83.23
	7	29.25	32.88	1702.08	2130.79	595.98	372.09	576.91	588.52	96.80	158.17
	8	34.36	20.56	1037.98	1444.42	418.53	367.98	324.82	405.92	77.61	110.31
	9	19.59	89.46	1159.11	1009.39	401.98	312.11	356.69	263.89	88.73	84.55
Zinc	1	54.00	85.85	2601.58	1831.21	1100.47	823.50	854.97	434.20	77.69	52.73
	2	183.80	260.73	2604.13	1194.61	1227.72	621.18	793.25	337.69	64.61	54.36
	3	319.60	75.25	2963.84	1073.22	1040.60	523.07	723.39	276.23	69.52	52.81
	4	358.30	251.43	3688.60	3619.02	1130.61	769.73	910.99	950.98	80.58	123.55
	5	459.56	261.77	2600.48	3840.09	984.36	738.76	673.34	1009.84	68.40	136.69
	6	537.67	223.25	4602.59	2090.64	1481.02	791.54	1088.36	556.27	73.49	70.28
	7	109.67	98.73	4451.17	2190.57	1174.96	618.59	1233.05	739.03	104.94	119.47
	8	122.15	125.75	3263.66	2964.68	1020.52	1019.70	828.79	928.17	81.21	91.02
	9	169.60	329.56	2261.98	1317.69	799.83	664.19	523.26	340.55	65.42	51.27

(SD = standard deviation, CV = coefficient of variation, S = surface, B = bottom)

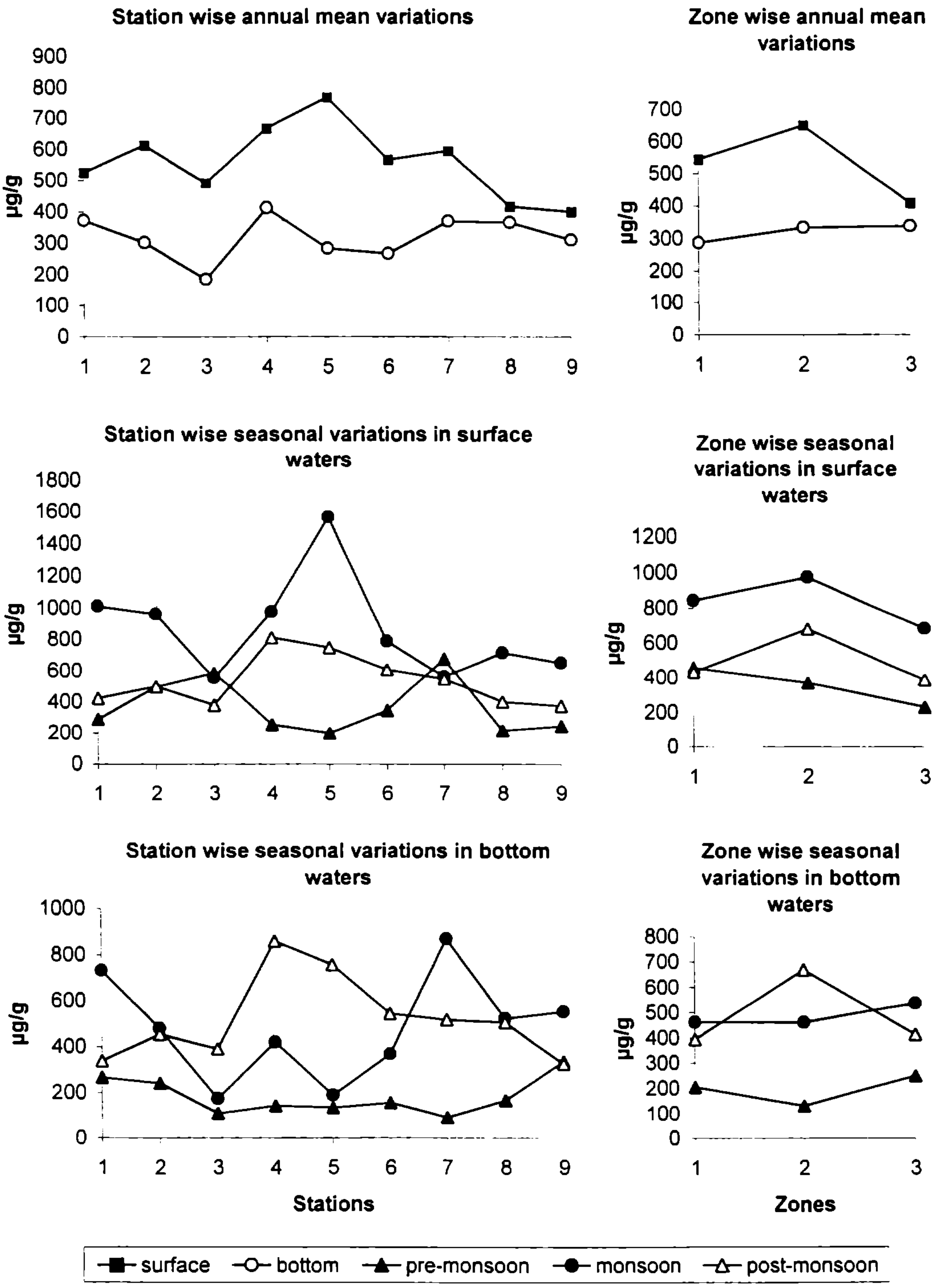


Figure 5.13. Seasonal and spatial variations of particulate lead.

from the fluvial estuarine region of Seine River (France). Nolting et al. (1996) observed particulate Pb in the range 29 to 396 µg/g from Lena River Estuary. Babukutty and Chacko (1995) reported a mean value of 148.55 µg/g of Pb_p from northern parts of Cochin estuarine system. In another study of Cochin Estuary, Ouseph (1992) observed Pb_p concentrations in the range 33 to 260 µg/g. Compared to these values, the concentrations of Pb_p observed in the present study was higher. Resuspension of lead rich sediments, long range transport of lead - rich SPM, and enhanced, though diffuse, atmospheric inputs of Pb were considered to have contributed to the elevated concentration of Pb_p observed in the study area. The depletion in the concentration of lead during the pre-monsoon season is probably because of reduced resuspension of lead-rich material under the low flow conditions. The comparatively higher concentrations of lead in suspended particulate matter in the monsoon season have been explained as partially due to the riverine input of lead rich suspended particulate matter and partially due to the resuspension of lead–rich fine bottom sediments under the high flow conditions during monsoon. The organisms ingest lead adsorbed onto particulate phase, which is solubilised by the acidic gastric juice and is rendered bio-available (Waldichuk, 1985). The range of lead concentration in the particulate phase per unit volume of water (0.26 to 15.01 µg/l) (Table 5.2) observed in the present study was lower than the values reported by Babukutty (1991) (0.6 to 9.71 µg/l) from the northern side of Cochin estuarine system. Particulate lead generally accounts for > 75% of residues in flowing waters and > 50% in standing waters (Whitehead et al., 1988; Zingde et al., 1988; Scoullos and Hatzianestis, 1989). In the present study, lead showed preference to the dissolved phase with an overall mean value of 25 % in the particulate phase (Table 5.3). Seasonality was observed in the partitioning behaviour of Pb_p with the monsoon season showing the least values in the particulate phase in surface waters (Figure 5.14).

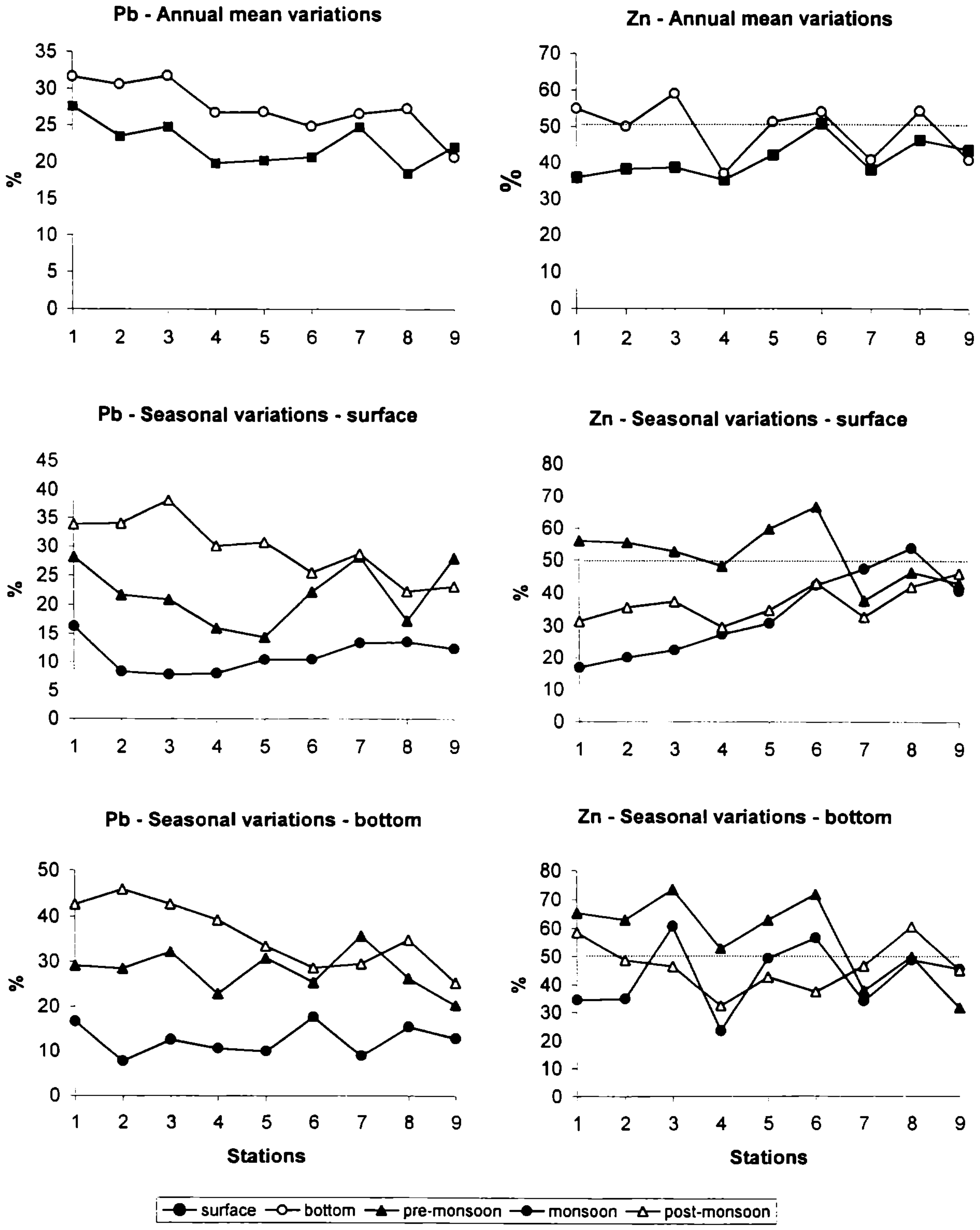


Figure 5.14 Percentage of particulate fractions of lead and zinc in water.

PARTICULATE ZINC (Zn_p)

Out of the ten metals studied, zinc recorded the highest mean concentration in particulate phase, both in surface and bottom waters, besides iron and manganese (Table 5.1). Zinc concentrations in the particulate phase varied by a factor of 85 (54.00 to 4602.59 µg/g) in surface waters and by a factor of 51 (75.25 to 3840.09 µg/g) in bottom waters. The mean concentration in surface water (1106 µg/g) was about one and a half times greater than that of bottom water concentration (730 µg/g). The lowest and highest surface values were recorded at stations 1 and 6 respectively and in bottom waters at stations 3 and 5 respectively (Table 5.9). Variations in station wise annual mean concentrations of particulate Zn are given in Figure 5.15. Figure 5.15 shows that bottom waters recorded lower particulate zinc concentrations in all the stations. Similar behaviour was also observed for the particulate concentrations of cadmium, cobalt, copper, chromium, iron, manganese, molybdenum, lead and nickel in the present study. Zn also behaved in a similar way to that of Cd, Co, Cr, Mn, Ni and Pb in the variations of zone wise annual mean concentrations in surface waters, which was characterised by an increase at zone 2 followed by a decrease at zone 3 than that of zone 1. Bottom waters showed a regular increase from zone 1 to zone 3 (Figure 5.15).

Seasonal variations were observed, but the variations were not uniform throughout the stations (Figure 5.15). In the pre-monsoon season, both surface and bottom waters recorded highest value of particulate zinc in zone 1 (Figure 5.15). In post-monsoon season, the highest particulate zinc concentration was observed in zone 2 followed by zone 3, the lowest being at zone 1. During monsoon season, zone 3 recorded lowest value in surface waters, whereas in bottom waters, zone 3 recorded the highest. At zone 1, the lowest concentration of particulate zinc could be seen in post-monsoon season, whereas the highest concentration was observed either in monsoon or pre-monsoon seasons. At zones 2 and 3, the pre-monsoon season recorded the

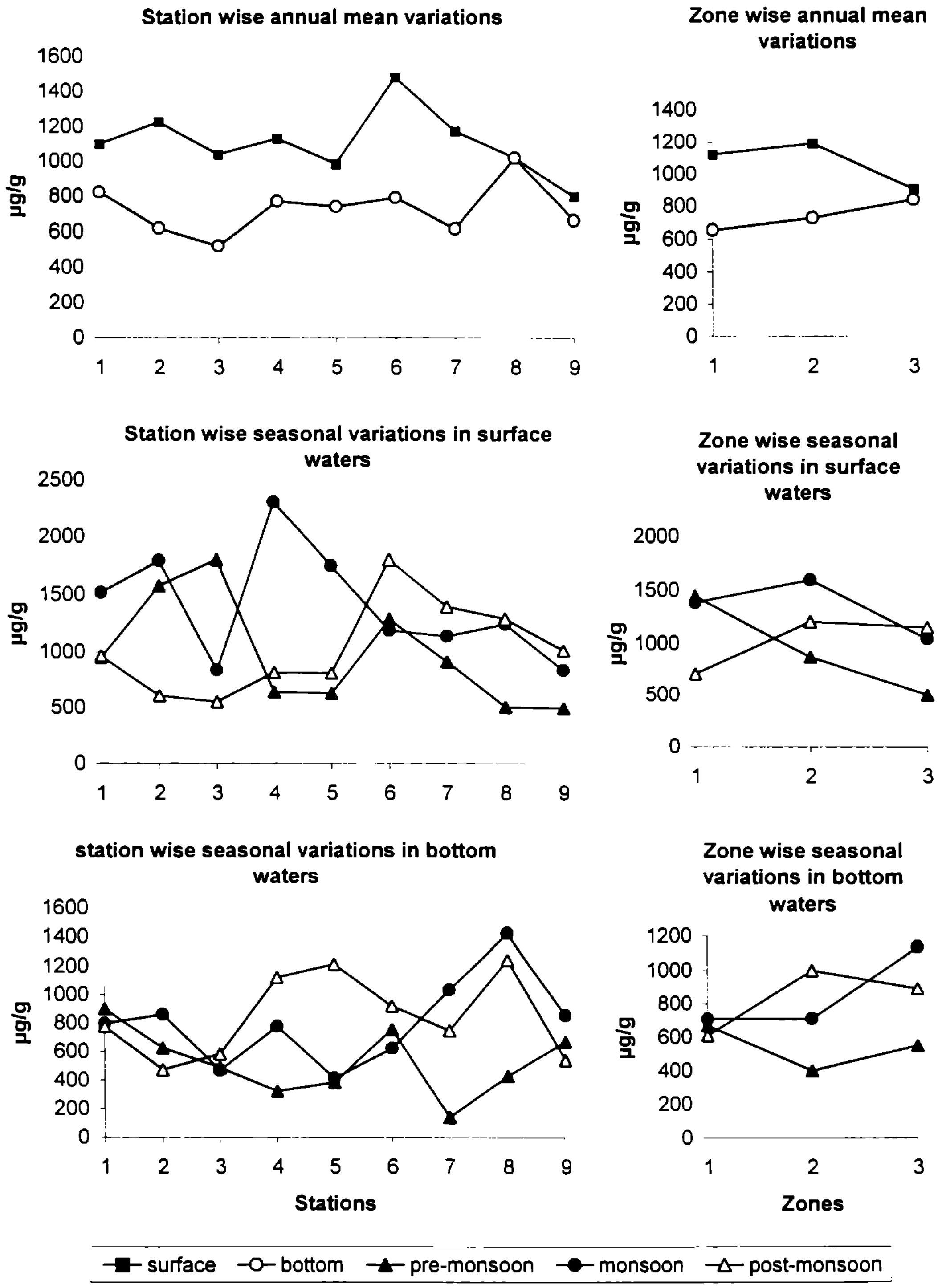


Figure 5.15. Seasonal and spatial variations of particulate zinc.

lowest value in surface and bottom waters, whereas highest value was observed either in monsoon or post-monsoon seasons.

Delfino and Otto (1986) observed that Zn content of SPM ranged from 200 to 1100 µg/g. The multi river average calculated by Martin and Meybeck (1979) was 350 µg/g. Jean-Francois et al. (1994) reported a mean concentration of 542.65 µg/g of particulate Zn from the fluvial estuarine region of Seine River. Nolting et al. (1996) observed particulate Zn in the range 156 to 1982 µg/g from Lena River Estuary. In a study of the northern part of Cochin Estuary, Ouseph (1992) found Zn concentrations in suspended matter varying from 125 - 3100 µg/g. Compared to this, the values observed for particulate Zn in the study area was higher as in the case of other trace metals studied. But the range of values (54 – 4602 µg/g) obtained in the present study was comparable to those reported from the Visakhapatnam coastal waters (Bay of Bengal) by Satyanarayana et al. (1985a). These values suggest that there is enrichment of zinc in the suspended particulate phase. The generally higher values of particulate Zn without a uniform seasonal trend throughout the stations suggest that resuspension of fine material enriched by Zn may be of greater influence in the transport of particulate Zn in the studied area. Another reason can be anthropogenic sources. The lower values of zinc per unit volume of water (in the range 1.95 to 28.10 µg/l) in the particulate phase as compared to the values reported by Babukutty (1991) (in the range 4.71 to 79.32 µg/l) suggest the reduced load of suspended solids in the water column of the study area. Carpenter et al. (1975) found Zn to prevail in the particulate phase during all seasons, whereas this study revealed that soluble Zn predominated in the monsoon and post-monsoon seasons but during the pre-monsoon season, the particulate phase predominated over the dissolved phase (Figure 5.14). In the present study, the percentage of particulate Zn was found to vary from 1.4 to 85.3 (Table 5.3). Matkar et al. (1981) reported 10.9 – 91.8 % of zinc in the dissolved phase from the Bombay Harbour area.

DISTRIBUTION COEFFICIENT (K_D)

The partitioning of trace metals between the solid and solution phases significantly influences their transport and behaviour in the estuarine environment (Morris et al., 1982; Olsen et al., 1982; Morris, 1986; Elbaz–Poulichet et al., 1987; Balls, 1988 & 1989; Laslett, 1995). The distribution of a metal between the dissolved and particulate phases can be expressed by distribution coefficient, or K_D, defined as the ratio of the concentration of metal per unit mass of particulate material (P) to the concentration of the metal per unit mass (or per unit volume) of water (C).

$$K_D = P/C$$

Thus, the relative affinity of trace metals for dissolved and particulate phases in an estuarine region can be evaluated from the respective partition coefficients (K_D). An elevated K_D value indicates affinity for the particulate phase. Ideally, the coefficients should reflect the distribution of metals in equilibrium between the two phases, and the exchange reactions (e.g. adsorption/desorption, oxidation/reduction, precipitation/dissolution or ingestion/excretion). It is frequently assumed that K_D reflects a heterogeneous reaction at equilibrium, but in practice kinetic constraints, imposed by reaction conditions, often prevent the equilibrium from being attained (Tappin et al., 1995). Trace metal K_Ds are highly sensitive to particle type and there is evidence to suggest that some phytoplanktons have a greater affinity for some metals (e.g. Cd, Zn) than lithogenic particles (Wartel et al., 1991; Turner et al., 1992a). K_D value is an effective way of summarizing the interplay between the dissolved and particulate phases and is of fundamental significance in the description of the geochemical properties of elements in the aquatic system and in pollution impact assessment (Martin and Whitfield, 1983; Sibley and Myttenaere, 1986; van der Kooij et al., 1991; Tappin et al., 1995; Wood et al., 1995). In estuaries, where river-ocean fluxes of constituents are modified by abundant anthropogenic inputs are sited, they are of particular relevance. K_D

can be derived from field measurements of dissolved and particulate constituents (Millward and Turner, 1995).

Considerable variations in K_D values occur for all the metals investigated (Table 5.10). Factors contributing to the variability include seasonal differences in the proportions of lithogenous and biogenous particles in suspended particulate matter, and variations in dissolved concentrations occurring independently of those in the composition of suspended particulate matter (Tappin et al., 1995). The dissolved/particulate partitioning of trace metals in estuaries is also influenced by many factors, like pH, changes in salinity, suspended particle concentration, the particle size and the nature of particles (Bourg, 1987; Pohl et al., 1998). Our understanding of the equilibrium processes influencing the partitioning into dissolved/SPM is still poor. Investigation of Santschi et al. (1997) showed the importance of colloidal and particulate organic matter in the partitioning of trace metals. They concluded, that the solution/particle partitioning of metal ions becomes controlled by solution/particle partitioning of the organic ligands. A high value of K_D indicates a strong affinity between the trace metal and particle. Manganese showed the strongest affinity for the suspended particulate matter, with a mean $\log_{10}K_D$ value of 7.35 (Table 5.10). Iron also showed a similar strong affinity to the particulate phase ($\log_{10}K_D$ = 6.19). For these two elements, the particulate percentages of the total load were usually greater than 99.4 % (Table 5.3). Though to a lesser extent, Co followed by Mo, showed affinity for particulate phase. Cr, Cu, Ni, Pb and Zn showed mean $\log_{10}K_D$ values in the range 4.52 – 5.02 and the mean particulate percentages of the total load in water for these elements were less than 50 %. Cd was the least associated with particles, with a mean $\log_{10}K_D$ value 3.76 with 94 % existing in the dissolved phase. A decrease of mean $\log_{10}K_D$ values from 7.35 to 3.76 from Mn to Cd (in the order Mn > Fe > Co > Mo > Cr > Zn > Cu > Ni > Pb > Cd) (Table 5.10) may be attributed to the different bio-geochemical behaviour of these elements in the estuary. Of the ten metals studied, Mn showed the greatest affinity for

Table 5. 10 Overall summary statistics on partition coefficients ($Log_{10}KD$)

Trace Metals	Min.		Max.		Mean		Mean of
	S	B	S	B	S	B	S & B
Cd	2.35	2.24	5.53	5.24	3.92	3.59	3.76
Co	3.97	3.79	7.12	6.62	5.55	5.45	5.50
Cr	3.75	3.60	6.50	6.35	5.10	4.94	5.02
Cu	3.53	3.61	6.16	5.77	4.99	4.77	4.88
Fe	4.42	4.65	7.23	6.81	6.19	6.19	6.19
Mn	5.83	4.69	9.15	8.68	7.48	7.21	7.35
Mo	2.91	2.74	6.89	6.52	5.22	5.09	5.15
Ni	3.15	3.19	5.88	5.60	4.90	4.55	4.72
Pb	2.97	3.00	5.57	5.55	4.65	4.40	4.52
Zn	3.66	3.82	5.95	5.68	5.07	4.87	4.97

(S =surface, B = bottom)

particulate phase followed by iron. Cadmium showed the greatest affinity for the dissolved phase. In a study of the Forth and Tay estuaries, Owens et al. (1997) observed distribution coefficients of trace metals in the order Pb > Mn > Zn > Ni > Cu > Cd. Though, the order is generally in agreement with the observations of the present study, lead is found to have a contrasting behaviour in the study area. In the present study, distribution coefficient of Cd ($\log_{10}K_D$) ranged from 2.24 to 5.53 with a mean value of 3.76 (Table 5.10). On a worldwide basis, the particulate cadmium/dissolved cadmium distribution coefficients ($\log_{10}K_D$) range from 4 to 5 (Yeats and Bewers, 1987). Values of $\log_{10}K_D$ of trace metals reported from different parts of the world are given in Table 5.11. Most of the values were found comparable, however, wider range of $\log_{10}K_D$ values of Mn, Fe, Cu and Ni were found in the present study.

Correlation among variables

To obtain a meaningful interpretation of the distribution of particulate trace metals, the correlation between particulate trace metals and other environmental parameters and also the inter-relationship between different particulate trace metals are discussed. The correlation values are given in Table 5.12. The variations of particulate trace metals with salinity are depicted in Figures 5.16 and 5.17 In general, the distributions of Cd, Fe, Cr, Cu, Mo, Ni, Pb and Zn in the particulate phase showed a non-linear pattern or an inverse relation with salinity ie. the concentrations were found to be decreasing with increase in salinity. This characteristic feature may be explained as due to the desorption and solubilization of particulate metals as salinity increases. The only exception to this behaviour was Co and Mn, which showed positive correlations with salinity. The correlations of Mn with salinity ($p < 0.05$ and < 0.001 in surface and bottom waters respectively) were found to be more significant than that of Co. Recently, Millward et al. (1999) in a study of Humber Estuary observed an inverse relation of particulate iron, manganese, zinc and nickel with salinity. The inverse relationship of particulate iron with salinity can

Table 5. 11 Ranges of $\log_{10} K_D$ values reported for some trace metals from different estuaries.

Area	Cd	Cu	Fe	Mn	Ni	Pb	Zn	References
Baltic Sea(mean)	4.4	4.9						Kremling and Petersen (1978)
Ocean(Calculated mean)	2.9	4.5				5.7		Martin and Whitfield (1983)
Scheldt	3.7 - 5.0	4.4 - 5.3				5.6 - 6.6		Valenta et al. (1986)
English estuaries and Coast	3.5 - 5.0	4.0 - 5.0				5.0 - 7.0		Balls (1989)
Rhine	4.7 - 5.6	4.1 - 5.0				5.7 - 6.4	4.0 - 5.2	Golimowski et al. (1990)
Wall	4.4 - 5.7	3.7 - 5.3				5.8 - 6.8	4.0 - 5.3	Golimowski et al.(1990)
Maas	5.5 - 6.5	4.7 - 5.8				5.8 - 7.1	4.9 - 5.4	Golimowski et al. (1990)
Weser(mean)		4.1		6.2	4.3	6.3	4.8	Turner et al. (1992b)
Seine				3.1 - 5.6			4.1 - 5.4	Boughriet et al. (1992)
Seine	3.9 - 4.0	4.5 - 4.7			4.2 - 4.4	6.1 - 6.3	4.4 - 4.7	Chiffoleau et al. (1994)
Mersey	4.2 - 5.1	4.7 - 5.0			3.8 - 4.4	5.0 - 5.4	4.4 - 4.5	Comber et al. (1995)
Humber	3.2 - 4.3	3.8 - 3.9			3.7 - 3.8		4.2 - 4.6	Comber et al. (1995)
Scottish Sea Loch	2.9 - 4.6	3.2 - 5.6	5.6 - 6.7	5.2 - 7.2	4.6 - 5.1	5.9 - 6.8	5.0 - 5.8	Hall et al. (1996)
Atlantic Ocean	5.1 - 6.2	4.5 - 5.9				4.7 - 6.4		Eckard Helmers (1996)
Forth	3.1 - 6.1	4.2 - 5.7		3.6 - 5.9	4.2 - 5.3	5.1 - 7.0	4.3 - 5.9	Owens et al. (1997)
Tay	3.3 - 5.7	4.3 - 4.8		4.3 - 6.0	4.4 - 4.8	5.4 - 7.1	3.9 - 6.3	Owens et al. (1997)
Kuttanad backwaters	2.2 - 5.5	3.5 - 6.2	4.4 - 7.2	4.7 - 9.2	3.2 - 5.9	3.0 - 5.6	3.7 - 6.0	This study

Table 5.12 Correlation values (r) of particulate trace metals among themselves and with other environmental parameters (n = 108)

	Cd_p		Co_p		Cr_p		Cu_p		Fe_p		Mn_p		Mo_p		Ni_p		Pb_p		Zn_p	
	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B	S	B
pH	-0.096	0.128	-0.365	-0.034	-0.084	0.148	0.050	0.351	-0.025	0.036	-0.302	-0.183	-0.044	0.229	-0.165	0.180	-0.158	0.131	0.047	0.260
DO	-0.038	0.082	-0.053	-0.197	-0.101	0.067	-0.098	0.026	-0.127	-0.160	0.103	-0.335	-0.146	0.136	0.026	0.014	-0.068	0.085	-0.098	-0.038
salinity	-0.189	-0.135	0.078	0.142	-0.245	-0.159	-0.219	-0.226	-0.257	-0.167	0.224	0.327	-0.256	-0.192	-0.126	-0.074	-0.221	-0.134	-0.226	-0.119
SPM	-0.322	-0.405	-0.215	-0.303	-0.430	-0.380	-0.298	-0.389	-0.386	-0.357	-0.180	-0.221	-0.310	-0.274	-0.425	-0.465	-0.322	-0.408	-0.350	-0.457
Zn_p	0.552	0.529	0.318	0.293	0.647	0.618	0.720	0.769	0.378	0.340	0.180	0.163	0.251	0.444	0.625	0.778	0.286	0.730		
Pb_p	0.650	0.795	0.263	0.158	0.686	0.831	0.377	0.591	0.477	0.285	0.091	-0.006	0.625	0.532	0.694	0.889				
Ni_p	0.824	0.759	0.447	0.291	0.758	0.770	0.511	0.650	0.443	0.247	0.423	0.202	0.416	0.458						
Mo_p	0.454	0.233	0.032	0.027	0.581	0.653	0.311	0.536	0.468	0.318	-0.170	-0.167								
Mn_p	0.106	-0.033	0.772	0.736	0.143	-0.003	0.057	-0.046	0.204	0.393										
Fe_p	0.376	0.091	0.434	0.692	0.698	0.478	0.359	0.174												
Cu_p	0.517	0.500	0.239	0.134	0.557	0.561														
Cr_p	0.746	0.616	0.393	0.264																
Co_p	0.230	0.096																		

(S = surface, B = bottom, SPM = suspended particulate matter, '$_p$' = represents particulate form of each metal studied).

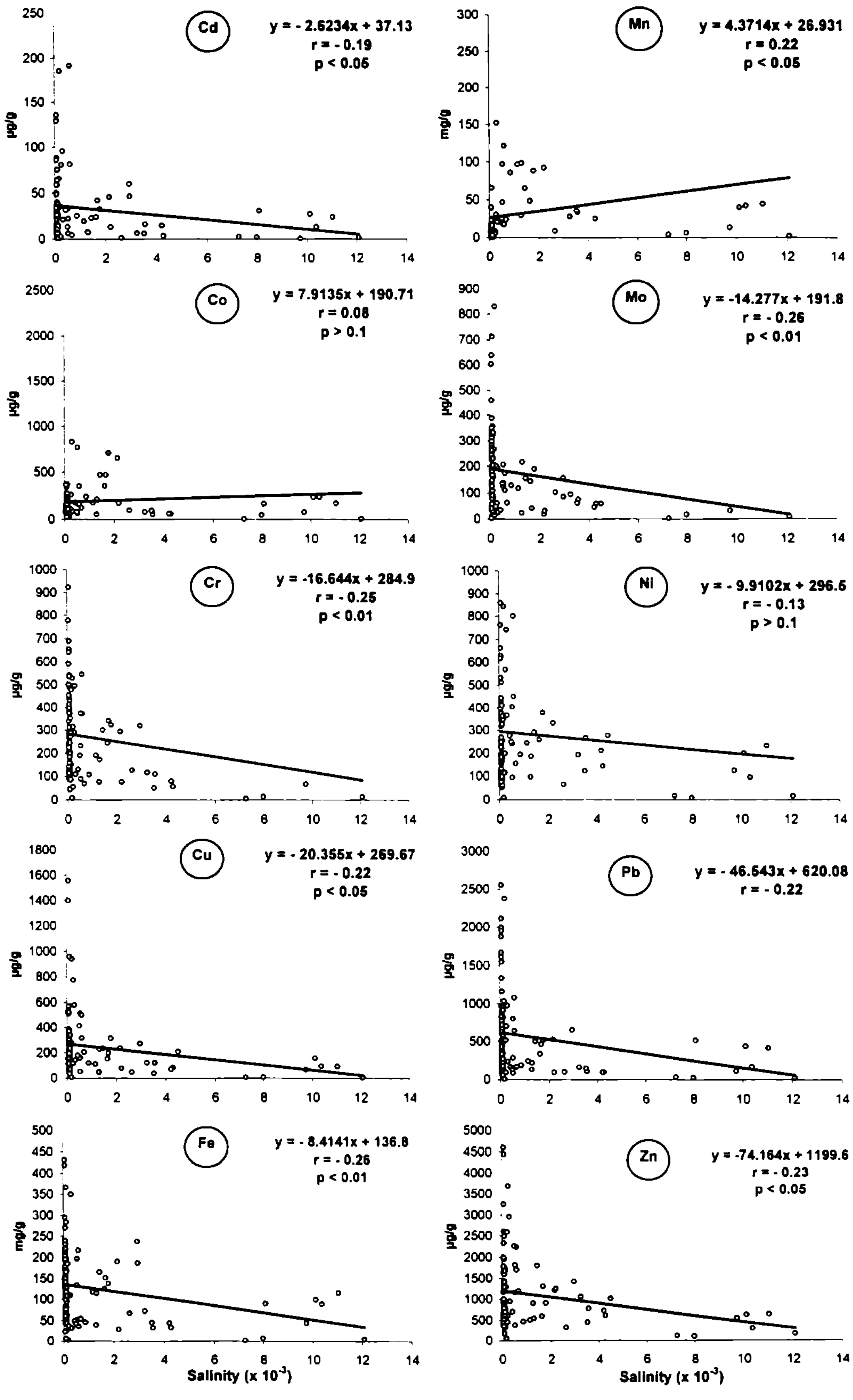


Figure 5.16. Particulate trace metals vs salinity correlation graph (surface water) (n = 108)

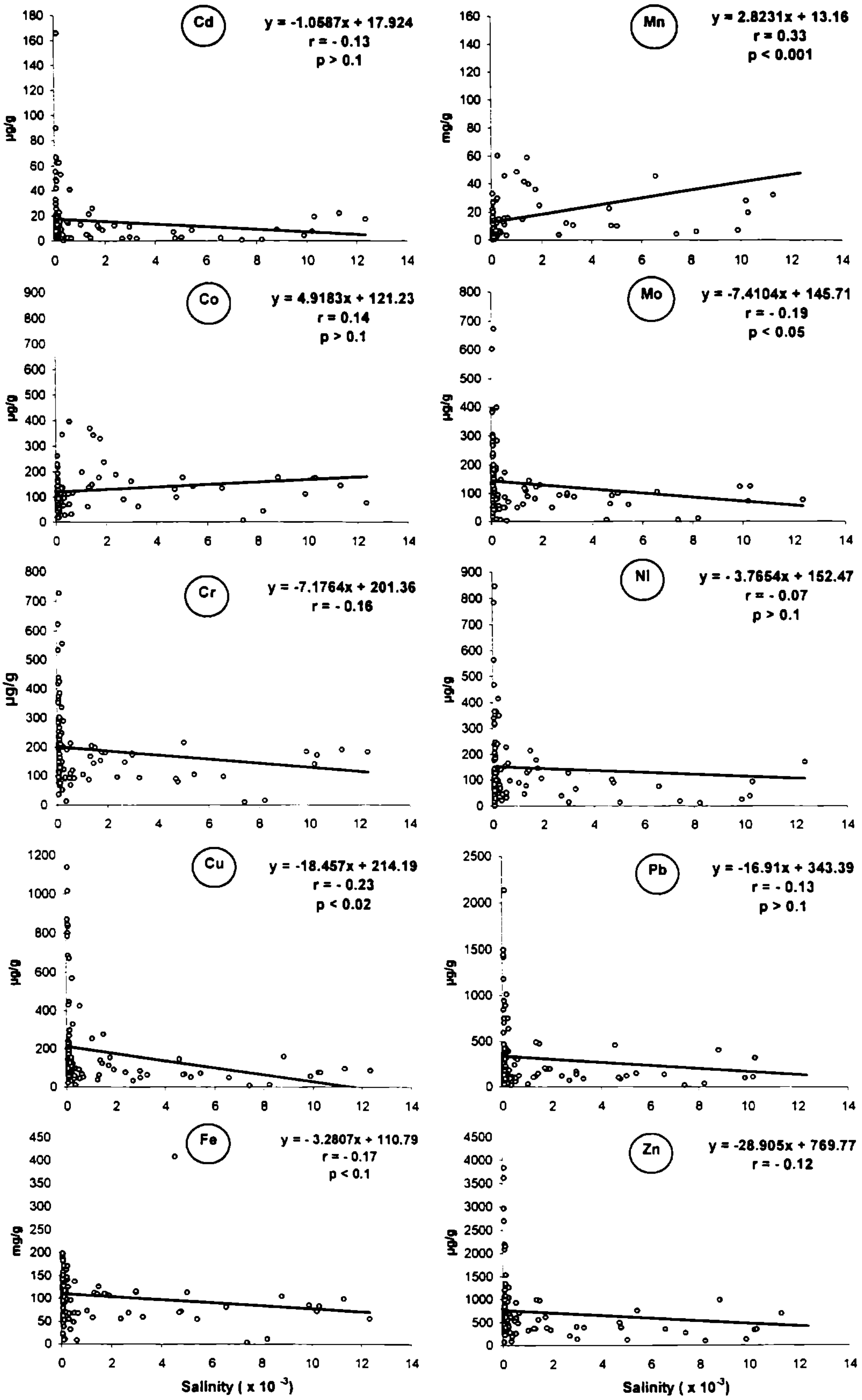


Figure 5.17 Particulate trace metals vs salinity correlation graph (bottom water) (n = 108)

be explained as due to the flocculation and subsequent settling of particulate form of iron with increase in salinity. There are overwhelming evidence, both from laboratory experiments and field investigations, that Cd bound onto suspended matter is (partially) desorbed when river water mixes with sea water (Regnier and Wollast, 1993). Speciation calculations suggest that desorption of particulate Cd during estuarine mixing is due to the formation of chlorocomplexes (Turner et al., 1981; Comans and van Dijk, 1988). Several field studies on the chemistry of dissolved Cd in the Scheldt Estuary have confirmed this hypothesis (Kerdijk and Salomons, 1981; Duinker et al., 1982b; Zwolsman and van Eck, 1990). This behaviour of cadmium is further supported by the fact that $\log_{10}K_D$ values of Cd showed highly significant ($p < 0.001$) negative correlation with salinity. A decrease in the concentration of particulate copper with salinity was also observed by Regnier and Wollast (1993). The behaviour of Mn and to a lesser extent that of Co was just the reverse of other elements. Mn showed positive correlation with salinity, 0.22 ($p < 0.05$) and 0.33 ($p < 0.001$) for surface and bottom waters respectively. In surface waters, Co did not show any significant correlation with salinity ($r = 0.08$), whereas in bottom waters, there was a slight positive correlation with salinity (0.14). Mn is an element, which is very soluble under reducing conditions, which precipitates as soon as the concentration of oxygen increases. Its behaviour can easily be understood in terms of the effect of redox and pH changes in the estuary, better oxidizing conditions corresponding to higher particulate Mn concentrations. The similarity in the behaviour of particulate Co with Mn was also reported by many workers (Heggie and Lewis, 1984; Gendron et al., 1986; Sundby et al., 1986; Kremling and Hydes, 1988). The affinity of cobalt for the manganese oxide phase and the dissolution of Mn oxides in a reductive environment are thought to be responsible for the similar behaviour. The generally observed non-linear distributions of particulate trace metals with respect to salinity are in part, attributable to physical processes such as particle settlement, resuspension of bottom sediment and particle/water exchange of metal and input from external sources to the estuarine mixing zone.

Trace metals tend to be associated with the major labile geochemical phases (e.g. Fe and Mn oxides and hydroxides) and it is the movement of such phases, which determine the transport of trace metals (Balls, 1986 & 1990; Windom et al., 1988; Hall et al., 1996). It is found in the present study that the trace metals are more closely correlated to Fe than to Mn (Figures 5.18, 5.19 5.20 and 5.21). Each element, except Cd and Cu in bottom waters, shows a significant correlation with Fe, which is stronger than that with Mn. A similar observation was made by Balls (1990) in the Clyde Estuary and Hall et al. (1996) from the Scottish Sea Loch. In the Kuttanad backwaters, it was found that all the particulate trace metals, except Mn, in surface waters showed good positive correlation with iron. In bottom waters, except Cd and Cu, all other metals showed good positive correlation with particulate iron (Figures 5.18 and 5.19). These results suggest that iron and manganese oxides are the main carriers of other trace metals in the area, except Cd and Cu. In a recent study of trace metals in suspended matter of Scheldt Estuary by Zwolsman and van Eck (1999), it was observed that Co and Ni get coprecipitated with Mn (hydro) oxide. There was a good positive correlation ($r = 0.423$, $p < 0.001$) of particulate Ni with that of particulate Mn in surface water (Table 5.12). Laslett and Balls (1995) observed that the chemistry of Ni was intimately linked with that of Mn in the Forth Estuary as a consequence of the chemistry of the two metals being dominated by the recycling pattern of Mn. The highly significant positive correlation of particulate cobalt ($p << 0.001$) with particulate Mn (Table 5.12) showed that the chemistry of cobalt in the Kuttanad backwaters is intimately linked with that of Mn. This is a consequence of the chemistry of cobalt being dominated by the recycling pattern of Mn.

It was observed that all the particulate trace metals studied showed an inverse relation with suspended particulate matter concentrations which was evident from the negative correlation of particulate trace metals with suspended particulate matter concentration (Table 5.12 & Figures 5.22 and 5.23). The

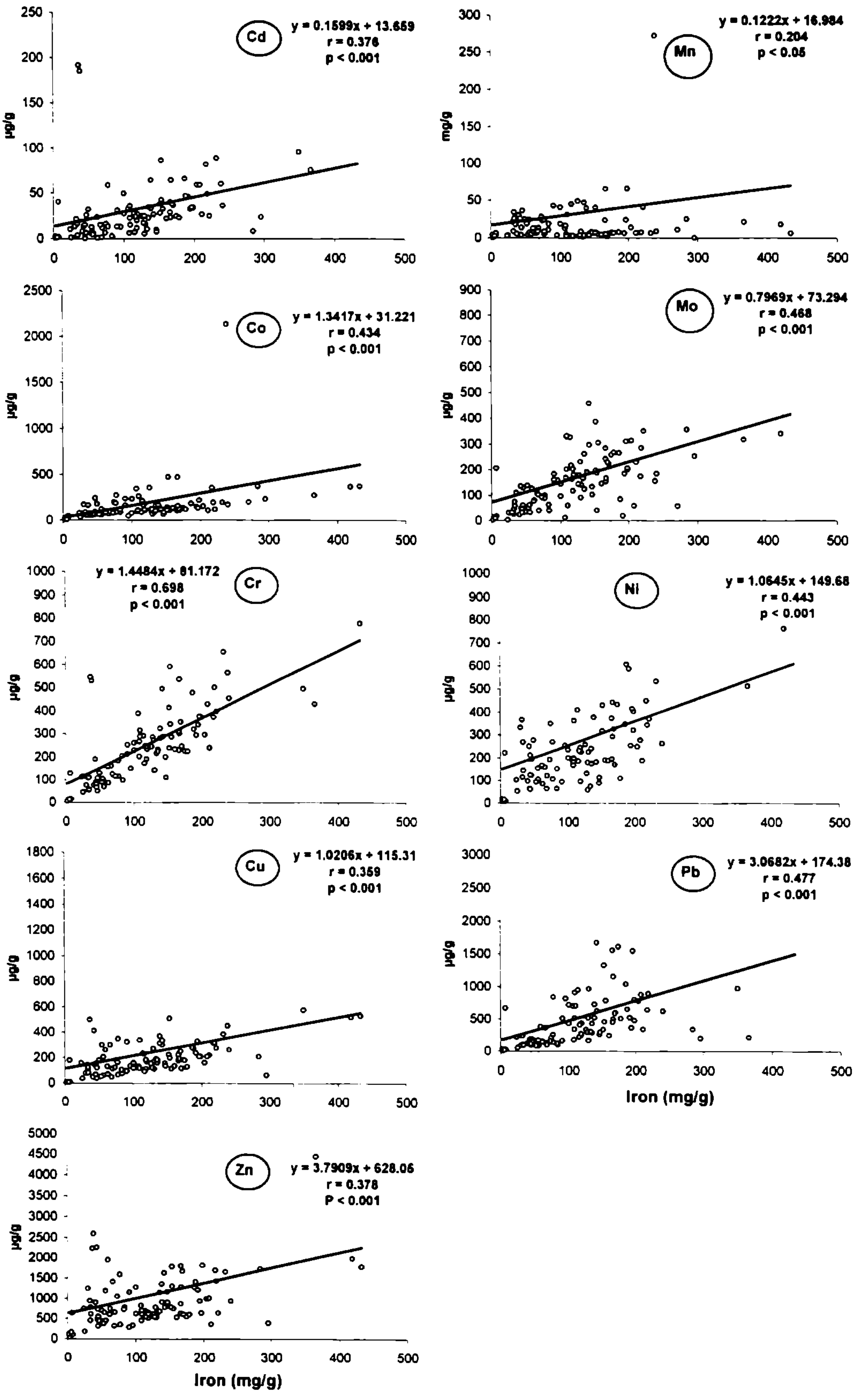


Figure 5.18 Particulate trace metals vs particulate Fe correlation graph (surface water, n = 108)

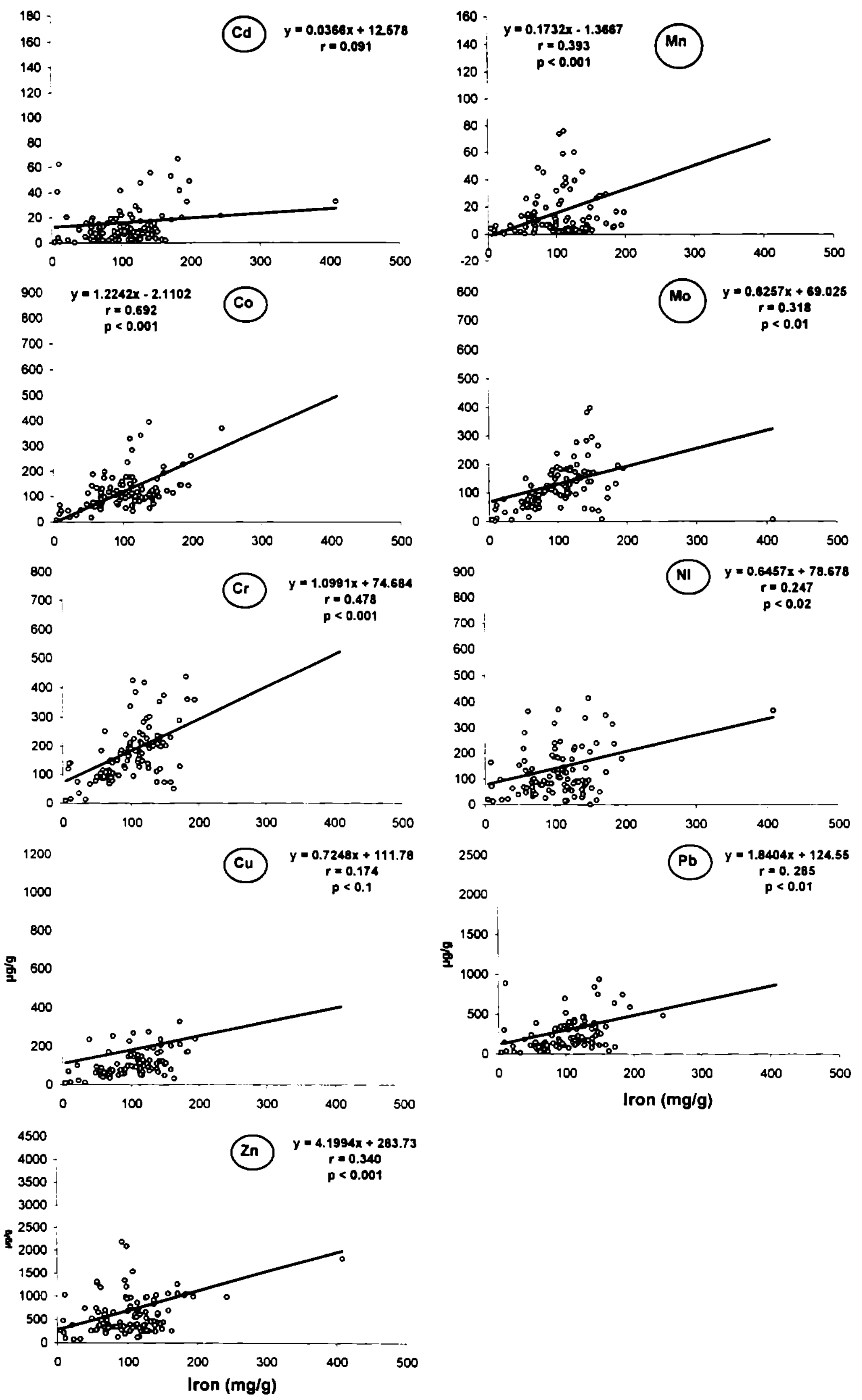


Figure 5.19 Particulate trace metals vs particulate Fe correlation graph (bottom water, n = 108)

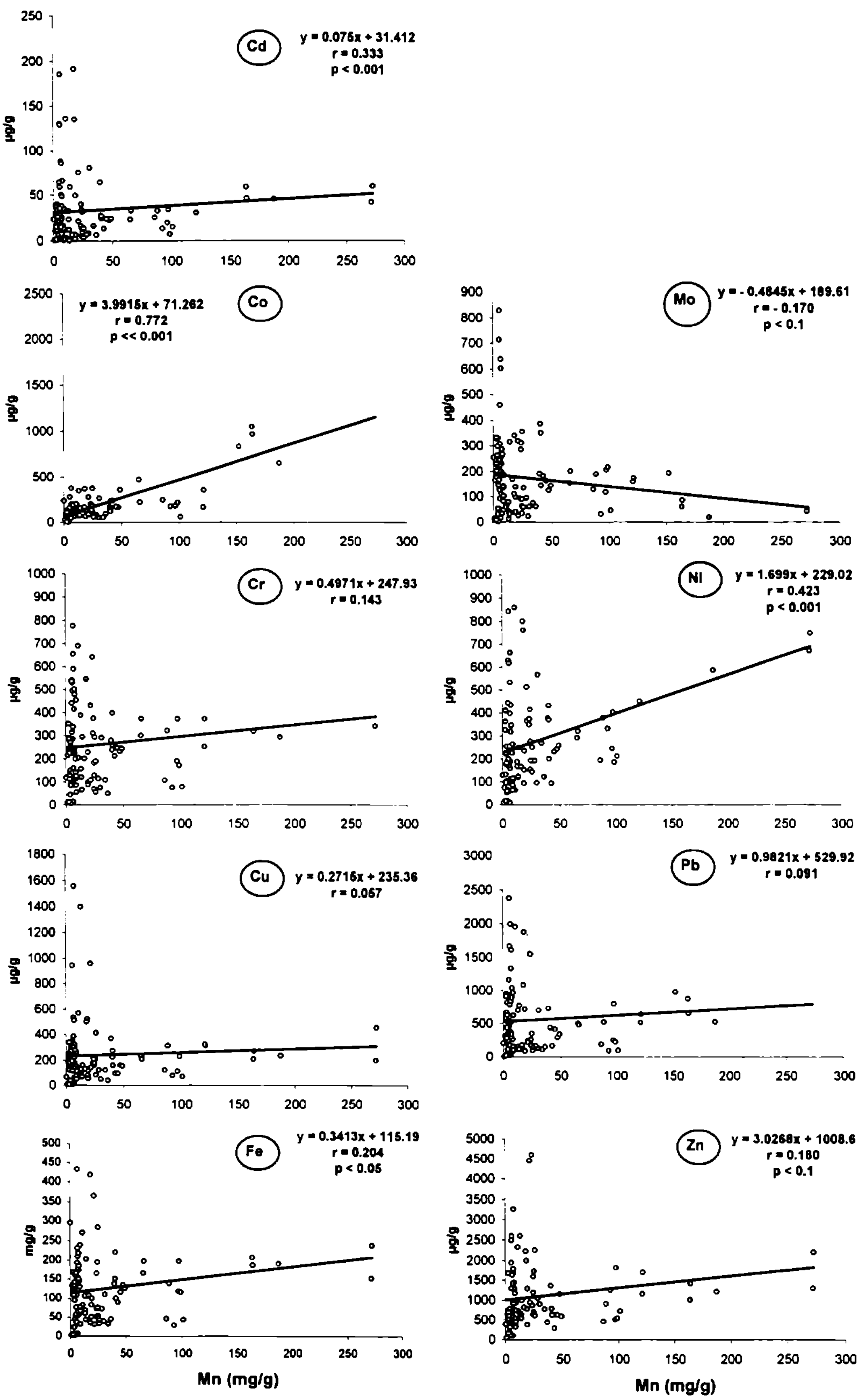


Figure 5.20 Particulate trace metal vs particulate Mn correlation graph (surface water, n =108)

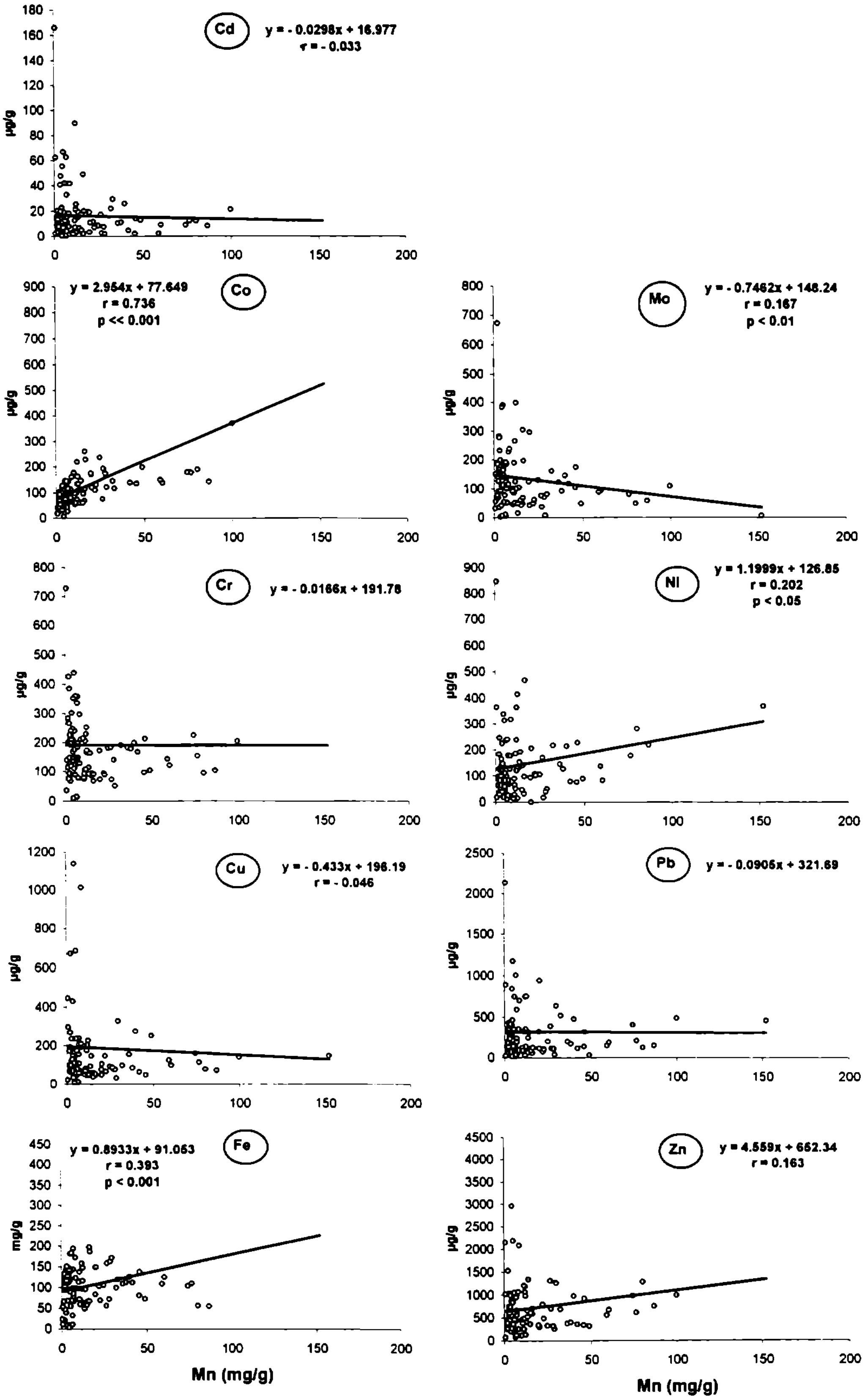


Figure 5.21 Particulate trace metal vs particulate Mn (bottom water, n = 108)

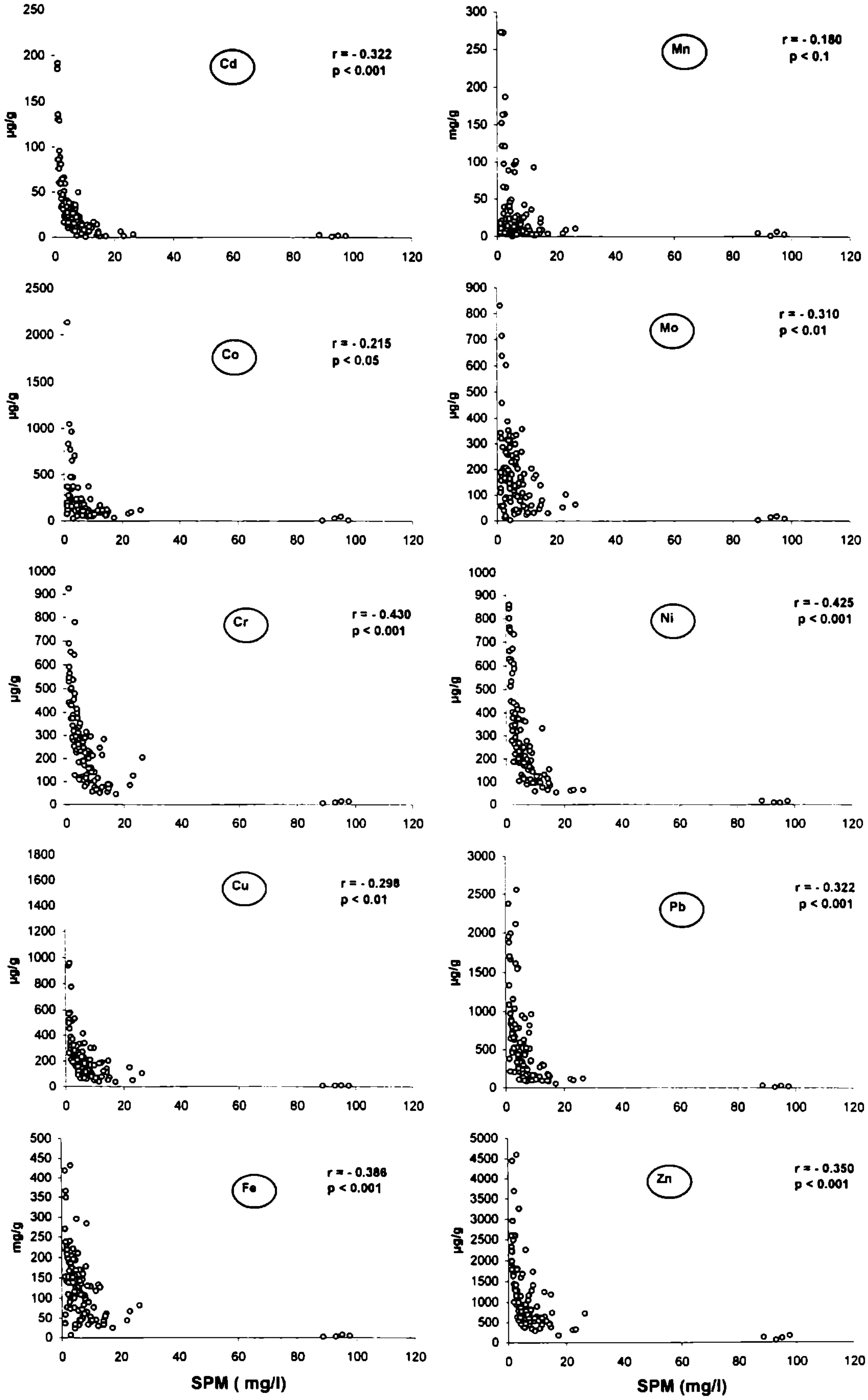


Figure 5.22 Correlation between particulate trace metals and suspended particulate matter concentrations (surface water, n = 108)

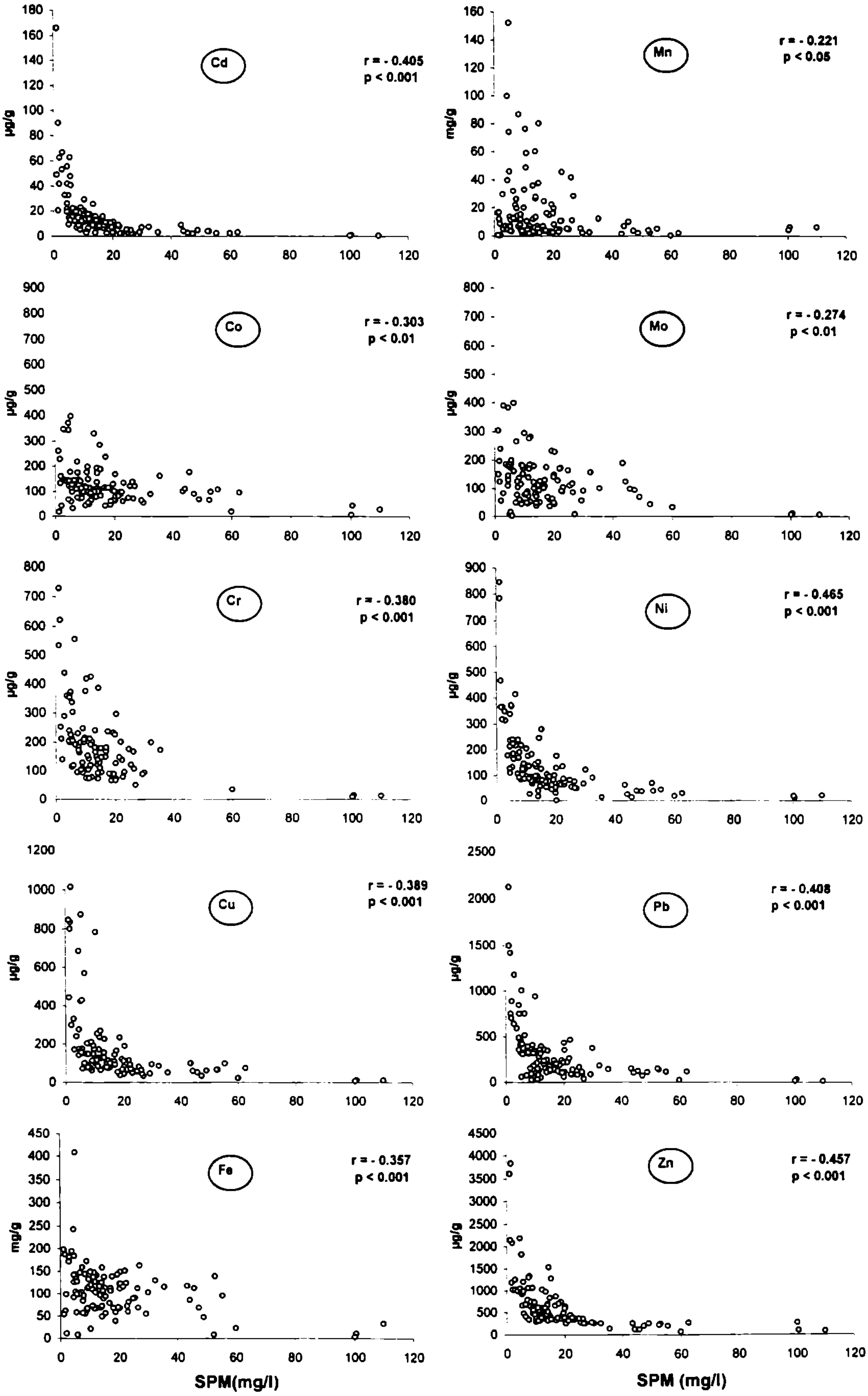


Figure 5.23 Correlation between particulate trace metals and suspended particulate matter concentrations (bottom water, n = 108)

decrease in particulate metal concentration with SPM concentration is the consequence of a higher proportion of the SPM being derived from resuspended sediments. Owens et al. (1997) also observed a similar behaviour of particulate trace metals from Tay Estuary.

From the present study, it was found that $\log_{10} K_D$ values of Cd and iron showed highly significant negative correlations ($p < 0.001$) with salinity. In the case of cadmium, this can be attributed to the desorption of Cd as it forms soluble chloro-complexes at high salinity. This effect has been observed both in mixing experiments (Turner et al., 1993) and in the field study (Comber et al., 1995; Owens et al., 1997). In the Kuttanad backwaters, effect of salinity on the partitioning of iron is found to have cadmium like behaviour since iron also showed a highly significant inverse relationship ($p < 0.001$) with salinity. No significant correlation was found between the partition coefficients for Mn and salinity. This indicates that salinity has practically no role in the partitioning of Mn in the Kuttanad backwaters.

Suspended particulate matter load in the water column was found to influence particle composition as well as partitioning behaviour. A decrease in K_D with increasing SPM loading is common for particle reactive elements and has been termed as the 'particle concentration effect' (Nevissi, 1986; Balls, 1989). The effect has been observed for Pb in the Weser Estuary (Turner et al., 1992b) and in the Forth Estuary (Owens et al., 1997) and for Cd in the Tay Estuary (Owens et al., 1997). In the present study, this type of behaviour was observed for Cd, Cu, Ni, Pb and Zn, which is evident from the highly significant correlation ($p << 0.001$) of $\log_{10} K_D$ with SPM loading in the surface and bottom waters (Table 5.13). Cr, Fe and Mo showed this behaviour in the surface waters only. The effect can be a consequence of higher proportion of the SPM being derived out of the resuspended sediments from the comparatively shallow water body.

Table 5.13 Correlation between $\log_{10}K_D$ values of trace metals and other environmental parameters

Trace Metal	Salinity		SPM		pH		DO	
	S	B	S	B	S	B	S	B
Cd	-0.346	-0.333	-0.552	-0.605	-0.047	0.316	-0.127	0.074
Co	0.072	0.187	-0.301	-0.221	0.035	0.054	0.053	-0.137
Cr	-0.269	-0.357	-0.380	-0.292	0.150	0.319	0.027	0.085
Cu	-0.273	-0.161	-0.649	-0.685	0.091	0.391	0.100	-0.006
Fe	-0.514	-0.426	-0.597	-0.301	0.212	0.268	-0.019	-0.026
Mn	-0.044	-0.003	-0.285	-0.305	0.247	0.183	0.209	-0.250
Mo	-0.265	-0.124	-0.383	-0.266	0.273	0.266	0.015	0.024
Ni	-0.152	-0.042	-0.624	-0.582	0.186	0.408	0.164	-0.204
Pb	-0.225	-0.094	-0.625	-0.535	0.003	0.292	0.035	-0.005
Zn	-0.138	-0.202	-0.477	-0.568	0.097	0.332	0.179	-0.107

CHAPTER 6

METAL PARTITIONING IN SEDIMENTS

6.1 INTRODUCTION

Heavy metals tend to be trapped in estuaries and are thus of particular concern in this environment. Metal concentrations in the particulate form are 3-5 orders of magnitude higher than in the dissolved form (Balls, 1989; Comber et al., 1995) and so the bulk of the trapped metals tend to accumulate within the estuarine sediments (Salomons and Forstner, 1984). Metals accumulated in this way may be subsequently released to the overlying water column as a result of either physical disturbance (Boughriet et al., 1992), or diagenesis (Petersen et al., 1995) or when the environmental conditions change (Izquierdo et al., 1997), and the sediments may persist as a source of pollutants long after the cessation of direct discharges. Therefore, monitoring of trace metal concentrations in sediments is an integral part of any environmental management programme. However, despite their importance, data on metal concentrations in the sediments of Kuttanad are very scarce.

The fertility of an aquatic system is regulated by the chemical environment and is defined by the bioavailability of various chemical species. In the estuarine environment, the sediment-water interaction / partition has a profound role in regulating the chemical and thereby the biological conditions. Any study in the estuarine system will be incomplete if it does not contain the processes that modify or regulate the chemical environment and parameters. Trace metals, because of its persistence and toxicity, are considered to be one of the most potential chemical species, which can modify the fertility of an aquatic system. Though considerable efforts were made on the assessment of the levels of many of the trace metals in the sediment as well as in the overlying water, only scanty data are available on the partitioned characters of trace metals in the sediments of the Indian estuaries.

Estuarine sedimentation

Sedimentary particles in suspension in estuaries are of relatively small size, and that less than 2 µm in diameter are mainly clays, which carry a negative surface charge arising from lattice discontinuities. A double layer of hydrated cations balances this total negative charge. The stability of this charge balance is directly dependent on the ionic concentrations in the bulk water, and as ionic strength increases, there is a tendency for the particles to flocculate as the charge equilibrium is disturbed (Aston and Chester, 1976). The rate of flocculation depends on the extent of particle collisions, and therefore, on the concentration of particle suspensions. Turbulent mixing enhances the collision of particles by Brownian motion (Aston and Chester, 1976).

Studies on the flocculation of clay mineral particles have indicated, in general, that river waters contain unflocculated clay particles, but flocculation occurs in saline waters, where an increase in the total ionic concentration tends to decrease the thickness of the electrical double layer. Below a critical thickness, flocculation occurs. Flocculation is a reversible phenomenon, and particles carried by estuarine circulation back into fresh water will tend to de-flocculate (Dyer, 1972). Thus, in estuaries, the movement of clay mineral mixtures across interfaces between fresh and saline waters at high current velocities usually results in the selective transport of the different clay species.

From the above considerations, it is clear that estuarine environments are not simply areas in which there is direct transport of materials between the continents and the oceans. The initial transfer takes place in estuaries and it is here that the first reactions occur between fresh water and sea water and their associated solids. However, these reactions are not necessarily directly reflected in estuarine sediments, which may in fact have a partially marine origin.

The transport of suspended and bedload materials in estuaries is complex; it is a function of the circulation and stratification of the estuarine waters. Further, it is often difficult to distinguish the bedload from the suspended load in an estuary because what at one stage of the tidal cycle may be bedload can become resuspended at another stage.

Chemical characteristics of estuarine sediments

Trace elements are introduced into estuaries in two principal forms, namely those associated with solid and colloidal materials, and those in solution. When trace elements associated with solid materials are considered, it is convenient to make a fundamental distinction between those elements held in lattice positions within detrital minerals, and those held in surface and non-lattice positions. This distinction is important and necessary because the two fractions show differences in their estuarine behaviour. The elements held in non-lattice positions are particularly susceptible to processes involving reactions between dissolved and particulate forms, with changes in physico-chemical parameters such as pH, Eh, ionic strength etc., which occur in the estuarine system.

From the laboratory experiments of Kharkar et al. (1968), it was shown that some trace elements adsorbed from solution by clay minerals in the river environment are released, to a greater or lesser extent, on contact with sea water. This release probably occurs through ion exchange reactions involving the major cations, such as Na^+ and Mg^{2+} The effect of desorption of trace constituents varies from one element to another. Thus, in addition to the trace elements brought into estuaries in solution, there is an additional source of dissolved material due to desorption from particulate matter reaching the estuarine environment. The desorbed trace elements can either be removed from solution again, or they may remain in solution and be transported by water circulation and eventually reach the open ocean. Trace elements may be removed from solution by a number of processes that include re-adsorption into inorganic and organic detritus and incorporation into estuarine biota. Once taken up by detritus and organisms, they may be either sedimented within the estuary, or may be carried in suspension to coastal and oceanic areas. The adsorption of trace elements from saline waters onto suspended clays, iron and manganese oxides, and organic particulates has been examined (Aston and Chester, 1973: Aston and Duursma, 1973). These studies have shown that although trace elements may be desorbed from river-borne detritus on entering saline waters, the adsorption of trace elements is also possible under saline conditions.

One important mechanism operative in the removal of trace elements from solution during estuarine mixing may be the formation of iron oxide coatings on clay particles, which have acted as negatively charged nuclei for the adsorption of hydrolysis products of iron. Oxides of iron and manganese are very efficient scavengers of trace elements and Aston and Chester (1973) have suggested that the oxide coatings formed on detrital particles in estuaries may remove trace elements from solution in the estuarine environment, and furthermore, they may also prevent the trace element desorption from ion exchange sites. Differences in local conditions, particle size and organic matter content can have a large effect on trace element concentrations (Hallberg, 1974; Brook and Moore, 1988).

Thus, it may be concluded that estuaries are an important stage in the transport of river-borne solids to the oceans. It is in these environments that the solids have their initial contact with saline waters, and some of the processes occurring have an important effect on the oceanic cycles of many elements.

Heavy metals like Zn, Cu, Pb, Ni, Co, Mn, Fe and Mo are natural constituents of sediments. Generally, the concentrations of these metals in river sediments reflect the occurrence and abundance of certain rocks or mineralized deposits in the drainage area of the river. At present, however, the anthropogenic input of certain heavy metals into the environment equals or exceeds the amount released by weathering.

A large part of anthropogenic discharge of metals into the environment becomes part of the suspended matter in rivers, which acts as an efficient scavenger for these metals. When flow velocity slackens, coarser-grained particles and aggregates will settle. This sedimentation takes place especially in estuaries. Therefore, sediments reflect the extent of pollution in a given area. However, part of the suspended matter, the very finely grained particles and colloidal material, has a very low settling velocity and may remain in suspension for long periods of time and so be transported over large distances. Generally, for most heavy metals, there is higher concentration in the suspended matter compared with that in the deposited sediment (Duinker et al., 1974; Borole et al., 1982; Ramesh et al., 1990; Biksham et al., 1991).

After deposition, the chemical environment of the sediment is different from that during transport. Generally, the pH is lower and the sediment often becomes anoxic. Together with other changes in the chemistry of the sediment, these factors can bring about some release of the heavy metals to the interstitial water (mobilization).

The bioavailability of many of the metals is so governed by the sedimentary sorption of these metals. The sediment contains a wide spectrum of inorganic clay minerals. These clay minerals contribute a large variety of sorption sites, which are of different chemical character and potential, to the sediment. Moreover, the organic matter, which forms part of the sediment, will be supplementing to the sorption sites. Thus, the sedimentary surface can be considered as a multitude of heterogenic sorption sites.

Though environmental pollution is clearly demonstrated by the high concentrations of heavy metals in water and aquatic sediments, a question arises as to what percentage of the total concentration of heavy metals in sediments will be available for release to the water over a long period of time. Knowledge of the total amount of metals does not indicate the risk of toxicity or the nature of the various geochemical processes which may be taking place. Moreover, such studies have not yielded information regarding the partitioning of trace elements between the various components of the sediments and their potential to affect water quality under different environmental conditions. Information on total metal concentrations alone is not sufficient because heavy metals are present in different chemical forms in sediments and only part of the metal present can be easily remobilized. The identification of the main binding mechanisms of trace metals not only helps our understanding of chemical processes involved, but also allows us to estimate the potential for mobilization and bioavailability of the metal (Hall et al., 1993; Fernandez-Turiel et al., 1994; Izquierdo et al., 1997).

The most widely used methods for determining the different forms of metals in sediments are based on sequential extraction procedures, whereby several reagents are used consecutively to extract operationally-defined phases from the sediment in a set sequence (Lopez-Sanchez et al., 1993). Partitioning studies are not only very useful for determining the degree of association of the metals in the 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. Metals with an anthropogenic origin are mainly obtained in the first extractions, while in the last stage of the process, the residual fractions are obtained, corresponding to metals with lithogenic origins (Izquierdo et al., 1997). Several workers have attempted to elucidate and predict the availability of metals from the sediment phase both by conventional and sequential extraction techniques (Luoma and Jenne, 1976; Bryan and Hummerstone, 1978; Luoma and Bryan, 1979; Tessier et al., 1979; Tessier et al., 1982; Luoma, 1983 & 1989; Samanidou and Fytianos, 1987; Tessier and Campbell, 1987; Rauret et al., 1988; Campbell and Tessier, 1989; Gunn et al., 1989; Nair et al., 1991; Nair and Balchand, 1993; Thomas et al., 1994; Izquierdo et al., 1997; Singh, 1999; Panda and Sahu, 1999; Mortimer and Rae, 2000).

Some of the earlier investigations carried out to assess the trace metal content of sediments of Cochin Estuary were Murty and Veerayya (1981), Venugopal et al. (1982), Paul and Pillai (1983a), Ouseph (1987), Nair et al. (1990) and Jayasree and Nair (1995). Of these, Murty and Veerayya (1981) studied the distribution pattern of Fe, Mn, Ti, Ni, Co and Cu in the sediments of Cochin Estuary and in the Vembanad Lake. This was the only study, which reported trace metal distribution from the southern upstream part of the Cochin Estuary. The present study was conducted during the period November-December 1969, before the construction of the salinity barrier at Thanneermukkam. This Chapter briefly describes the trace metal levels (Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn) in the surface sediments of the Kuttanad backwater system and their association with different chemical phases of the sediments.

6.2. MATERIALS AND METHODS

Details regarding sampling location, sampling interval and chemical analyses of the samples are furnished in Chapter 2, except the difference that the analyses of samples during the collection of March–96 and September–96 could not be included for partitioning studies of trace metals in sediments due to some technical difficulties. As discussed in Chapter 2, the fractions of trace metals identified are,

1. The exchangeable fraction
2. The reducible fraction
3. The organic fraction including residual fraction

The numbers representing the fractions are used (in Figures and text) along with the chemical symbol of the element to represent the respective fractions of the element for discussion. Total metal concentration has been denoted by adding the subscript T to the chemical symbol of the metal. Thus, Cd_1, Cd_2, Cd_3 and Cd_T represent the exchangeable fraction, reducible fraction, organic plus residual fraction and the total cadmium respectively in sediments.

6.3. RESULTS AND DISCUSSION

The monthly data on total cadmium, cobalt, chromium, copper, iron, manganese, molybdenum, nickel, lead and zinc in sediments are given as Annexure 4 and the monthly data of different fractions of the above trace metals in the sediments are given as Annexure 5. The overall summary statistics on the total content of Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn in the sediments, giving the minimum, maximum, mean, standard deviation and percentage coefficient of variation are furnished in Table 6.1. Table 6.2 gives the overall summary statistics on different fractions of the above mentioned trace metals. Concentrations (total) of some trace metals in sediments reported from different parts of the world are given in Table 6.3. Of the ten metals studied, the most abundant was iron followed by manganese and the least abundant metal was cadmium. The observed order of abundance was iron > manganese > chromium > zinc > molybdenum > cobalt > lead > nickel > copper > cadmium. The concentrations of these metals varied widely; the minimum variation (% C.V. = 40.19) was recorded in the case of zinc and the maximum (% C.V. = 60.79) was recorded in the case of copper (Table 6.1).

Table 6.1 Overall summary statistics on total metal distribution in sediments (n = 108)

Trace Metal	Min.	Max.	Mean	SD	% CV
Cadmium	0.47	5.23	2.00	1.19	59.43
Cobalt	5.41	171.51	61.01	32.81	53.79
Chromium	13.00	283.73	156.29	76.05	48.66
Copper	3.09	69.55	31.73	19.28	60.79
Iron	0.50	18.26	6.88	3.68	53.46
Manganese	0.07	1.38	0.54	0.29	53.76
Molybdenum	6.39	194.72	88.47	49.93	56.44
Nickel	8.89	91.55	52.71	23.45	44.49
Lead	5.08	103.85	54.96	22.62	41.17
Zinc	21.06	276.55	138.81	55.78	40.19

(Fe in %, Mn in mg/g, others in µg/g, SD = standard deviation, CV = coefficient of variation)

Table 6.2 Overall summary statistics on distribution of trace metals in different chemical fractions of sediment.

Fractions	Concentration (µg/g)					Percentage		
	Min.	Max.	Mean	SD	%CV	Min.	Max.	Mean
Cd_1	< 0.01	0.35	0.11	0.10	96.31	0.01	34.48	7.44
Cd_2	0.05	1.19	0.41	0.20	49.33	1.48	93.28	28.15
Cd_3	0.03	4.33	1.48	1.14	77.17	4.75	98.18	64.41
Co_1	0.04	5.00	1.65	1.19	72.01	0.04	10.24	3.17
Co_2	1.45	24.81	12.56	6.29	50.05	4.44	49.24	23.87
Co_3	3.92	163.83	48.13	30.63	63.64	44.39	95.53	72.97
Cr_1	0.20	7.75	2.68	2.06	76.69	0.13	13.18	2.28
Cr_2	1.03	36.63	17.43	9.27	53.16	3.59	31.62	11.98
Cr_3	11.08	268.41	143.18	69.87	48.80	67.62	95.94	85.74
Cu_1	< 0.01	0.46	0.10	0.10	96.20	< 0.01	2.01	0.37
Cu_2	0.08	4.43	1.13	1.11	97.77	0.41	9.69	3.33
Cu_3	2.90	65.53	31.84	18.81	59.06	90.08	99.53	96.30
Fe_1	0.15	1756.99	372.63	446.09	119.71	< 0.01	3.42	0.55
$*Fe_2$	1.19	40.02	14.53	8.31	57.18	4.84	69.89	24.94
$*Fe_3$	3.85	168.47	55.47	34.58	62.34	30.09	95.16	74.52

(* Fe_2 and $*Fe_3$ are in mg/g, SD = standard deviation, CV = coefficient of variation)

Table 6.2 (Contd.) Overall summary statistics on distribution of trace metals in different chemical fractions of sediment

Fractions	Concentration (µg/g)					Percentage		
	Min.	Max.	Mean	SD	%CV	Min.	Max.	Mean
Mn_1	2.62	431.33	173.18	102.99	59.47	2.92	57.28	32.97
Mn_2	22.77	360.59	129.79	70.31	54.18	7.83	77.63	26.82
Mn_3	2.30	1196.70	243.77	214.32	87.92	1.78	86.67	40.21
Mo_1	0.91	3.57	2.25	0.62	27.62	1.15	27.90	4.14
Mo_2	2.07	14.43	7.54	2.84	37.68	3.76	37 16	11.50
Mo_3	2.54	182.55	77.48	46.75	60.33	39.77	94.76	84.36
Ni_1	0.89	10.52	4.29	2.40	55.89	1.42	34.43	9.53
Ni_2	6.03	29.83	16.14	5.52	34.19	14.30	76.80	35.80
Ni_3	0.13	68.01	33.29	18.81	56.52	1.08	80.62	54.67
Pb_1	0.03	10.27	3.08	2.96	95.97	0.04	35.65	6.34
Pb_2	1.90	31.02	12.92	6.47	50.08	4.85	61.46	23.98
Pb_3	0.82	81.95	41.82	18.60	44.48	7 10	94.60	69.68
Zn_1	0.07	8.08	1.28	1.73	134.88	0.05	4.78	0.85
Zn_2	1.88	34.32	15.67	7.87	50.21	2.39	32.97	11.66
Zn_3	16.16	250.07	126.07	51.59	40.92	66.00	97.49	87.50

(SD = standard deviation, CV = coefficient of variation)

Table 6.3 Mean (or range of) values of trace metals in sediments reported from different parts of the world (μg/g)

Location	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Average Shale	0.3	20	100	50			80	20	90	Turekian and Wedepohl (1961)
Gulf of Mexico shelf		5.0	49.0	10.0			29.0	24.0		Holmes (1973)
Clyde Sea	0 - 1.5			3.0 - 17.0				12.0 - 45	34 - 102	Steele (1973)
Sewage site			102	142			23	173	252	Carmody et al. (1974)
Turkey point, Florida	0.33			10.0			25.0	2.0	5	Segar and Pollenberg (1974)
Narragansett Bay	0.5	4.7	46.0	53.0			18.0	44.0	110	Eisler et al. (1977)
Baffin Bay coastal						120 - 660				Campbell and Loring (1980)
Greece						204 - 2334				Chester and Voutsinou (1981)
California (Municipal outfall zone)	12.0		260.0	164.0			52.0	102.0	332	Hershelman et al. (1981)
Southern part of CES		30 - 82		3.0 - 100	2.2 - 73.7	120 - 600	10.0 - 60			Murty and Veerayya (1981)
Narmada Estuary				136	89.0	1097	81		140	Borole et al. (1982)
Tapti Estuary				128	76.0	1125	70		125	Borole et al. (1982)
Northern part of CES		10.0 - 43		17 - 71		73 - 318	22 - 82		103 - 664	Venugopal et al. (1982)
World average (top soils)	0.4	8	70	30	40.0	1000	50	35	90	Martin and Whitfield (1983)
Northern part of CES	0.8 - 18			5.0 - 61	4.4 - 29.1	15 - 640	3.0 - 45		116 - 1385	Paul and Pillai (1983a)
Northern part of CES	0.1 - 6.5	2.0 - 42	5.0 - 96	8.0 - 63	3.1 - 90.6	44 - 1439	14 - 85	3.0 - 46	10.0 - 417	Mallik and Suchindan (1984)
Bombay Harbour	10	50	124	105	86.0	1140	111	48	155	Patel et al. (1985)
Visakhapatnam outer Harbour	11	11		41	58.0	490	37	104	4240	Satyanarayana et al. (1985b)
Indian average (river sediment)		31	87	28	29.0	605	37		16	Subramanian et al. (1985)
Thana Creek, India	2.3	32	51	115	70.0	867	117	52	146	Mahajan et al. (1987)
Ulhas Estuary, India	2.3	44	86	97	63.6	230	93	37	149	Mahajan et al. (1987)
Ashtamudi, Kerala				60	1.8		12	38	60	Nair et al. (1987)
Northern part of CES	0.5 - 8.4		7 - 130					10.0 90	35 - 780	Ouseph (1987)
Godavary River		47	126	82	57.0	1070	51	11	54	Subramanian (1987)
Black Sea						127 - 620				Andreev and Simeonov (1988)

Table 6.3 (contd.) Mean (or range of) values of trace metals in sediments reported from different parts of the world (μg/g)

Location	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Godavary Estuary			128	119	76.0	1294	91	5		Biksham and Subramanian (1988)
Belgium						98 - 136		12.0 - 16	45 - 59	Fatima et al. (1988)
Ganges Estuary			98	44	42.0	732	49	32	151	subramanian et al. (1988)
Mindhola Estuary				113		1109	92	19	157	Zingde et al. (1988)
Indonesian coast	0.1 - 0.2			40 - 50				25 - 35		Everarts (1989)
Guipuzcoa, Spain	0.1- 0.3		5 - 160	10.0 - 230						Legorburu et al. (1989)
Cauvery Estuary, India	1.8		229	33	34	1310	379	38	75	Subramanian et al. (1989)
Beufort sea		10.5	70.0	44.0	280.0	377	33.0		99	Sweeney and Naidu (1989)
Spencer Gulf, S. Aust.	0 - 270									Tiller et al. (1989)
Red Sea	0.8 -9			3.0 - 28					2.0 - 180	Abu-Hilal and Badran (1990)
Humber Estuary, UK			214 - 422	70 - 206					319 - 914	Grant and Middleton (1990)
Northern part of CES	0.3 - 4.0	3.0 - 22	3.0 - 18	1.0 - 42			11 - 123	8.0 - 40	23 - 245	Nair et al. (1990)
Krishna River		32	82	35	25.0	906	32		26	Ramesh et al. (1990)
Cork Harbour, Ireland	< 0.1		8.5	11			12	18.5	67	Berrow (1991)
Caribbean Sea, Panama	5.0 - 8		4.0 - 30	2.0 - 17	17 - 525		74 - 123	18 - 45	8.0 - 40	Guzman and Jimenez (1992)
Northern part of CES	0.3 - 8.4	1.0 - 25	4.0 - 100	1.0 - 50	2.8 - 20.2	7 - 170	2.0 - 71	3.0 - 50	14 - 259	Nair (1992)
Shelf of Pakistan	2		25	23	50	210	72.0	17	98	Tariq et al. (1994)
Northern part of CES	0.51	2.9	1	0.35	0.803	11	3.00	2.7	14	Jayasree and Nair (1995)
Sydney, Australia	0 - 2.4		5.0 - 69	7		8.0 - 117	2.0 - 50	4.0 - 43	2.0 - 120	Leigh (1996)
Sheldt Estuary	< 0.1 - 44.8		31 - 322	<1 - 207			1.0 - 84	1 - 338	4 - 1325	Zwolsman et al. (1996)
Tees Estuary	5.9	34	224	103			41	307	392	Jones and Turki (1997)
Damodar River bed			22	27	14.9	390	11		39	Singh (1999)

(Fe* in mg/g, CES = Cochin estuarine system)

CADMIUM

Total cadmium in sediment (Cd_T)

In the Kuttanad region, the overall mean value of total cadmium in the sediment (Cd_T) was 2 µg/g and was found to vary from 0.47 to 5.23 µg/g of dry sediment (Table 6.1). The station wise summary statistics on Cd_T are given in Table 6.4. The highest value was observed at station 6 and the lowest at station 9. The highest and lowest station wise annual mean concentrations were also observed at stations 6 and 9 respectively and it ranged from 1.51 to 2.46 µg/g (Table 6.4). The station wise annual mean concentration showed an increasing trend from station 1 to station 6 and then decreased towards station 9 (Figure 6.1).

The seasonal distribution of cadmium (Figure 6.1) showed strong incorporation into the sediments during the monsoon season, as the seasonal average was generally higher for all the stations during this season. The lowest seasonal average was observed in the post-monsoon season for all stations. The distribution pattern of Cd in the study area is such that there is slight enrichment of Cd in the sediments of zone 2 and there is impoverishment in the level of Cd in sediments of zone 3 (Figure 6.1). The increase of Cd concentration in the sediments of the low saline region of zone 2 can be attributed to the flocculation and sedimentation of particulate matter in this zone. The decrease of Cd concentration at zone 3 is largely due to the sandy nature of the sediments in this area (Figure 3.17 in Chapter 3).

Cadmium in uncontaminated fresh water sediments is generally detected at 0.1-1.0 µg/g dry weights, increasing to 4 -10 µg/g in contaminated areas (Mohapatra, 1988; Mudroch et al., 1988). Cadmium in the sediments of the Rhine River (The Netherlands) averaged 20 µg/g (Beukema et al., 1986). Cadmium is appreciably enriched in coastal marine

Table 6.4 Station wise summary statistics on Cd concentrations in sediments (μg/g)

	Stations	Min.	Max.	Mean	SD	CV
Total cadmium	1	0.63	3.59	1.78	1.09	61.52
	2	0.89	3.56	1.93	1.01	52.05
	3	0.58	3.35	1.99	1.12	56.19
	4	0.52	4.13	2.20	1.23	56.03
	5	0.89	4.59	2.39	1.33	55.45
	6	1.01	5.23	2.46	1.38	56.05
	7	0.79	3.87	2.06	1.14	55.29
	8	0.49	3.70	1.64	1.30	78.90
	9	0.47	3.60	1.51	1.08	71.50

		Absolute concentration (μg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of cadmium	1	0.01	0.26	0.13	0.11	84.45	0.50	34.48	9.34
	2	0.00	0.30	0.14	0.12	86.72	0.01	25.45	8.64
	3	0.01	0.35	0.15	0.13	89.24	0.24	25.78	9.24
	4	0.01	0.31	0.12	0.11	94.99	0.17	19.67	6.25
	5	0.01	0.30	0.12	0.11	92.13	0.33	20.01	5.75
	6	0.01	0.24	0.12	0.10	83.96	0.43	16.22	5.82
	7	0.00	0.28	0.11	0.10	90.04	0.31	21.25	5.73
	8	0.00	0.26	0.09	0.08	96.81	0.40	31.20	8.94
	9	0.01	0.17	0.07	0.06	90.25	0.34	31.69	7.23
Reducible fraction of cadmium	1	0.31	0.76	0.53	0.13	24.98	17.60	87.05	40.51
	2	0.26	0.87	0.52	0.17	33.15	7.32	77.91	34.84
	3	0.20	0.69	0.51	0.13	26.44	5.91	93.28	37.26
	4	0.18	0.61	0.39	0.15	38.81	5.35	53.91	25.01
	5	0.25	0.68	0.43	0.14	31.82	5.39	58.62	23.31
	6	0.13	0.67	0.41	0.17	41.10	3.52	50.26	21.63
	7	0.11	0.90	0.41	0.21	50.07	3.01	57.91	25.07
	8	0.06	1.19	0.28	0.33	117.16	2.53	49.63	24.84
	9	0.05	0.40	0.20	0.10	49.44	1.48	38.82	20.87
Organic cum residual fraction of cadmium	1	0.07	2.60	1.11	1.00	90.27	9.65	81.12	50.16
	2	0.16	3.28	1.34	1.09	81.28	17.76	92.18	56.53
	3	0.03	3.12	1.31	1.17	88.86	4.75	93.24	53.50
	4	0.27	3.40	1.66	1.23	73.72	44.52	94.48	68.73
	5	0.36	4.33	1.85	1.31	70.62	40.25	94.28	70.94
	6	0.48	3.52	1.79	1.12	62.69	45.97	96.00	72.55
	7	0.31	3.61	1.69	1.19	70.34	39.34	96.58	69.20
	8	0.10	3.49	1.25	1.21	96.45	19.17	96.97	66.22
	9	0.15	3.53	1.29	1.15	89.01	30.11	98.18	71.90

(SD = standard deviation, CV = coefficient of variation)

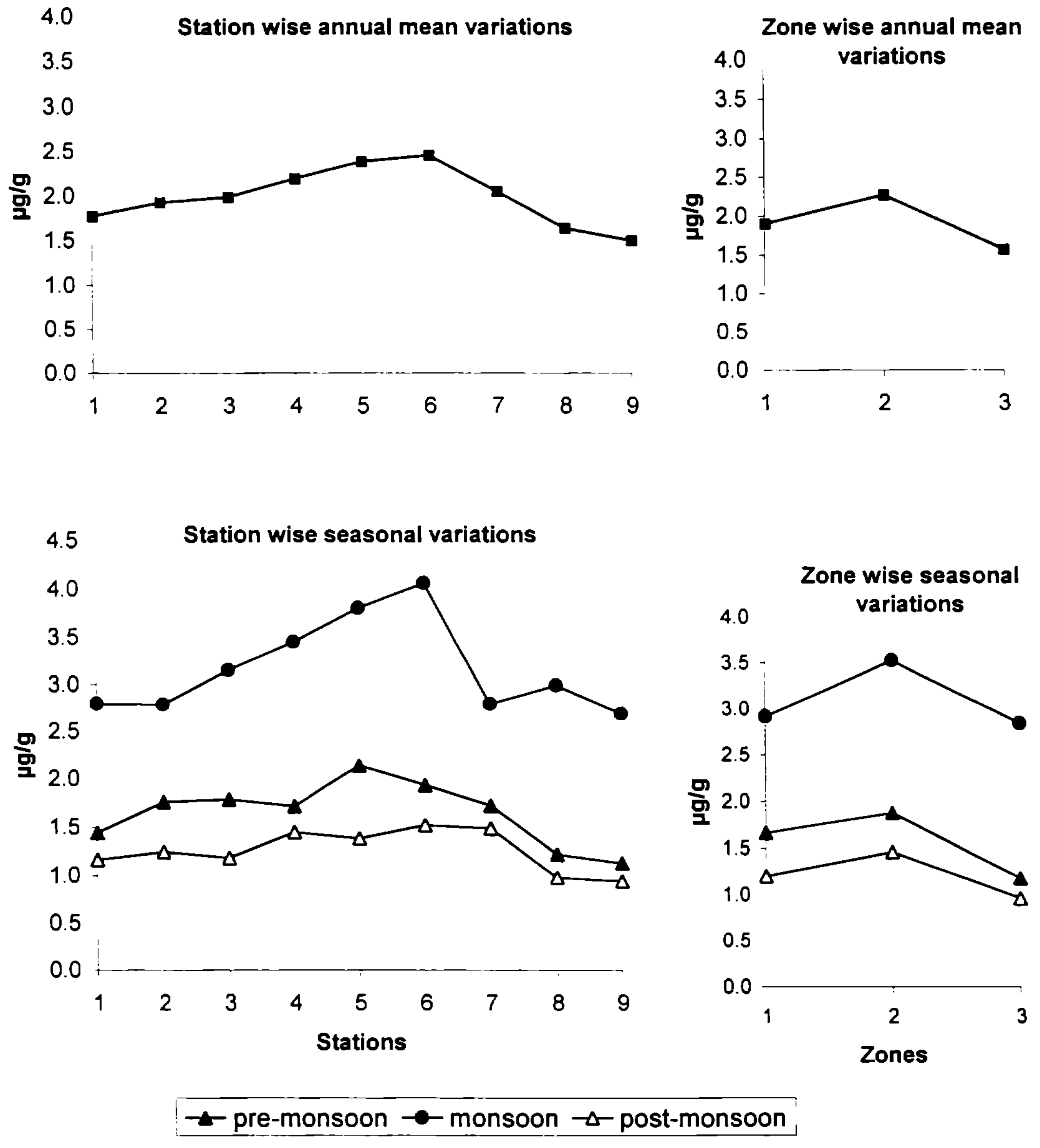


Figure 6.1 Seasonal and spatial variations of total cadmium in sediments.

waters and sediments. The mean value of cadmium recorded in the present study (2.00 µg/g) is slightly higher than the mean value (1.66 µg/g) observed by Nair (1992) from a study in the down stream of Cochin Estuary. Jayasree and Nair (1995) have reported a still lower value of cadmium (0.51 µg/g) from Cochin Estuary. Nair et al. (1990) observed a mean value of 0.61 µg/g from the same estuary. Comparing the above three studies in Cochin Estuary with the present study, it can be seen that there is a slight enrichment of cadmium in the southern upstream part of the Cochin estuarine system.

The exchangeable fraction of cadmium (Cd_1)

The concentrations of exchangeable fractions of cadmium varied upto a maximum concentration of 0.35 µg/g (Table 6.2). Relatively, the values ranged to a maximum of 34.48 percent of total cadmium, with a mean value of 7.44 percentage. The range of values is slightly on the higher side when compared to the values reported by Nair (1992) from the northern part of Cochin estuarine system, which were in the range 1.40 to 18.89 % of total cadmium, with a mean value 5.76 %. The exchangeable fraction of Cd showed pronounced enhancement in the post-monsoon and monsoon seasons at all stations (Figure 6.2). All stations showed very low values in pre-monsoon season, (0.44% to 0.73%) and the concentrations were almost equal in all stations. In monsoon and post-monsoon seasons, stations of zone 1 recorded comparatively higher values than zone 2, whereas zone 3 recorded the lowest among the zones (Figure 6.2). A more or less similar trend was also observed in the percentage wise distribution pattern of Cd_1 fraction (Figure 6.2). The Cd_1 fractions exhibited wider variability (Coefficient of variation = 96.31 percent) (Table 6.2). The comparatively higher values of Cd_1 fraction in the riverine zone and in zone 2 in the monsoon and post-monsoon seasons are primarily due to the reactive nature of cadmium being received by the estuary from the rivers. One of the reasons for the marked decrease in the percentage of Cd_1

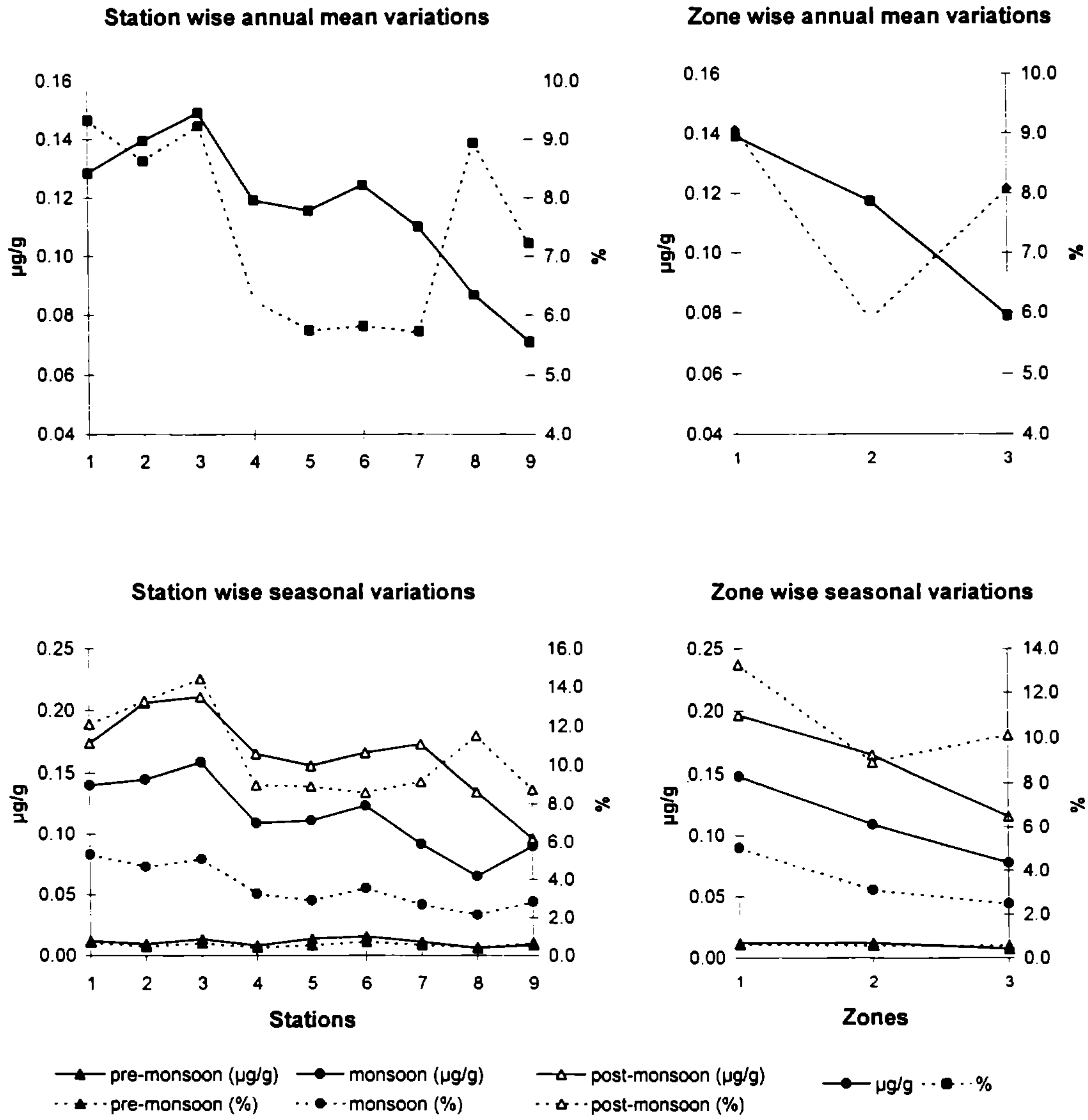


Figure 6.2 Spatial and temporal variations of exchangeable fractions of Cd (Cd_1) on absolute (µg/g) and relative (%) basis.

fractions in pre-monsoon season may be the transformations undergone by this fraction under the influence of increasing salinity. The depletion of exchangeable Cd at higher salinities could be either due to exchange with Ca and Mg or due to complexation of Cd by chloride ions at higher salinities (Bourg, 1983).

The station wise annual mean concentrations were in the range 0.07 to 0.15 µg/g (Table 6.4). The lowest was observed at station 9 and the highest at station 3. Figure 6.2, which also gives the trend in station wise annual mean concentration, showed that the riverine stations (station 1, 2 and 3) had comparatively higher exchangeable fraction of cadmium and showed a decreasing tendency towards station 9. Or, in other words, the exchangeable fraction of cadmium was slightly higher in the fresh-water zones than in the estuarine zones. Nair et al. (1991) also observed that exchangeable Cd was predominant in the fresh water zone and gradually decreased in content with increasing salinity.

The reducible fraction of cadmium (Cd_2)

The reducible fraction of cadmium (Cd_2) ranged from 0.05 µg/g (at station 9) to 1.19 µg/g (at station 8) (Table 6.4) in the study area. Percentage wise, the values ranged from 1.48 to 93.28 percentage of Cd_T (Table 6.4). On an average, 28.15 percentage of Cd_T was found in the Cd_2 fraction (Table 6.2), which is about 4 times that of the Cd_1 fraction. The station wise annual mean concentrations ranged from 0.20 µg/g at station 9 to 0.53 µg/g at station 1 (Table 6.4). The station wise annual mean concentrations at stations 1 to 3 remained almost same (in the range 0.51 µg/g to 0.53 µg/g). Similarly, the Cd_2 fraction at stations 5 to 7 also were found almost closer (range 0.41µg/g to 0.43 µg/g). An overall decreasing trend was found from station 1 to station 9 in the case of annual mean concentration of Cd_2 fraction (Figure 6.3). In other words, the annual mean concentrations of the riverine stations of zone 1 were the highest and the

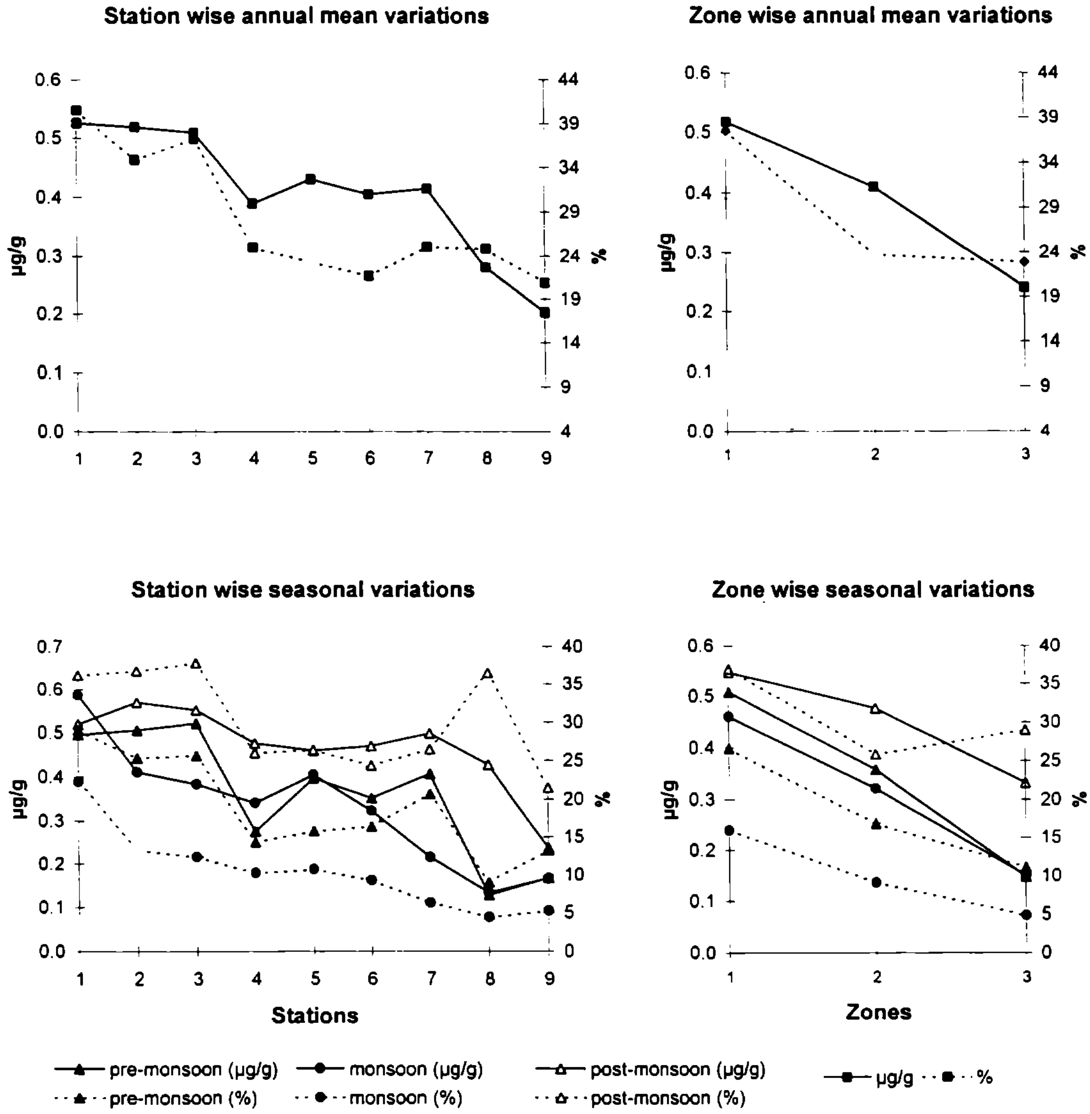


Figure 6.3 Spatial and temporal variations of reducible fractions of Cd (Cd_2) on absolute (µg/g) and relative (%) basis.

stations of zone 3, were the lowest (Figure 6.3). But the zone wise seasonal distribution pattern of Cd_2 fraction in percentage in the post-monsoon season was found slightly different in the sense that zone 3 recorded slightly higher values than that of zone 2. Station 8 showed maximum scatter in values, which is evident from the comparatively high standard deviation (0.33) and high coefficient of variation (117) (Table 6.4). The concentrations of Cd_2 fraction in pre-monsoon and monsoon seasons did not exhibit any definite trend in seasonal variations, but always remained less than that of post-monsoon season except at station 1 where the highest seasonal average was in monsoon period. Contrary to this, the concentrations in relative terms showed definite seasonal variability, showing the highest values in post-monsoon season and lowest values in monsoon season. The mean value (28.15 %) of Cd_2 fraction recorded in the present study is lower when compared to values reported by Forstner (1982), Calmano and Forstner (1983), Hong and Forstner (1983), Samanidou and Fytianos (1987) and Pardo et al. (1990) for similar fraction of Cd but it is higher than the values reported by Nair (1992) (15.61%) from other parts of the Cochin Estuary. This indicates the enrichment of Cd associated with Fe-Mn oxide bound phase in the upstream part of Cochin Estuary. The higher values of Cd_2 fraction in this part of the Cochin Estuary can be explained on the basis of relatively high abundance of freshly precipitated Fe and Mn oxides in this area.

The organic cum residual fraction of cadmium (Cd_3)

The investigation into the fractionation of cadmium in Kuttanad area revealed that the organic cum residual fraction of cadmium (Cd_3) varied from a minimum of 0.03 µg/g at station 3 to a maximum of 4.33 µg/g at station 5 (Table 6.4). This range of value is proportional to 4.75 to 98.18 percentage of total Cd. On an average, 64.41 percentage of total cadmium was found in the Cd_3 fraction. The annual mean concentrations were found to be varying from 1.11 µg/g (at station 1) to 1.85 µg/g (at station 5) (Table 6.4). The annual mean concentration of Cd_3 fraction showed an increasing trend from station 1 to station 5 and then decreased towards station 9, the peak of the concentration graph being at station 5 (Figure 6.4). Unlike that of Cd_1 and Cd_2 fractions, the annual mean concentration of Cd_3 fraction (absolute value) was found higher at zone 2 than that of zone 1 (Figure 6.4). Definite seasonal variations also could be observed in the distribution of Cd_3 fraction (Figure 6.4). Unlike the trend observed for the Cd_1 and Cd_2 fractions where a post-monsoon hike was observed generally in all stations, a pronounced seasonal depletion was observed in the post-monsoon season for the Cd_3 fractions with a range of values 0.61 to 1.29 µg/g in this season. Pronounced monsoonal hike in the concentrations of Cd_3 fractions (in µg/g) was observed for all the stations, with a range of values 1.91 to 3.28 µg/g. The percentage wise distribution of Cd_3 fraction also recorded lower values during post-monsoon season, but monsoon and pre-monsoon seasons did not show much difference in percentage of organic cum residual fraction of cadmium, though a slight increase was observed in the monsoon season. In a study of the northern part of the Cochin estuarine system, Nair (1992) observed 78.63 percentage of Cd_3 fraction in the surface sediments as against the 64.41 % observed in the present study. Many of the reported values in the similar fraction of Cd were in the range 8 to 43 % (Tessier et al., 1980; Calmano and Forstner, 1983; Samanidou and Fytianos, 1987; Pardo et al., 1990).

COBALT

Total cobalt in sediment (Co_T)

Total concentration of cobalt in the sediments of Kuttanad area varied from 5.41 to 171.51 µg/g of dry sediment (Table 6.1). Table 6.5 gives the station wise summary statistics on total Co in sediments. As in the case of cadmium, the lowest and highest values were recorded at stations 9 and 6 respectively (Table 6.5). Station wise annual mean concentrations varied from 15.17 to 95.66 µg/g of dry sediment (Table 6.5).

Table 6.5 Station wise summary statistics on Co concentrations in sediments (µg/g)

	Stations	Min.	Max.	Mean	SD	CV
Total cobalt in sediment	1	33.74	69.85	55.24	10.38	18.78
	2	30.24	78.65	57.51	16.07	27.95
	3	42.17	113.56	67.35	18.87	28.02
	4	73.69	118.60	88.02	12.31	13.99
	5	52.73	120.18	91.30	17.60	19.28
	6	68.26	171.51	95.66	28.72	30.03
	7	20.42	119.74	61.23	25.94	42.37
	8	10.67	60.28	17.59	13.68	77.73
	9	5.41	34.46	15.17	7.58	50.00

		Absolute concentration (µg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of cobalt	1	0.17	4.07	2.06	1.20	58.43	0.30	8.63	3.67
	2	0.88	4.38	2.57	1.05	40.66	1.31	7.49	4.43
	3	1.06	5.00	3.04	1.26	41.37	0.93	7.61	5.12
	4	0.79	3.57	2.30	0.86	37.43	0.67	4.55	2.59
	5	0.80	2.49	1.52	0.56	37.02	0.87	2.64	1.58
	6	0.06	2.77	1.28	0.84	65.31	0.04	3.68	1.42
	7	0.26	1.60	0.98	0.49	49.71	0.21	3.11	1.72
	8	0.15	1.81	0.72	0.51	71.11	1.31	10.24	4.39
	9	0.04	1.12	0.50	0.35	70.23	0.29	8.83	3.60
Reducible fraction of cobalt	1	11.49	23.97	17.74	4.19	23.64	24.45	49.24	32.45
	2	10.20	24.59	17.40	4.59	26.40	16.14	37.95	28.17
	3	8.71	24.81	17.95	4.17	23.23	14.72	36.73	28.75
	4	7.83	23.53	14.72	4.60	31.28	8.63	26.99	16.74
	5	7.46	22.08	13.58	5.16	38.01	8.53	26.29	14.74
	6	5.24	15.01	11.06	3.09	27.92	4.44	18.24	12.27
	7	4.21	15.98	9.67	3.90	40.37	7.04	30.03	15.86
	8	2.59	23.39	6.04	6.20	102.57	18.76	46.82	31.81
	9	1.45	9.15	4.90	2.26	46.24	22.36	42.51	34.00
Organic cum residual fraction of cobalt	1	16.16	47.82	35.96	9.36	26.02	47.89	72.63	63.88
	2	22.27	54.15	42.43	10.70	25.22	57.00	79.99	67.41
	3	24.38	92.99	44.00	18.78	42.70	57.81	81.89	66.13
	4	56.78	107.54	72.89	14.77	20.27	70.84	90.67	80.67
	5	43.88	106.56	78.82	17.31	21.96	71.47	89.32	83.68
	6	55.25	163.83	84.66	31.19	36.84	80.94	95.53	86.31
	7	22.08	103.50	53.45	22.36	41.84	68.63	91.79	82.42
	8	5.93	35.08	11.23	8.56	76.20	44.39	78.68	63.79
	9	3.92	24.18	9.68	6.24	64.50	50.08	77.35	62.41

(SD = standard deviation, CV = coefficient of variation)

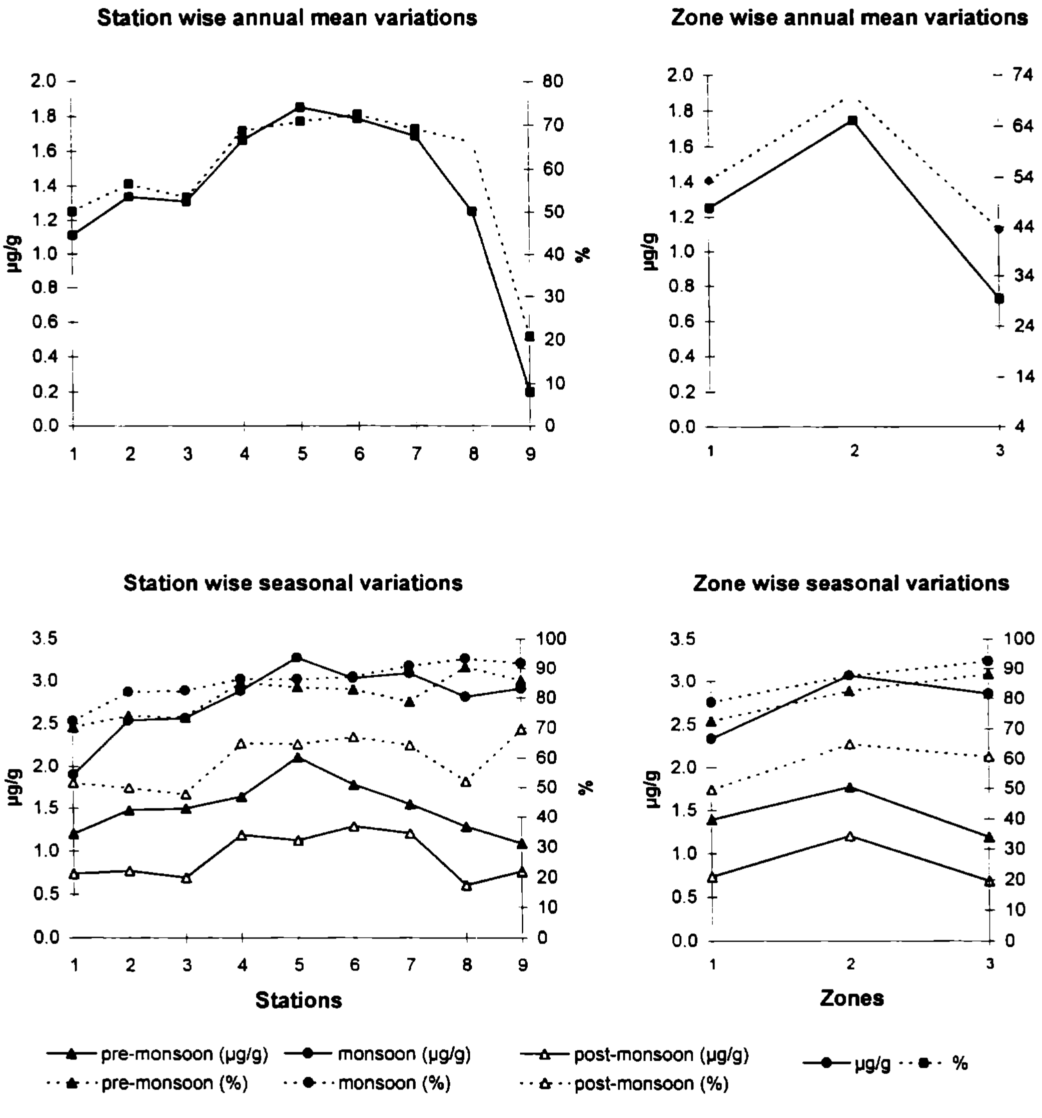


Figure 6.4 Spatial and temporal variations of organic cum residual fractions of Cd (Cd_3) on absolute (µg/g) and relative (%) basis.

Similar to that of cadmium, cobalt also showed an increasing trend in the annual mean concentration from station 1 to station 6 and then decreased to station 9 (Figure 6.5). The station wise annual mean values were the highest at the low saline zone (zone 2) and lowest at zone 3 (Figure 6.5).

Seasonal variations in the concentrations of total cobalt in sediments could be observed in all stations but not uniform throughout (Figure 6.5). The lowest seasonal averages in pre-monsoon and monsoon seasons were observed at station 8 but in post-monsoon it was at station 9. The highest seasonal averages in pre-monsoon and post-monsoon seasons were recorded at station 6 and that in monsoon also station 6 recorded high values but highest was at station 4. The seasonal averages and the annual mean concentrations at stations 8 and 9 were significantly lower when compared to the corresponding concentrations at other stations. The analyses of data on a zonal basis (Figure 6.5) showed that the spatial distribution pattern is more or less similar to that of cadmium. Both metals showed enrichment in sediments of zone 2 than in sediments of the fresh water region of zone 1. As in the case of cadmium, the impoverishment of values in the sediments of zone 3 was observed for cobalt also. The most probable reason for this is again the textural characteristics of the sediments of this region, which is richer in particles greater than 63 µm. The comparatively higher values of cobalt in zones 1 and 2 exhibit the high affinity of cobalt for silt-clay associations, as these zones are rich in silt and clay.

Cobalt in uncontaminated fresh water sediments is generally found at 1-10 µg/g dry weight, increasing to 25-50 µg/g in anthropogenically contaminated areas. Residues in Hamilton Harbour, situated in a highly industrialized part of eastern Canada, averaged 6.5 µg/g (range 2.3-11 µg/g) in shallow water near the shore, increasing to 38 µg/g (range 17-58 µg/g) in deposition basins (Poulton, 1987). Hutchinson and Fitchko (1974) reported that outlet sediments of Great Lake tributaries contained < 5 µg in the majority of samples, with only 10% of the samples

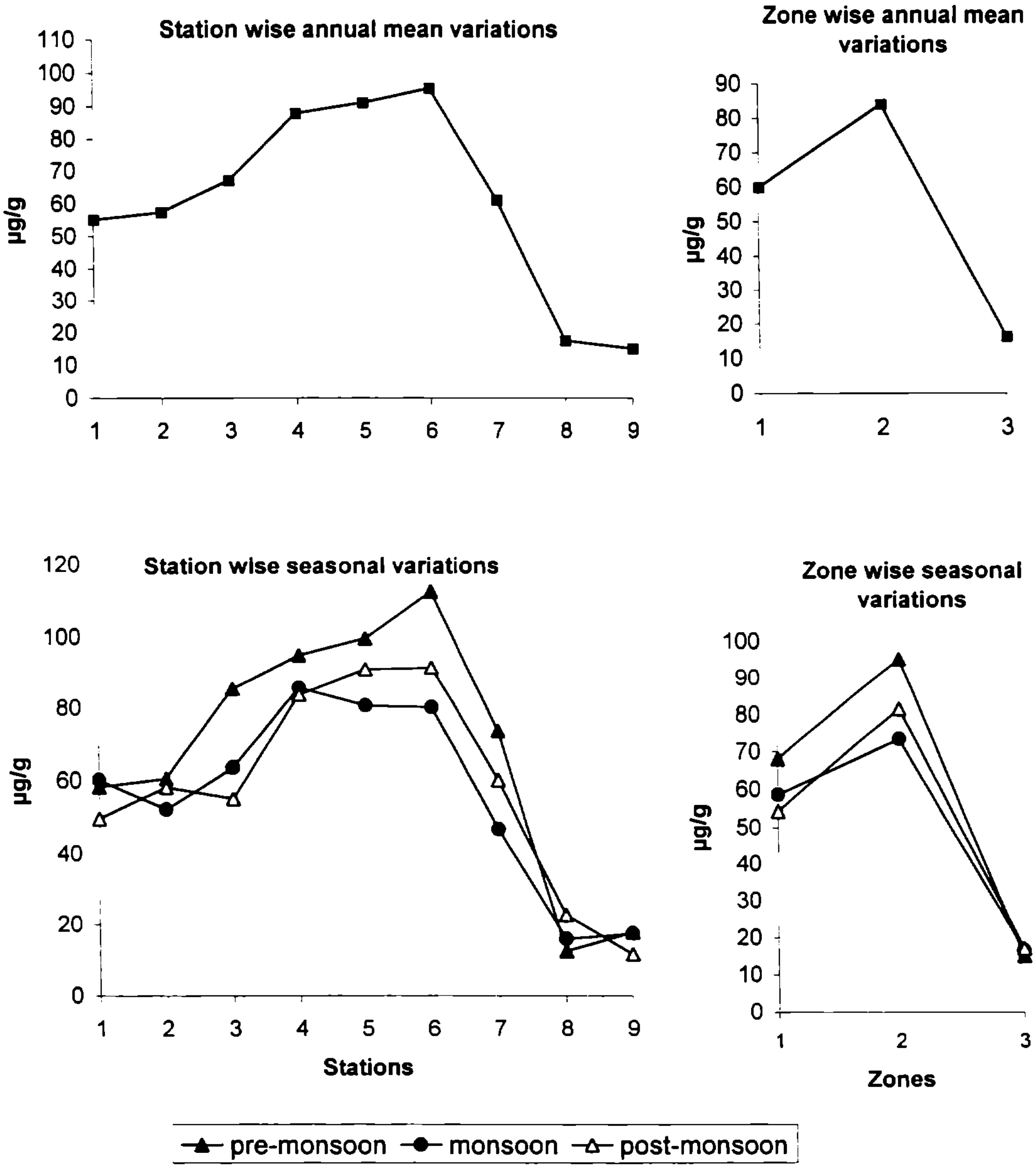


Figure 6.5 Seasonal and spatial variations of total cobalt in sediments.

exceeding 25 µg/g. Appreciably higher residues, averaging 37 µg/g (range 33-40 µg/g), were found in Thane Creek, which receives industrial wastes from the city of Bombay (Mohapatra, 1988). Even higher levels (upto 57 µg/g) were found in the sediments of lakes near coal-burning generating plants (Wilson et al., 1986). Residues of 12-34 µg/g of cobalt have been reported for the Indian Ocean (Moore, 1991), whereas sediments in the Baltic Sea and North Sea contain cobalt at 8 and 6-25 µg/g, respectively (Duursma, 1973). Nair et al. (1990) have reported a mean value of 5.87 µg/g and Jayasree and Nair (1995) reported a mean value of 2.1 µg/g of cobalt from other parts of Cochin Estuary. Compared to this, the mean value recorded in the present study (61.01 µg/g) (Table 6.1) is appreciably higher. This again shows that there is an appreciable enrichment of metal concentration in the southern upstream part of Cochin Estuary. The wide difference in the values observed in the present study and that reported by Nair et al. (1990) and Jayasree and Nair (1995) could be due to the difference in the location of study area. The present study area differs from other parts of the Cochin estuarine system in that for an appreciable period of time in a year, the water body is isolated from the rest of the estuary by preventing the entry of saline water into the region and thus, leading to restriction on the flushing of the system with saline water. This causes the settling of fine grained suspended particles, which are enriched in cobalt. The higher values of cobalt in the pre-monsoon season in zones 1 and 2 are indicative of the anthropogenic input of cobalt in this area.

The exchangeable fraction of cobalt (Co_1)

The absolute values of exchangeable fraction of cobalt (Co_1) ranged from 0.04 to 5.00 µg/g and the relative values varied from 0.04 to 10.24 percentage of total cobalt (Table 6.5). The mean value (1.65 µg/g or 3.17 % of Co_T) recorded in the present study was comparable to the values reported by Nair (1992) (0.18 µg/g or 2.40 %) from other parts of Cochin Estuary. Similar values were reported by Gibbs (1973) from Yukon River

(4.7%), Lee (1985) from Keum Estuary (3.7%) and Pardo et al. (1990) from Pisuerga River (4.67%). The station wise annual mean concentrations (Table 6.5) varied from 0.50 to 3.04 µg/g, the lowest being at station 9 and the highest at station 3. The annual mean concentrations showed an increasing trend from station 1 to 3 and then showed a regular decreasing trend towards station 9 (Figure 6.6), showing the concentration peak at station 3. Zone wise, the maximum annual mean concentration was recorded at zone 1, zone 3 recording the lowest value. Seasonal average concentrations of exchangeable cobalt are also plotted in Figure 6.6. Pre-monsoon season showed lowest seasonal average concentration of exchangeable cobalt in all stations in absolute and in relative terms. The seasonal variations were more evident in the riverine zone (zone 1). Seasonal variations were not very pronounced in the stations of zones 2 and 3. Contrary to this, the percentage of exchangeable cobalt fraction showed clear variations at zone 3 (Figure 6.6). One interesting feature observed in the case of Co is that the percentage of Co_1 fraction was higher at zone 3 than at zone 2. Nair (1992) also observed a similar increasing trend in the percentage of Co_1 fraction towards the downward direction of the estuary. Nair (1992) attributed this behaviour to the solubility of cobalt minerals under saline conditions. In the present study, as the maximum increase in the percentage of Co_1 was observed in the post-monsoon season, followed by monsoon season, enhanced solubility of cobalt minerals under saline conditions cannot be ascribed as the only reason for the observed phenomenon. During the monsoon and post-monsoon seasons, cobalt in more mobile form may be reaching the estuarine sediments of zone 3 from the nearby paddy fields, thus reducing the significance of the salinity factor. The comparatively lower percentage of Co in the exchangeable fraction showed that cobalt is not much labile in the sediments of Kuttanad.

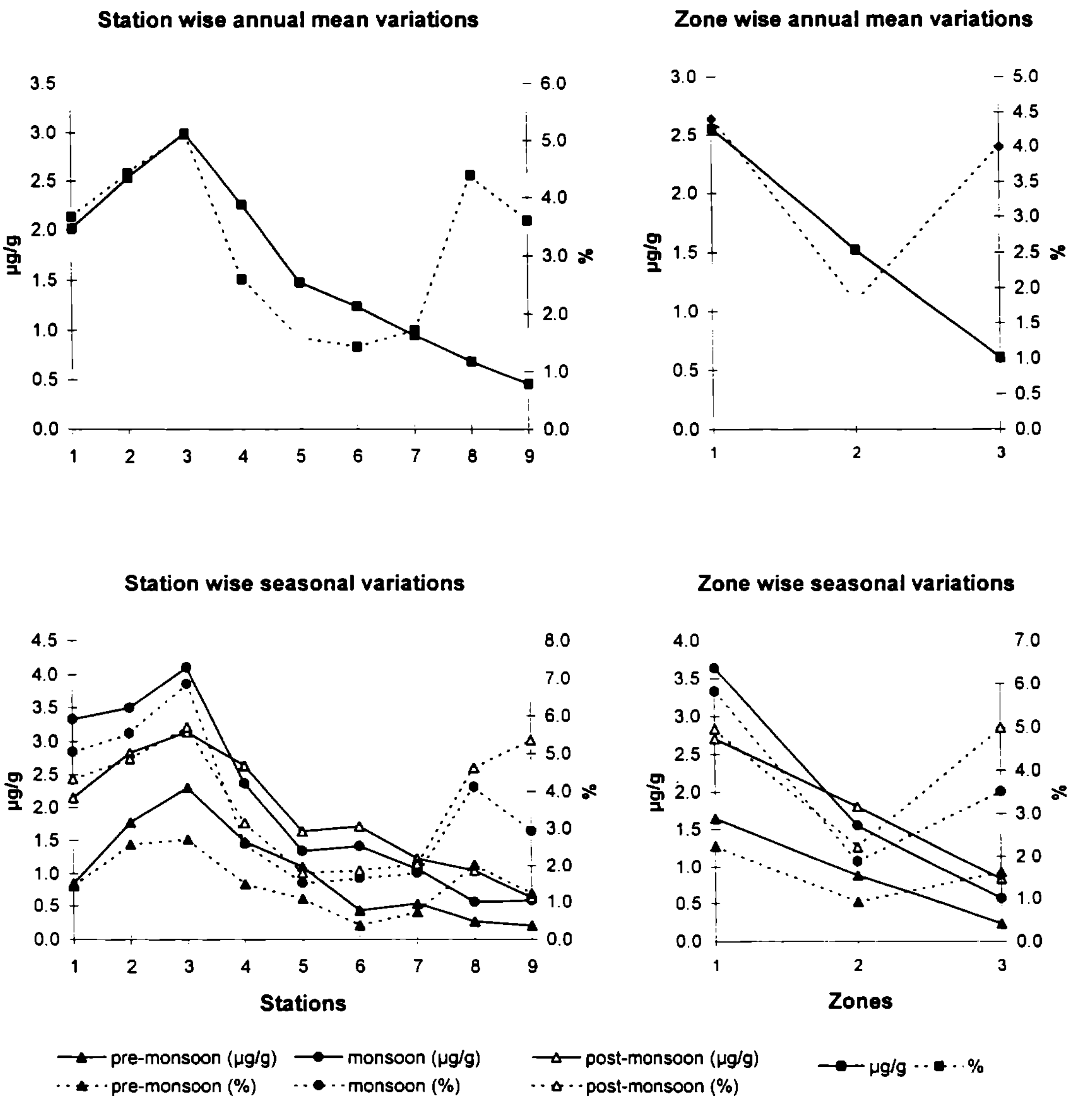


Figure 6.6 Spatial and temporal variations of exchangeable fractions of Co (Co_1) on absolute (µg/g) and relative (%) basis.

The reducible fraction of cobalt (Co_2)

The reducible fraction of cobalt (Co_2) varied from 1.45 to 24.81 µg/g of sediment, lowest was at station 9, and the highest at station 3 (Table 6.5). Relatively, the variation was found from 4.44 to 49.24 percentage of total cobalt (Table 6.5). On an average, 23.87 percentage of total cobalt was found in this fraction (Table 6.2). The station wise highest (17.9 µg/g) and the lowest (4.9 µg/g) annual mean concentrations were also observed at stations 3 and 9 respectively (Table 6.5). The station wise annual mean concentrations at stations 1 to 3 were close together (in the range 17.4 µg/g to 17.9 µg/g). From station 3 onwards, the annual mean concentration showed a gradual decreasing trend towards station 9 (Figure 6.7). As in the case of Cd_2 fraction, Co_2 fraction also recorded maximum values in the stations of zone 1 and lowest values in the stations of zone 3. This fraction of Co did not show a pronounced seasonal variability (Figure 6.7), but still many of the stations recorded lower values in the monsoon season and slightly higher values in the post-monsoon season. Zone 3 showed a clear hike in the percentage of Co_2 fraction during post-monsoon period. As observed in the case of Co_1 fraction, the percentage of Co_2 fraction also showed a clear hike at zone 3 than zone 2. As in the case of Cd, maximum scatter was observed at station 8 (coefficient of variation 102.57) (Table 6.5). The overall mean value of Co_2 fraction (23.87 %) observed in the present study is higher than the values reported by Nair (1992) from other parts of Cochin Estuary for similar fraction of Co (6.44%) and also higher than the values reported by Pardo et al. (1990) from Pisuerga River (14.74 %) and Lee (1985) from Keum Estuary (18.6%). But much higher values were reported by Tessier et al. (1980) for Co_2 fraction from St. Francois River (47 %) and Yamaska River (31 %) and by Gibbs (1973) from Yukon (29.2). In aquatic systems, cobalt is usually removed from water column by co-precipitation with oxyhydroxides of Fe and Mn (Gibbs, 1973; Schor, 1985; Bowers and Huang, 1987). The comparatively higher percentage of reducible fraction of cobalt recorded in the present

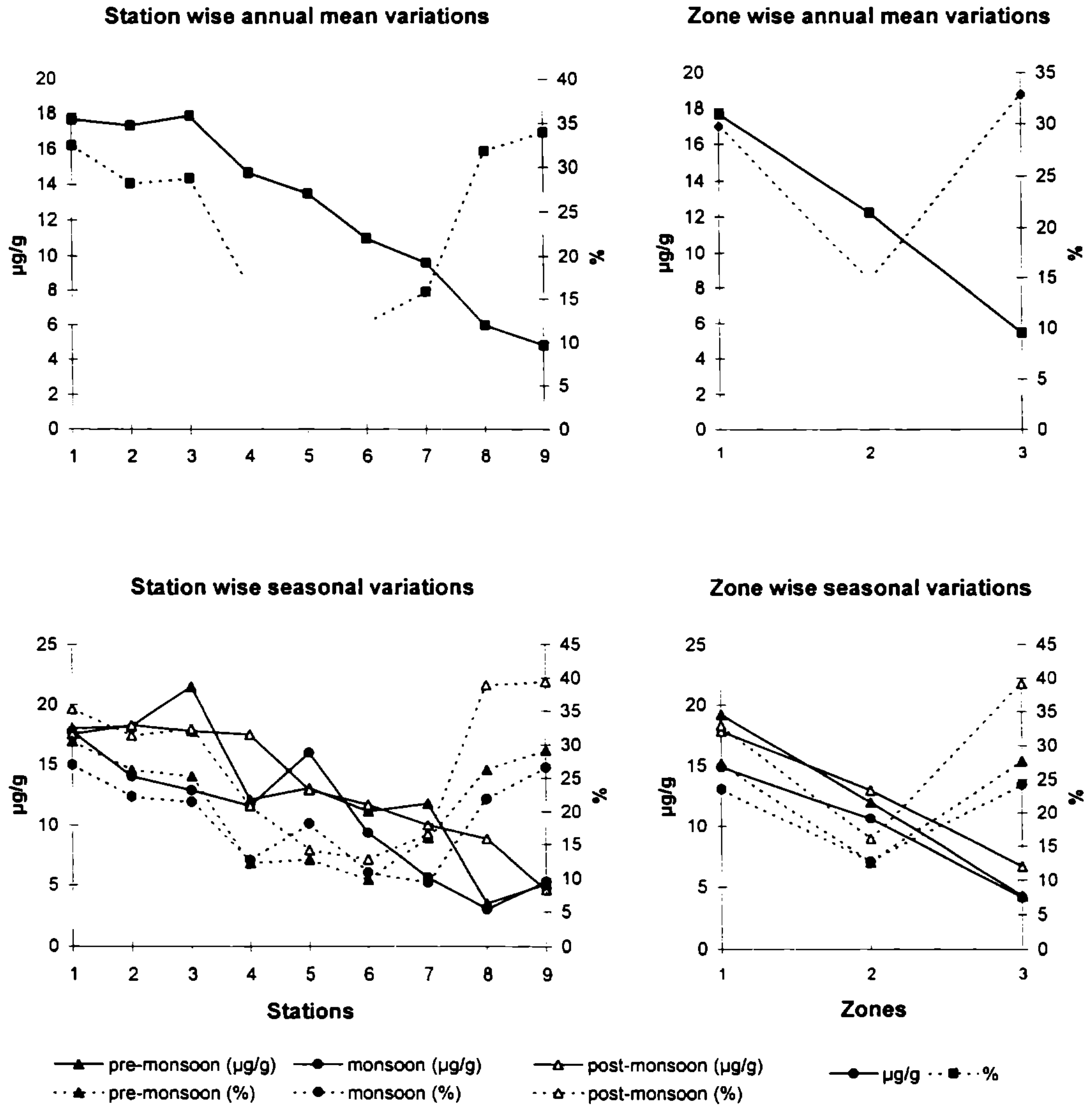


Figure 6.7 Spatial and temporal variations of reducible fractions of Co (Co_2) on absolute (µg/g) and relative (%) basis.

study when compared to the values reported from other parts of the same estuary may be attributed to the co-precipitation of Co along with freshly precipitated Fe and Mn, which are found abundantly in this part of the estuary (Fe and Mn are discussed later).

The organic cum residual fraction of cobalt (Co_3)

The distribution of organic cum residual fraction of cobalt (Co_3) in the estuary was found more or less similar to the distribution of organic cum residual fraction of Cd. As observed in the case of Cd_3, a pronounced hike in the concentration of Co_3 fraction was also observed for stations of zone 2. This can be seen both in the case of annual mean concentrations and in the case of seasonal mean values. The relatively higher values of Co_3 fractions in zone 2 may be due to the association of cobalt with the organic matter, which is found relatively high in this zone. This study showed that the Co_3 fraction varied from 3.92 µg/g at station 9 to 163.83 µg/g at station 6 (Table 6.5). Percentage wise, the values varied from 44.39 to 95.53 percentage of the total cobalt (Table 6.5). The overall mean value (72.97 %) is higher than that observed for Cd (Table 6.2). The station wise annual mean concentration showed an increasing trend from station 1 to station 6 and then decreased towards station 9 (Figure 6.8). Values recorded at stations 8 and 9 were considerably lower than the values at other stations. Unlike that of Cd_3 fraction, seasonal variations were not very clear in the case of Co_3 fractions. It was also observed that when zone 3 recorded relatively higher percentage of Co_1 and Co_2 fractions in post-monsoon season, the Co_3 fraction recorded relatively lower percentage in this season. The mean Co_3 value (48.13 µg/g) recorded in the present study is much higher than the similar fraction of Co_3 (8.61 µg/g) reported by Nair (1992) from other parts of Cochin Estuary. This comparatively high concentration of Co_3 fraction in this area is primarily due to the high organic matter content in these sediments and also the fine texture of sediments in most of the stations, especially in zone 2. The relative abundance of Co_3

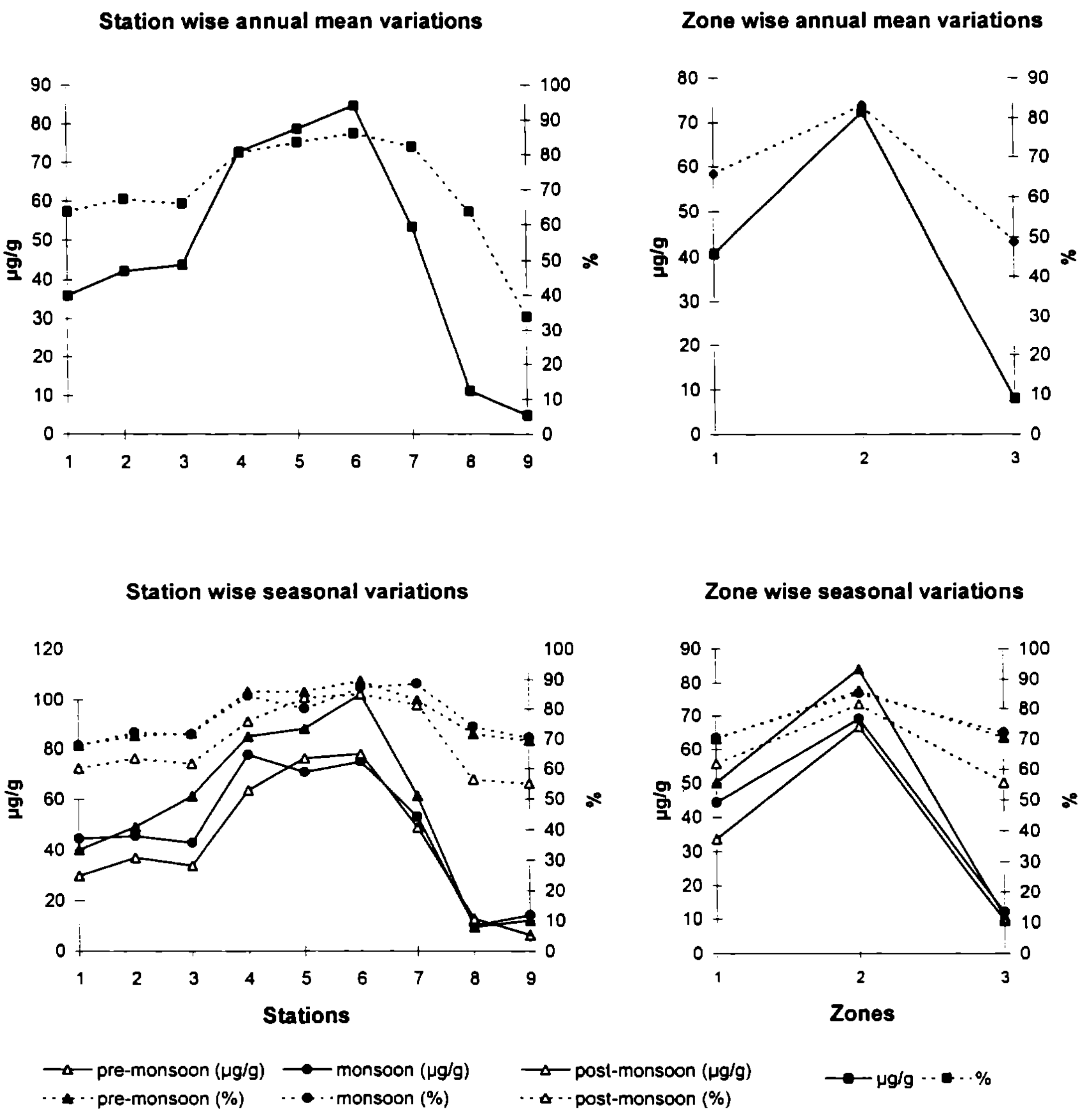


Figure 6.8 Spatial and temporal variations of organic cum residual fractions of Co (Co$_3$) on absolute (µg/g) and relative (%) basis.

fraction in the total Co is more or less comparable to the values reported by Gibbs (1973) from Yukon (64.3 %), Tessier et al. (1980) from Yamaska River (63 %) and St. Francois River (48 %), whereas 77.7 % of Co_3 fraction was reported form Keum Estuary by Lee (1985) and 80.63 % of Co_3 from Pisuerga River by Pardo et al. (1990).

CHROMIUM

Total chromium in sediment (Cr_T)

This study showed that concentrations of total chromium in sediment ranged from 13.00 to 283.73 µg/g, the lowest value being at station 9 and the highest at station 5 (Table 6.6). The station wise annual mean concentrations of total chromium varied from 31.36 to 221.12 µg/g (Table 6.6). Station 9, which recorded the lowest value, also recorded the lowest annual mean concentration. Station 4 recorded the highest annual mean concentration, though the highest value was observed at station 5. The trend in the variations of annual mean concentrations of total chromium in sediment (Figure 6.9) showed that the values increased from station 1 to station 4 and then decreased towards station 9, though a slight increase was observed at station 6. As in the case of many other metals, the annual mean concentrations at stations 8 and 9 (41.49 and 31.36 µg/g respectively) were significantly lower than that in the rest of the stations (range 143.35 to 221.12 µg/g).

Seasonal variations of total chromium in sediments were observed and are also represented in Figure 6.9. In most of the stations (stations 2 to 7), the monsoon season recorded the lowest values. Highest seasonal averages were observed in post-monsoon season except in stations 1 and 9 where the monsoon season recorded the highest values.

The mean value of chromium content in sediments observed in the present study is 156.29 µg/g dry weight of sediment. This value is

Table 6.6 Station wise summary statistics on Cr concentrations in sediments (µg/g)

	Stations	Min.	Max.	Mean	SD	CV
Total chromium in sediment	1	146.00	200.28	170.84	19.53	11.43
	2	79.87	247.82	184.65	55.33	29.97
	3	161.77	249.22	203.91	22.58	11.08
	4	161.55	265.18	221.12	26.77	12.11
	5	142.90	283.73	203.85	34.01	16.68
	6	148.27	262.34	206.05	34.77	16.87
	7	37.47	195.16	143.35	51.42	35.87
	8	13.55	157.96	41.49	37.80	91.10
	9	13.00	73.44	31.36	14.98	47.78

		Absolute concentration (µg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of chromium	1	0.20	6.23	3.35	2.22	66.50	0.13	3.52	1.82
	2	0.54	5.82	3.03	1.98	65.39	0.32	3.25	1.47
	3	0.65	7.75	3.75	2.67	71.22	0.31	3.84	1.70
	4	0.44	5.94	2.82	2.18	77.34	0.19	2.56	1.12
	5	0.45	5.14	2.79	1.88	67.26	0.21	2.85	1.27
	6	0.41	6.25	3.34	2.10	63.05	0.28	3.21	1.41
	7	0.32	6.44	2.52	1.95	77.53	0.22	4.14	1.68
	8	0.20	5.33	1.97	1.71	86.86	0.58	12.07	4.79
	9	0.23	4.31	1.77	1.48	83.43	0.76	13.18	5.27
Reducible fraction of chromium	1	20.38	36.63	26.57	5.57	20.98	10.18	20.58	15.29
	2	18.50	36.15	25.46	5.72	22.48	8.08	17.47	12.49
	3	15.69	35.57	27.03	5.38	19.91	8.05	17.92	13.18
	4	11.35	25.82	17.43	5.19	29.79	4.28	11.80	7.71
	5	8.50	28.56	18.72	6.80	36.32	3.97	16.33	9.10
	6	7.14	20.98	15.52	3.97	25.56	3.59	11.88	7.66
	7	7.06	23.88	13.49	5.25	38.96	4.02	19.10	9.47
	8	3.03	30.40	7.35	8.23	111.98	9.64	25.11	15.87
	9	1.03	9.49	5.33	2.62	49.11	7.91	31.62	17.04
Organic cum residual fraction of chromium	1	120.97	174.96	144.85	18.192	12.56	75.92	87.36	82.89
	2	134.96	209.38	176.94	27.786	15.70	81.67	91.47	86.04
	3	131.75	217.62	176.00	21.662	12.31	81.44	91.16	85.13
	4	180.46	249.41	209.56	20.579	9.82	87.68	94.05	91.17
	5	142.06	268.41	190.61	33.236	17.44	81.22	94.60	89.63
	6	132.17	242.37	192.16	35.589	18.52	85.97	95.94	90.93
	7	53.01	175.60	138.09	41.904	30.35	80.41	95.76	88.85
	8	17.28	122.23	34.95	31.387	89.80	71.22	89.78	79.33
	9	11.08	61.20	25.43	13.875	54.57	67.62	86.07	77.69

(SD = standard deviation, CV = coefficient of variation)

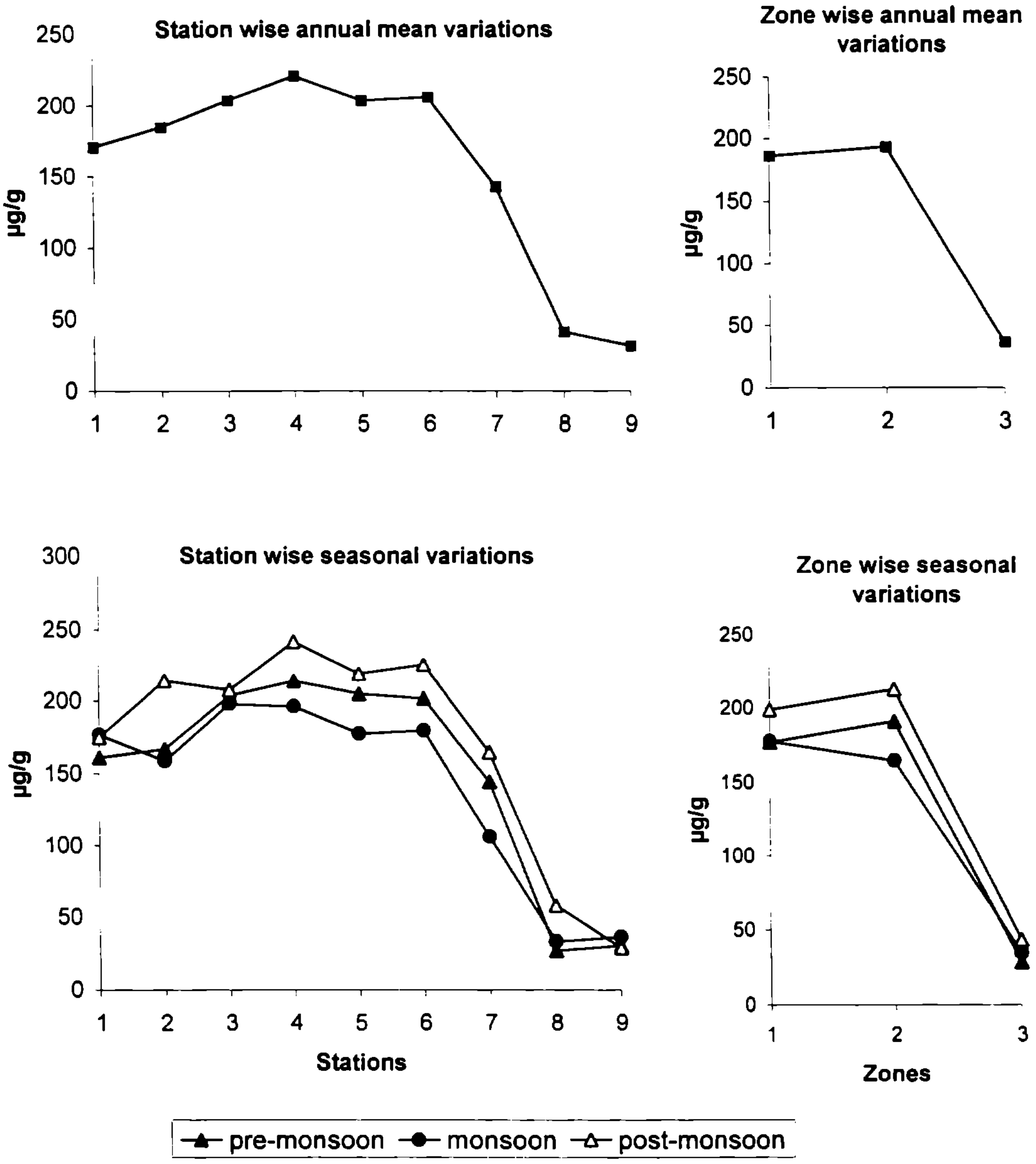


Figure 6.9 Seasonal and spatial variations of total chromium in sediments.

found to be higher than the mean value reported by Nair et al. (1990) from the downstream of Cochin Estuary, which was 17.96 µg/g. But the value is more or less comparable to the mean value reported from Indian rivers, Godavari (126 µ g/g) by Biksham and Subramanian (1988), and Cauvery (129 µg/g) by Vaithiyanathan et al. (1993) and at the same time higher than the world average (Martin and Meybeck, 1979) which is 100 µg/g. Higher levels of chromium content in sediments were also reported from Bombay Harbour (124 µg/g) by Patel et al. (1985), from Cauvery Estuary (229 µg/g) by Subramanian et al. (1989) and from Krishna Estuary (174 µg/g) by Subramanian et al. (1989). Total Cr in the surficial sediments of the depositional basins of the Great Lakes ranges from 8 to 362 µg/g dry weight, compared to background concentrations of 9-86 µg/g (Mudroch et al., 1988). Mohapatra (1988) reported that total Cr in the sediments of a polluted creek near Bombay (India) averaged 39.9 µg/g dry weight (range 24.2-74.5 µg/g). Sediment samples taken from the Belgium part of the North Sea and the Sheldt Estuary, gave concentrations of 44-114 µg/g, depending on sediment particle size (Araujo et al., 1988), whereas much higher levels (upto 1,600 µg/g) were found in sediments offshore of Los Angeles in 1981 (Stull and Baird, 1985). Those extremely high residues were due to the presence of a nearby sewage outfall.

The distribution pattern of chromium in the study area was such that there was an increase in metal concentration in the fresh water and low saline regions of zones 1 and 2 (Figure 6.9). The higher metal content in this region may be attributed to the decrease in the grain size of sediment that are evident from the higher percentage of silt and clay in these sediments. The considerably lower values of chromium in the sediments of zone 3 can be related to the coarse sandy nature of the sediments in this area.

The exchangeable fraction of chromium (Cr_1)

The range of concentrations of the absolute values of Cr_1 fraction was from 0.20 to 7.75 µg/g and the relative variation was from 0.13 to 13.18 percentage of the total chromium (Table 6.6). The overall mean value of Cr_1 fraction was 2.68 µg/g, which corresponds to 2.28 % of the Cr_T (Table 6.2). The variations of the station wise annual mean concentrations of exchangeable fractions of chromium (Figure 6.10) showed that the lower limit of the concentration was observed at station 9 (1.77 µg/g) and the upper limit recorded at station 3 (3.75 µg/g). Except the two high values at stations 3 and 6, station wise annual mean concentrations of Cr_1 fraction showed a decreasing trend from station 1 to station 9. Seasonal variations (Figure 6.10) were characterized by the decline in concentrations during pre-monsoon period and elevation in concentration during post-monsoon period. The percentage wise distribution did not show much difference in values during post-monsoon and monsoon periods but the pre-monsoon values remained to be the lowest among the seasons. It was also observed that the range of values in pre-monsoon season (0.25 to 1.20 µg/g) was much less when compared to the range of values in monsoon (1.92 to 4.82 µg/g) and post-monsoon seasons (2.29 to 4.76 µg/g). As in the case of Co_1 fractions, higher percentage of exchangeable fraction of chromium were observed in zone 3, especially in monsoon and post–monsoon seasons. The comparatively lower percentage of Cr_1 fraction (Mean = 2.28 % of Cr_T) is in agreement with the non-mobility generally assigned to chromium above pH 4.0 (Nair, 1992). The seasonal hike in monsoon and post-monsoon seasons may be due to the input of Cr in the more mobile form during the land runoff. The relatively constant value of Cr_1 fraction in pre-monsoon season showed that the role of salinity is not very significant in the mobility of chromium in this estuary. The mean percentage of the exchangeable fraction of Cr observed in the present study area (2.28 %) is comparable to the value (2.3 %) reported by Gibbs (1973) from Yukon River. Still lower values were reported by Forstner (1982) from Rhine River

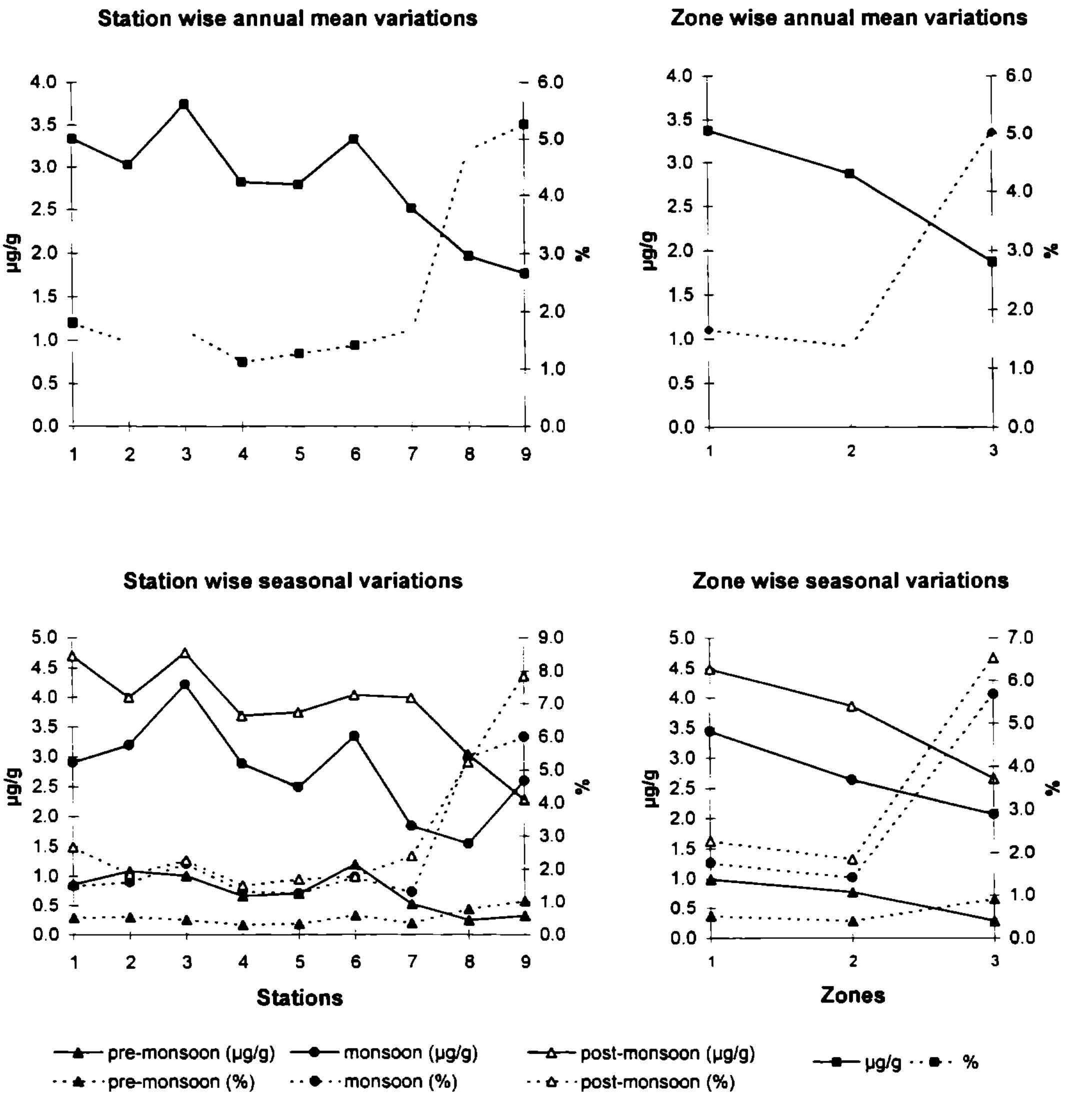


Figure 6.10 Spatial and temporal variations of exchangeable fractions of Cr (Cr_1) on absolute (µg/g) and relative (%) basis.

(0.1 %), Hong and Forstner (1983) from Yellow River (0.1 %), Samanidou and Fytianos (1987) from Axios River (0.52 %) and Elliot et al. (1990) from Pennsylvania sludge (1 %). Higher percentage of Cr_1 fraction was reported from Krka Estuary (range 11 to 39 %) by Prohic and Kniewald (1987). Slightly higher percentage of Cr_1 fraction recorded in the present study when compared to the values reported by Nair (1992) from other parts of Cochin Estuary (0.95%) showed that Cr is slightly more reactive in the southern upstream part of Cochin Estuary.

The reducible fraction of chromium (Cr_2)

The reducible fraction in sediments showed variations from 1.03 to 36.63 µg/g, the lowest being at station 9 and the highest at station 1 (Table 6.6). The whole range of values corresponds to a variation from 3.59 to 31.62 % of total Cr. The overall mean value of this fraction of chromium was 11.98 percentage and 17.43 µg/g (Table 6.2). This was found to be less than the corresponding percentage of the similar fraction of Cd and Co, though the absolute mean concentration (17.43) is higher than that of Cd_2 and Co_2. Station 9 also recorded lowest annual mean concentration (5.33 µg/g) but the highest was observed at station 3 (27.03 µg/g) (Table 6.6). The annual mean concentrations recorded at stations of zone 1 were almost comparable (range 25.46 to 27.03 µg/g). From stations 3 to 9, there was a decreasing trend in annual mean concentration, the decrease being much higher at stations 8 and 9 (Figure 6.11). Maximum scatter of values were observed at station 8, which recorded a coefficient of variation of 112. All stations, except station 5, recorded lower seasonal average values in monsoon period than in post-monsoon and pre-monsoon periods. The seasonal variations were not very vivid in absolute and relative terms as observed in Cr_1 fractions but slightly lower values were observed in monsoon season in many of the stations (Figure 6.11). One unique feature observed in the case of Cr_2 is that stations of zone 3 recorded higher percentage of Cr_2 fractions during all seasons. But such a hike was not

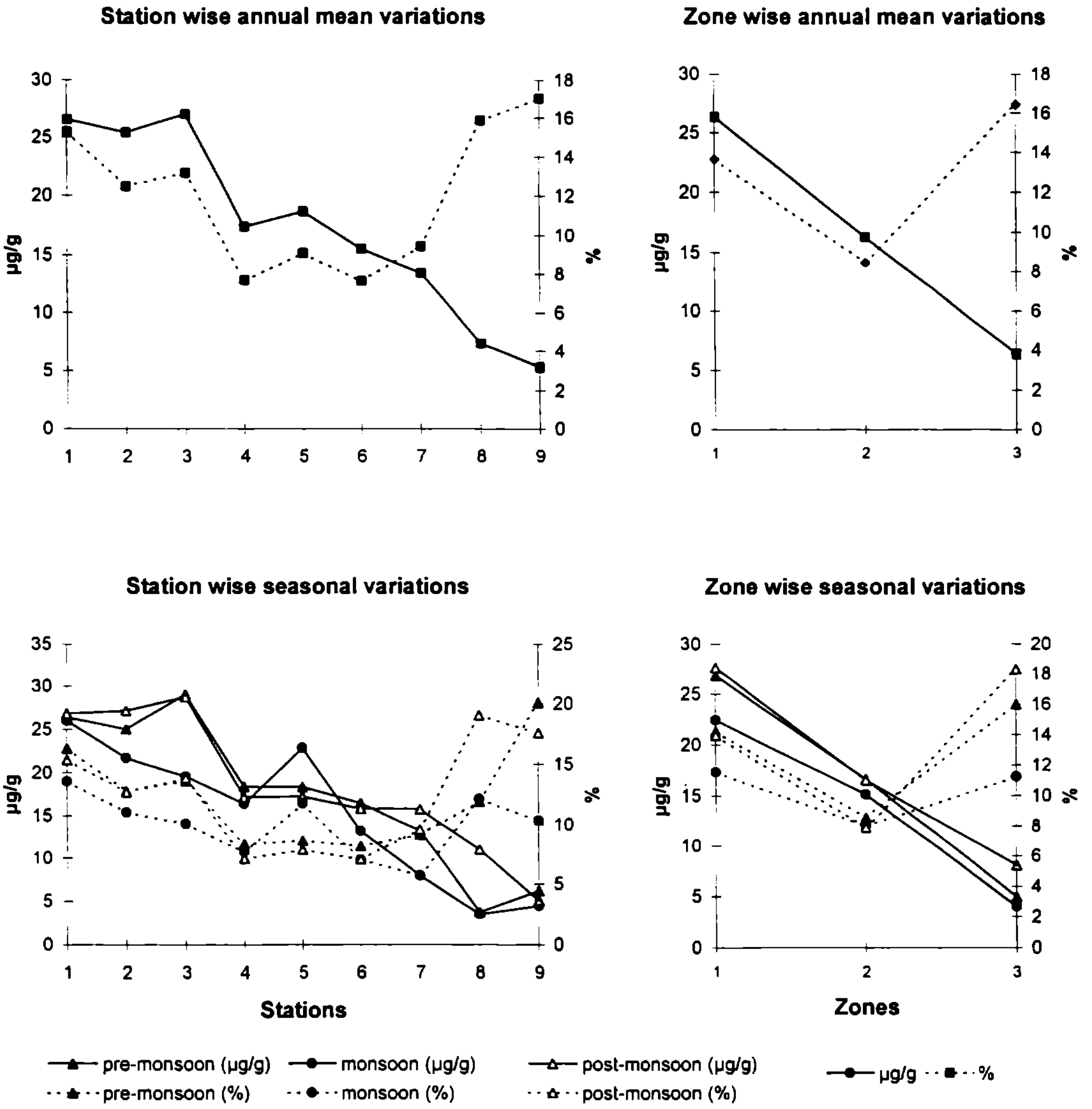


Figure 6.11 Spatial and temporal variations of reducible fractions of Cr (Cr_2) on absolute (μg/g) and relative (%) basis.

observed in absolute concentrations. Similar observation was made in the case of Co_2 fractions also. The mean percentage of Cr_2 fraction recorded in the present study is found to be much higher than the value (0.80) reported by Nair (1992) from other parts of the Cochin Estuary. It was also found higher than the values reported from Yukon River (7.2 %) by Gibbs (1973), Rhine River (0.4 %) by Forstner (1982), Yellow River (2 %) by Hong and Forstner (1983) and Axios River (9.04 %), Axios Estuary (10.32), Aliakmon River (4.23 %) and Aliakmon Estuary (3.52 %) by Samanidou and Fytianos (1987). Cr (III) has a strong tendency to adsorb onto particulates (McGrath and Smith, 1990). The relatively higher percentage of the reducible fraction of Cr observed in the present study can be due to the adsorption of Cr (III) on iron-manganese oxide coatings, which eventually settle at the bottom, and also due to coprecipitation of Cr (III) along with iron-manganese oxy-hydroxides.

The organic cum residual fraction of chromium (Cr_3)

From the study of the fractionation of chromium in the sediments of Kuttanad area, it was seen that the organic cum residual fraction of chromium (Cr_3) ranged from 11.08 to 268.41 μg/g in absolute concentration, the lowest being at station 9 and the highest at station 5 (Table 6.6). On a relative basis, concentration range falls between 67.62 to 95.94 % of the total chromium (Table 6.6). The overall mean percentage of this fraction (85.74 %) was found to be higher than that of the corresponding percentage of Cd and Co (Table 6.2). The station wise annual mean concentrations were found to vary from 25.43 μg/g at station 9 to 209.56 μg/g at station 4 (Table 6.6). In the case of Cr_3 fractions, stations of zone 3 recorded considerably lower annual mean concentrations (34.95 and 25.43 μg/g respectively) when compared to other stations (range 138.09 to 209.56 μg/g). Unlike the distribution pattern of Cr_1 and Cr_2 fractions, stations of zone 2 recorded highest annual mean concentrations (Figure 6.12). This may be due to the association of Cr with the stable organic complexes as this zone is rich in organic matter

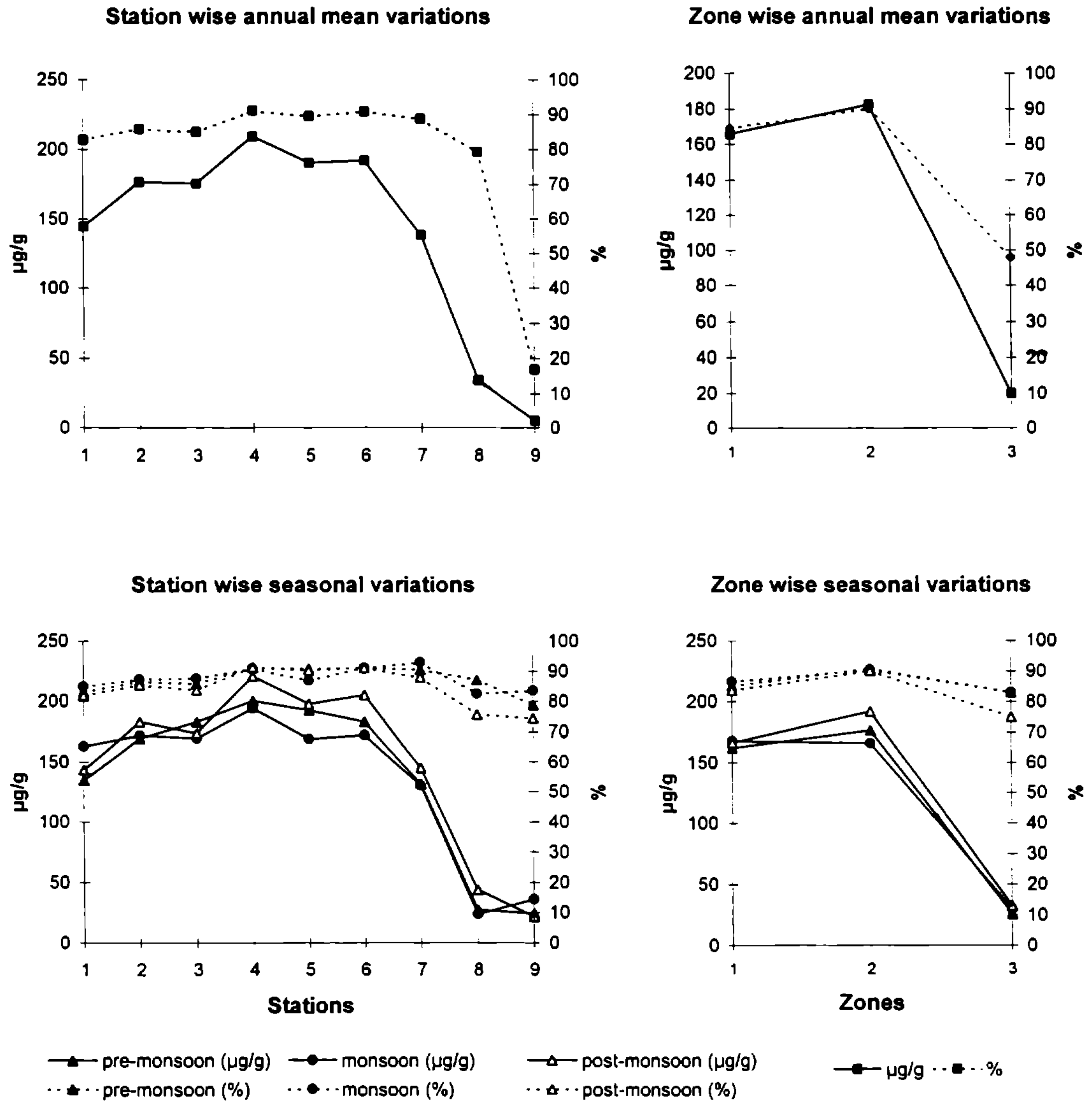


Figure 6.12 Spatial and temporal variations of organic cum residual fractions of Cr (Cr_3) on absolute (µg/g) and relative (%) basis.

(Chapter 3, Table 3.11). The ability of Cr to form stable organic complexes has been reported from sewage amended sites (Lake et al. 1989; Nair, 1992). Variations of Cr_3 among the seasons were not much evident (Figure 6.12), but rather uniformity in the distributional pattern had been exhibited along the stations in all the three seasons. The percentage wise distribution also not showed any seasonal differentiation. The mean percentage of the organic cum residual fraction of Cr reported in the present study (85.74 %) was lower than that reported by Nair (1992) from other parts of Cochin Estuary (98.26 %) and also lower than the values reported from Rhine River (99.4 %) by Forstner (1982), Yellow River (98 %) by Hong and Forstner (1983) and Axios River (90.44 %), Axios Estuary (89.49 %), Aliakmon River (95.54 %) and Aliakmon Estuary (96.26 %) by Samanidou and Fytianos (1987) and Pennsylvania sludge (97 %) by Elliot et al. (1990).

COPPER

Total copper in sediment (Cu_T)

The mean value of copper recorded in the surficial sediments of the studied area is 31.73 µg/g with a range of values from 3.09 to 69.55 µg/g (Table 6.1). The lowest and highest values were recorded at stations 9 and 2 respectively (Table 6.7). Station 9 recorded the lowest annual mean concentration (6.89 µg/g), but the highest annual mean concentration (58.11 µg/g) was observed at station 3 (Table 6.7). The annual mean concentration showed an increasing trend from station 1 to 3 followed by a gradual decrease towards station 9, the maxima of the concentration graph being at station 3 (Figure 6.13). Thus, the riverine zone (zone 1) recorded the highest annual mean and the estuarine zone (zone 3) recorded the lowest annual mean (Figure 6.13) concentrations of total copper in sediments.

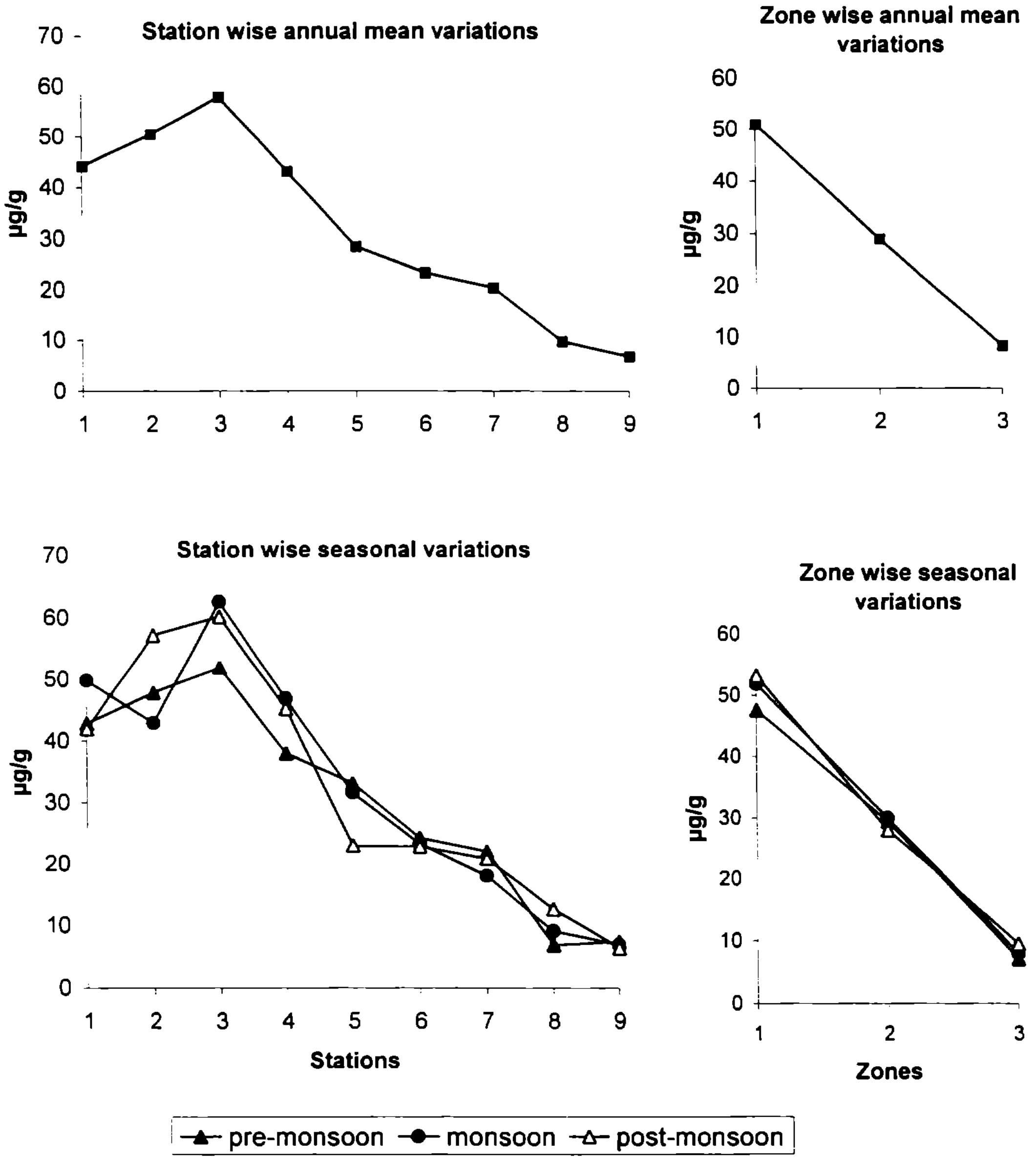
The seasonal distribution pattern is evident from Figure 6.13. A conspicuous difference in the values is not evident among the three

Table 6.7 Station wise summary statistics on Cu concentrations in sediments (μg/g)

	Stations	Min.	Max.	Mean	SD	CV
Total copper in sediment	1	35.00	60.78	44.26	7.36	16.63
	2	20.86	69.55	50.58	16.94	33.49
	3	32.12	68.44	58.11	11.50	19.78
	4	22.15	54.22	43.27	7.97	18.42
	5	13.74	35.91	28.57	6.85	23.97
	6	17.34	34.49	23.46	4.88	20.79
	7	6.83	35.79	20.54	8.30	40.43
	8	4.14	31.90	9.85	7.29	73.97
	9	3.09	12.42	6.89	2.69	39.12

		Absolute concentration (μg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of copper	1	0.01	0.22	0.12	0.08	67.71	0.03	0.44	0.24
	2	0.02	0.40	0.17	0.10	60.48	0.03	0.67	0.31
	3	0.01	0.46	0.22	0.16	72.17	0.01	0.73	0.35
	4	0.00	0.37	0.12	0.10	82.68	0.00	0.69	0.26
	5	0.02	0.15	0.09	0.06	64.39	0.05	1.13	0.34
	6	0.01	0.18	0.08	0.06	67.75	0.06	0.84	0.35
	7	0.01	0.14	0.07	0.05	66.22	0.05	0.81	0.36
	8	0.01	0.16	0.05	0.05	88.23	0.13	1.15	0.49
	9	0.01	0.09	0.04	0.03	74.37	0.11	2.01	0.61
Reducible fraction of copper	1	0.48	2.34	1.32	0.50	37.71	1.23	4.85	2.95
	2	1.00	4.43	2.62	1.25	47.86	2.07	8.54	4.62
	3	1.40	4.03	2.55	0.92	36.04	2.09	7.36	4.31
	4	0.92	3.80	1.68	1.08	64.24	2.16	7.18	3.73
	5	0.30	0.86	0.62	0.19	30.75	1.28	5.77	2.39
	6	0.19	0.59	0.40	0.14	34.02	0.86	3.06	1.73
	7	0.13	0.68	0.32	0.17	53.29	0.41	2.43	1.57
	8	0.08	0.84	0.33	0.21	64.23	0.77	5.68	3.47
	9	0.17	0.80	0.34	0.18	53.63	2.03	9.69	5.22
Organic cum residual fraction of copper	1	33.49	59.01	43.57	7.46	17.11	94.95	98.73	96.81
	2	37.59	65.50	53.70	10.31	19.20	90.90	97.70	95.07
	3	39.58	65.53	57.44	8.74	15.21	92.53	97.90	95.34
	4	21.15	50.05	42.22	7.91	18.73	92.31	97.57	96.01
	5	12.79	35.14	27.98	7.59	27.13	93.10	98.63	97.27
	6	16.66	33.95	23.50	5.20	22.14	96.10	99.09	97.93
	7	14.29	35.54	21.86	7.68	35.15	96.75	99.53	98.07
	8	5.18	30.89	9.75	7.54	77.38	94.15	99.00	96.04
	9	2.90	11.53	6.56	2.77	42.30	90.08	97.73	94.17

(SD = standard deviation, CV = coefficient of variation)


Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations

Zone wise seasonal variations

Figure 6.13 Seasonal and spatial variations of total copper in sediments.

seasons, in contrast to the behaviour of Cd, Co and Cr. The seasonal average value was found highest at station 3 during all the three seasons. The lowest seasonal average in monsoon and post-monsoon seasons was observed at station 9 but in pre-monsoon season it was at station 8. The trend observed in the variation of station wise annual mean concentrations was also observed in the case of seasonal average concentrations with an exception in monsoon season at station 2 which showed lower value than station 1. The spatial distribution pattern of copper is found to be different from that of cadmium, cobalt and chromium in that when the latter showed enrichment of metal concentrations in zone 2, copper showed enrichment of the metal levels in the fresh water region of zone 1 (Figure 6.13).

Since copper has a strong affinity for clays, iron and manganese oxides, and carbonate materials, residues are often elevated in sediments, in both fresh and marine waters. For example, total Cu in the sediments of Hamilton Harbour in eastern Canada ranged from 34 to 210 µg/g dry weight (Poulton, 1987). Similarly, in a review of literature on the Great Lakes, Mudroch et al. (1988) reported Cu_T values in the range 206-109 µg/g, 5-207 µg/g, 3-78 µg/g, 15-54 µg/g and 30-173 from the depositional basins of Ontario, Erie, Huron, Michigan, and Superior respectively. Highly polluted parts of Chesapeake Bay (USA) contain total Cu in the range 250-1500 µg/g dry weight (Sinex and Wright, 1988), while in San Francisco Bay, residues of 37-380 µg/g have been reported (Luoma and Philips, 1988). Concentration factors (sediment residue/water residue) typically exceeded 100 in both marine and fresh waters. Many of the above results are comparable and often higher than the range of values (3.09 to 69.55 µg/g) observed in the present study, but at the same time, higher than the mean copper value (10.19 µg/g) reported by Nair et al. (1990) from the downstream part of Cochin Estuary, when compared to a mean value of 31.73 µg/g observed in the present study. This value is appreciably lower than the values reported from the river sediments of Godavari (73 µg/g) by Biksham and Subramanian (1988), Mahanadi (57 µg/g) by Chakrapani and Subramanian (1990) and Tapti (126 µg/g) by

Subramanian (1987). However, the value is found to be slightly higher than the Indian average of 28 µg/g (Subramanian, 1987). The distribution pattern of total copper in sediments showed that the values were relatively higher in the reiverine zone (zone 1). This means that rivers are the major source of input of copper in the Kuttanad backwaters. Copper may be introduced anthropogenically in this area from fertilizers and fungicides, which are extensively used in the catchment area. Bordeaux mixture (a slurry of copper sulphate and hydrated lime) and copper oxychloride are the two major inorganic fungicides containing copper which are extensively used by rubber farmers in the catchment area of the upstream part of the rivers. This is mainly responsible for the high value of copper in the riverine stations (zone 1). The appreciably lower values of copper in the sediments of zone 3 are attributed to the sandy nature of the sediments in this area.

The exchangeable fraction of copper (Cu_1)

The Cu_1 fractions were distributed in very small amounts, the absolute mean value being 0.10 µg/g (Table 6.2). The relative mean value is 0.37 %, with a maximum value of 2.01 % (Table 6.2). The lowest value and the lowest station wise annual mean concentration (0.04 µg/g) of exchangeable fraction were observed at station 9 (Table 6.7). Similarly, the highest recorded value and the highest annual mean concentration (0.22 µg/g) of the exchangeable fraction of copper were seen at station 3. The trend in the variation of the annual mean concentration of the exchangeable fraction of copper in sediment is given in Figure 6.14. It shows that the concentration exhibited an increasing trend from station 1 to station 3 and then showed a decreasing trend towards station 9. Figure 6.14 also shows the variations of station wise seasonal mean concentrations. Irrespective of stations, lowest seasonal averages were observed in pre-monsoon period. In general, higher exchangeable fraction of copper was observed during the monsoon season (Figure 6.14). The percentage wise distribution pattern (Figure 6.14) showed an increase at zone 3 during monsoon and post-monsoon seasons. This may be due to

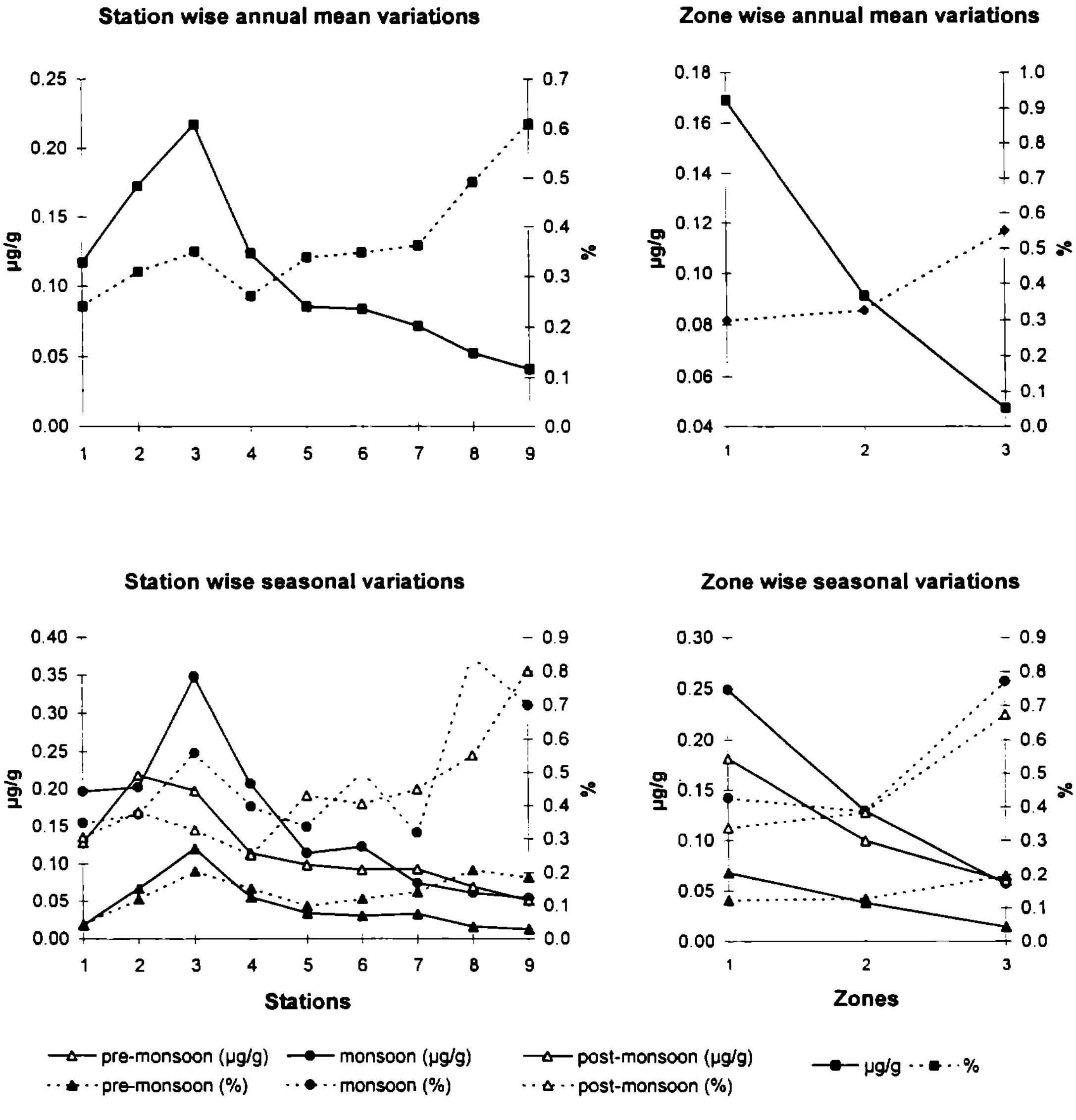


Figure 6.14 Spatial and temporal variations of exchangeable fractions of Cu (Cu_1) on absolute (µg/g) and relative (%) basis.

the reactive from of copper entering the estuary from the paddy fields through fertilizers and insecticides during this period. The comparatively lower concentration of Cu_1 fraction in zones 2 and 3 during pre-monsoon season can be due to two reasons. One is the release of exchangeable copper from sediments in the low saline region. In the low saline region, Ca and Mg ions compete with Cu for the ion-exchangeable site in sediment particles, releasing copper from sediments (Salomons and Bril, 1990; Salomons and Eagle, 1990). Another reason is the lack of enough exchangeable sites in sediment particles especially in sediments of zone 3. Compared to the earlier reported value (2.08 %) from other parts of Cochin Estuary by Nair (1992), the mean value obtained in the present study (0.37 %) is very low. Similarly, it was found lower than the values reported from Yukon (2.3 %) by Gibbs (1973), Yamaska River (1 %) by Tessier et al. (1980), St. Francois River (1.2 %) by Tessier et al. (1980), Rhine River (2.7 %) by Forstner (1982) and Neckar River (3 %) by Calmano and Forstner (1983). Similarly, the values reported by Lee (1985), Prohic and Kniewald (1987), Samanidou and Fytianos (1987) and Elliot et al. (1990) were found to be higher than the values observed in the present study. The reduced concentration of exchangeable fraction of copper observed in the present study area suggests the strong tendency of copper to remain in solution forming stable organic complexes especially in fresh water domains. Martin and Meybeck (1979) found that 10 to 50 percent of total copper exists in the dissolved form. Shibu et al. (1990) observed that the fresh water regime of the other parts of Cochin Estuary contained 69 percent of copper in the dissolved fraction.

The reducible fraction of copper (Cu_2)

As observed for Cu_1, Cu_2 fractions also were distributed in relatively low amounts, the values ranging from 0.08 µg/g at station 8 to 4.43 µg/g at station 2 (Table 6.7). In relative terms, the values ranged from 0.41 to 9.69 percentage with a mean value of 3.33 percentage (Table 6.2). Among the ten metals studied, copper recorded the lowest mean percentage (3.3 %) in the reducible fraction. The station wise annual mean concentration was found to vary from 0.32 µg/g at station 7 to 2.62 µg/g at station 2. The annual mean concentrations at stations 2 (2.62 µg/g) and 3 (2.55 µg/g) were almost comparable and were the two highest values recorded. The annual mean values recorded at stations 5 to 9 were considerably lower (in the range 0.32 to 0.62 µg/g) than the values recorded at stations 1 to 4 (Figure 6.15). Seasonal variations were more pronounced at stations 2 and 3 in absolute and relative terms than in other stations (Figure 6.15). Percentage wise seasonal variations were evident at stations of zone 3 and it can also be seen that there was an increase in the percentage of Cu_2 fractions at zone 3 than at zone 2; similar observation was also made to that of Co_2 and Cr_2. Stations 1 and 2 recorded lower concentration and lower percentage during pre-monsoon season and stations 8 and 9 recorded lower percentage of Cu_2 fraction during pre-monsoon season. A similar lower percentage of Cu_2 fraction was also observed by Nair (1992) from a study of other parts of Cochin Estuary (3.46 %).

The organic cum residual fraction of copper (Cu_3)

Variation of the absolute concentrations of organic cum residual fraction of copper (Cu_3) in the sediments of the surveyed area was found in the range 2.90 to 65.53 µg/g (Table 6.7), whereas the variation of the annual mean concentrations of the same fraction was in the range 6.56 to 57.44 µg/g (Table 6.7). The lowest value as well as the lowest annual mean concentration was observed at station 9, while station 3 recorded the highest value as well as highest annual mean concentrations. The trend in the variations of station wise annual mean concentrations of Cu_3 fraction is given in Figure 6.16, which showed that there was an increasing trend from station 1 to station 3 followed by a gradual decrease towards station 9. Seasonal variations were not very clear in most of the stations. Station 1 showed slightly high seasonal average in monsoon season. The mean percentage of Cu_3 fraction was the highest for similar fractions among the

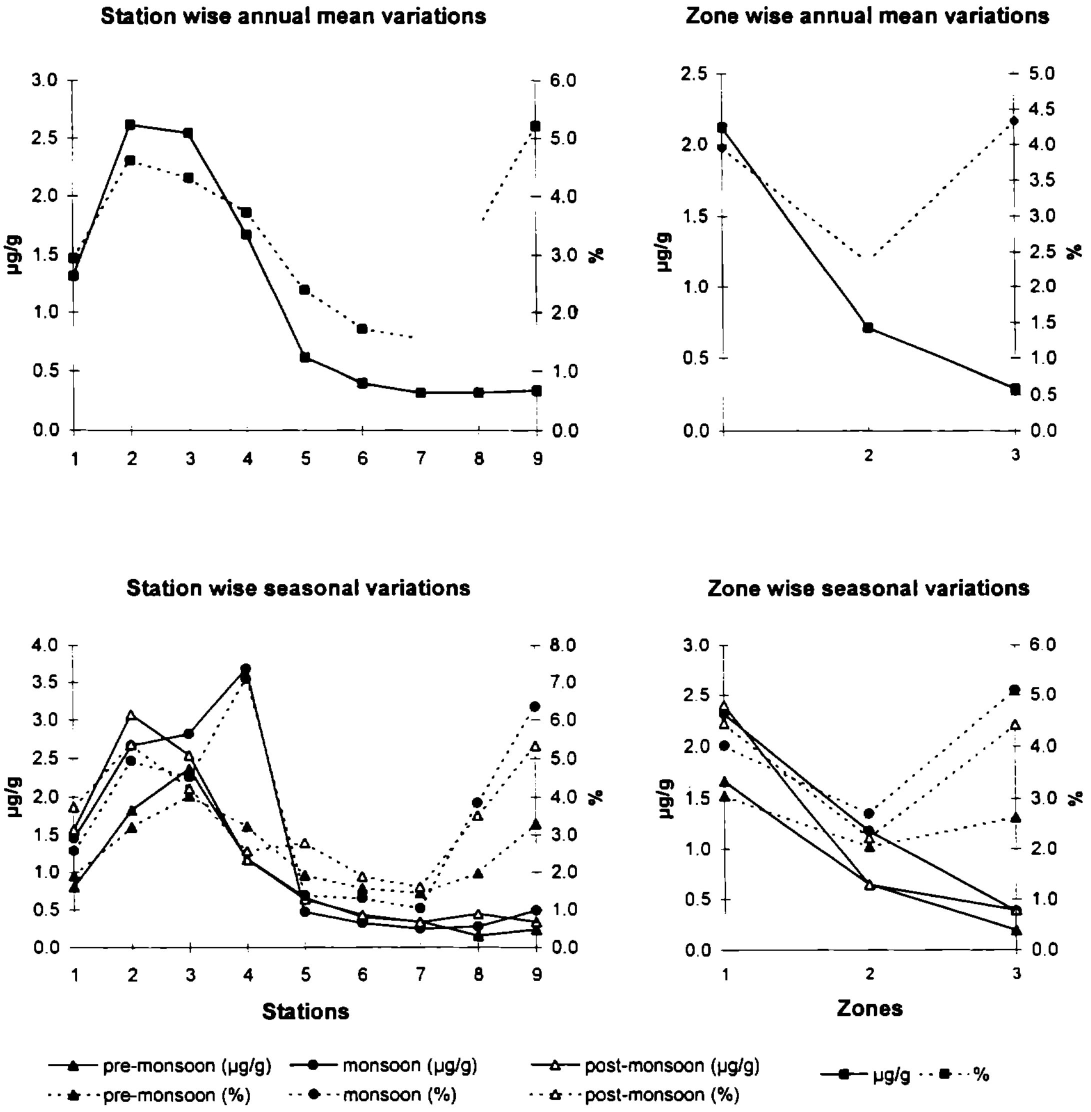


Figure 6.15 Spatial and temporal variations of reducible fractions of Cu (Cu_2) on absolute (µg/g) and relative (%) basis.

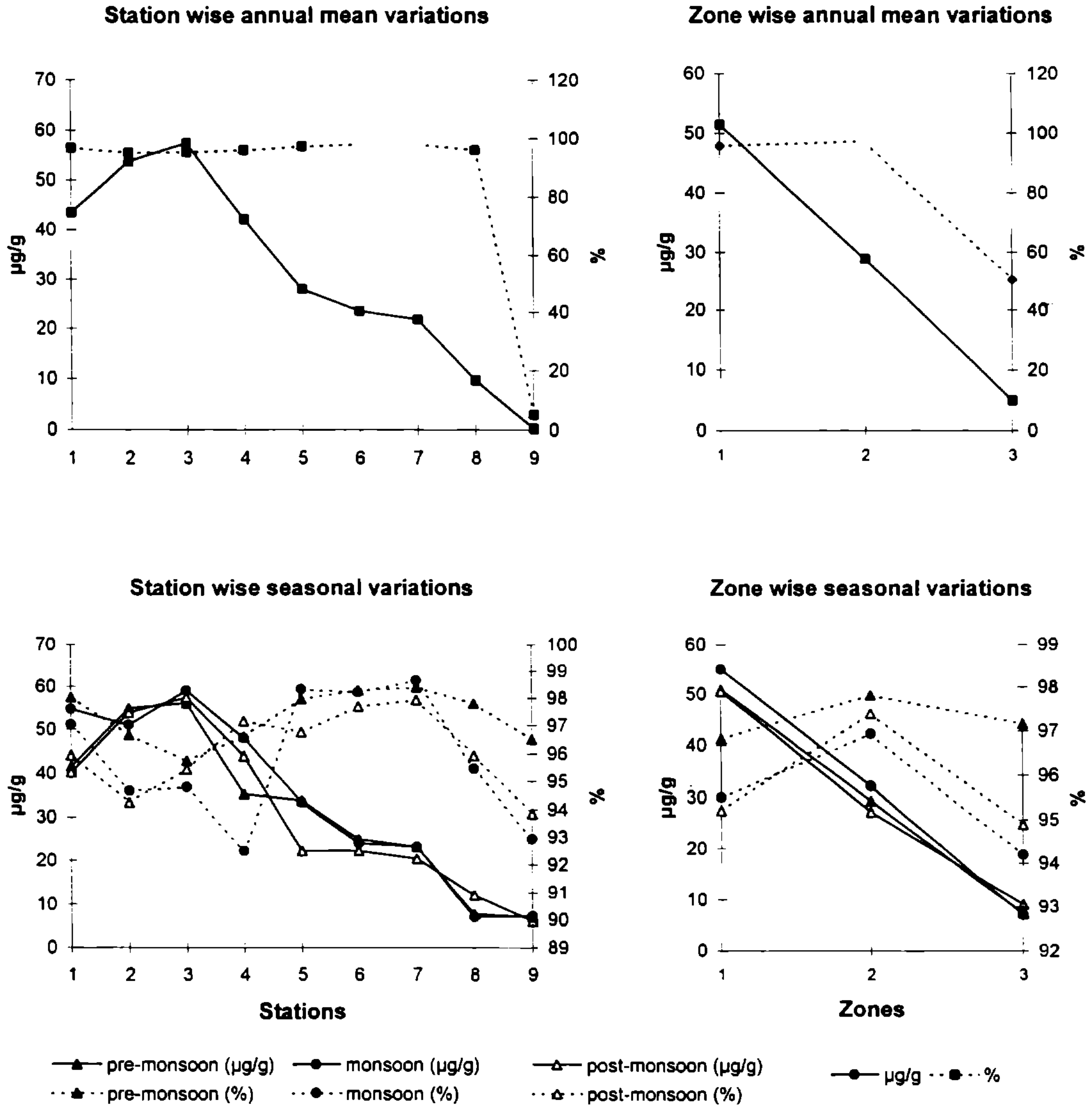


Figure 6.16 Spatial and temporal variations of organic cum residual fractions of Cu (Cu_3) on absolute (µg/g) and relative (%) basis.

10 metals studied (Table 6.2). The mean residual fraction of Cu reported from other parts of the Cochin Estuary by Nair (1992) was only 9.3 µg/g. The relatively high percentage of Cu_3 fraction is attributed to the association of a significant amount of Cu with organic matter. Many workers (Brannon et al., 1977; Tessier et al., 1980; Hong and Forstner, 1983; Samanidou and Fytianos, 1987; Pardo et al., 1990; Nair, 1992; Singh, 1999) have reported higher percentage of total copper bound to organic matter.

IRON

Total iron in sediment (Fe_T)

The concentration of iron in the surficial sediments of the area surveyed was found to vary from 0.50 % to 18.26 %, the lowest being at station 9 and the highest at station 5 (Table 6.8). The station wise annual mean percentage of total iron in sediment was in the range 1.44 to 11.02 % (Table 6.8). The lowest annual mean percentage was also observed at station 9 and the highest at station 5 (Table 6.8). The station wise annual mean percentage showed an increasing trend from station 1, reached a maximum value at station 5 and then decreased towards station 9 (Figure 6.17). The low saline zone (zone 2) was characterised by a distinct elevation in the total iron content in sediments (Figure 6.17), a behaviour similar to that of Co_T (Figure 6.2). As in the case of many other metals, the values at stations 8 and 9 were significantly lower (1.75 and 1.44 % respectively) when compared to the annual mean percentage at other stations (6.41 to 11.02 %).

The station wise seasonal average of total iron in sediments are also graphically represented in Figure 6.17 The range of values were 1.08 to 11.52 %, 1.64 to 9.25 % and 1.20 to 11.97 % in pre-monsoon, monsoon and post-monsoon seasons respectively. Station 8 recorded the lowest percentage of total iron in the pre-monsoon and monsoon seasons,

Table 6.8 Station wise summary statistics on Fe concentrations in sediments

	Stations	Min.	Max.	Mean	SD	CV
Total iron in sediment (%)	1	5.64	7.71	6.41	0.58	8.99
	2	3.25	8.41	6.77	1.77	26.15
	3	6.16	8.53	7.23	0.58	8.08
	4	8.82	10.92	9.67	0.62	6.41
	5	5.71	18.26	11.02	3.14	28.49
	6	7.92	14.10	10.93	1.98	18.09
	7	2.66	9.97	6.69	2.23	33.28
	8	0.91	5.61	1.75	1.29	73.65
	9	0.50	3.52	1.44	0.74	51.16

		Absolute concentration					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of iron (µg/g)	1	8.38	1756.99	595.71	640.38	107.50	0.01	2.65	0.95
	2	78.71	1452.08	631.60	541.62	85.75	0.13	2.07	0.90
	3	118.21	1329.13	860.83	323.40	37.57	0.17	2.16	1.19
	4	288.36	1206.16	590.16	301.21	51.04	0.29	1.17	0.60
	5	7.52	979.08	366.47	329.98	90.04	0.01	0.59	0.28
	6	0.43	253.46	65.23	91.56	140.38	0.00	0.30	0.07
	7	0.47	536.30	131.55	175.91	133.72	0.00	0.71	0.18
	8	1.13	288.64	61.58	99.78	162.03	0.01	2.29	0.39
	9	0.15	383.52	36.66	115.06	313.83	0.00	3.42	0.36
Reducible fraction of iron (mg/g)	1	12.88	32.71	21.68	7.35	33.90	20.03	50.44	33.87
	2	10.51	30.43	19.64	6.42	32.68	12.50	47.09	27.10
	3	8.80	28.21	19.59	6.54	33.40	13.12	37.86	27.02
	4	5.51	32.32	16.16	7.53	46.59	6.26	35.58	16.76
	5	10.25	40.02	17.88	9.47	52.98	7.65	42.57	16.95
	6	4.39	24.44	12.37	5.34	43.14	4.84	28.60	11.81
	7	6.13	19.89	12.31	4.74	38.52	8.97	53.26	20.01
	8	2.09	13.61	5.71	3.73	65.29	16.27	50.17	33.68
	9	1.19	12.01	5.41	3.71	68.58	22.50	69.89	37.25
Organic cum residual fraction of iron (mg/g)	1	28.05	53.43	42.33	9.56	22.59	46.90	79.91	65.18
	2	33.46	72.54	53.95	12.67	23.48	51.78	86.27	72.00
	3	42.89	62.21	51.84	7.23	13.95	60.81	85.82	71.79
	4	58.17	95.23	80.19	10.30	12.84	64.04	93.30	82.65
	5	43.69	168.47	95.01	34.80	36.63	56.85	92.25	82.77
	6	60.76	129.16	97.12	22.95	23.63	71.11	95.16	88.12
	7	12.72	87.20	58.12	20.82	35.83	46.54	91.02	79.81
	8	6.36	42.24	11.90	10.78	90.63	49.77	83.71	65.93
	9	3.85	23.17	8.76	5.70	65.03	30.09	77.49	62.39

(SD = standard deviation, CV = coefficient of variation)

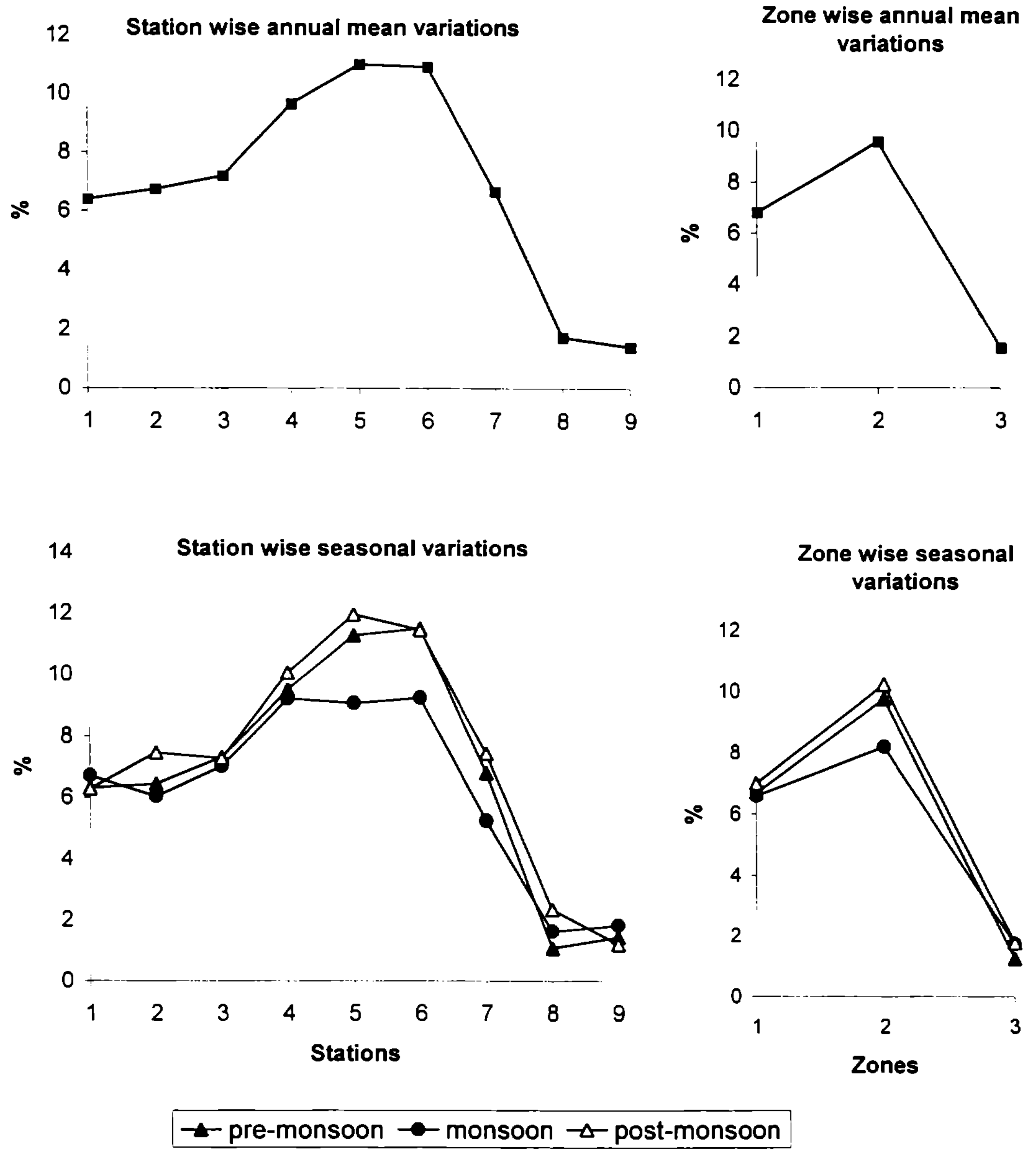


Figure 6.17 Seasonal and spatial variations of total iron in sediments.

whereas the lowest percentage in post monsoon season was recorded at station 9. The highest seasonal average of total iron in sediment was observed at station 6 in pre-monsoon and monsoon periods, whereas the highest average in post-monsoon season was at station 5. Generally, post-monsoon season recorded the highest percentage of total iron in sediments. Percentage of iron at stations 5 and 6 showed considerable decrease in monsoon season compared to the corresponding values in pre-monsoon and post-monsoon seasons. As observed in the case of annual mean concentration, the values at stations 8 and 9 were significantly lower than the values in other stations.

The discharge of municipal effluents into the ocean off Los Angeles resulted in surficial sediment iron residues of about 3.5% dry weight (Stull and Baird, 1985), while the concentrations of iron in North Sea sediments off the Belgium coast ranged from 0.9 -1.5% (Araujo et al., 1988). Similarly, high concentrations (0.7-1.8%) were reported for offshore areas of the Arabian Gulf (Samhan et al., 1987), the Ganges Estuary (1.2-4.6%) (Subramanian et al., 1988), and Bombay Harbour (6.2-7.6%) (Mohapatra, 1988). The mean value of iron in the sediments observed in this study (6.88%) is comparatively on the higher side when compared to the results. The pattern of spatial distribution is similar to that of cadmium, cobalt and chromium. It can be seen that iron levels were higher in the low saline stations of zone 2 (Figure 6.17). The flocculation and sedimentation of iron as a result of increase in ionic strength at stations where river water just meets saline water has been reported (Hart and Davies, 1981; Sharp et al., 1984). This can be one of the reasons for the increased concentration of sedimentary iron in zone 2. The decrease in sand content and high percentage of silt and clay in this zone may be another reason for the higher percentage of iron in this area. As in the case of Cd, Co and Cr, the lower values of iron in the sediments of zone 3 are attributable to the coarse sandy nature of the sediments in this area. Many elements including phosphates are scavenged by iron through adsorption onto particles. Since iron plays an important role in the fate of trace metals and nutrients, a breach in the iron-redox cycle may ultimately lead to the mobilization of toxic agents in the environment. Therefore, the relatively higher percentage of iron in the surficial sediments of Kuttanad should be viewed with some concern.

The exchangeable fraction of iron (Fe_1)

The concentrations of exchangeable fraction of iron (Fe_1) were found to vary from 0.15 to 1757 µg/g, with a mean value of 372.63 µg/g (Table 6.2). The exchangeable fraction of iron varied upto a maximum of 3.42 % of the total iron with a mean value of 0.55 %. These values were found slightly higher than the Fe_1 values reported by Nair (1992) from other parts of Cochin Estuary. Nair (1992) recorded Fe_1 values in the range 0.01 to 0.23 % with a mean value of 0.06 %. Many of the workers have reported lower values of Fe_1 fractions from different parts of the world. Some of them are Gibbs (1973) (0.01 %); Tessier et al. (1980) (0.01 %); Forstner (1982) (0.10 %); Hong and Forstner (1983) (0.10 %) and Samanidou and Fytianos (1987) (0.14 % - 0.23). But higher percentage of Fe_1 fractions were also reported from two different sites of Mobile Bay (1.35 % and 0.97 %) by Brannon et al. (1977).

Station 9 and station 3 remained to be the locations where the lowest and highest annual mean concentrations of exchangeable fractions of iron in sediments were recorded (Table 6.8). The annual mean concentrations at stations 1 to 5 were remarkably higher (in the range 366.47 to 860.83 µg/g) than the values at stations 6 to 9 (36.66 to 131.55 µg/g). Seasonal variations of exchangeable fractions of iron in sediments could be seen from Figure 6.18. The exchangeable fractions of iron at stations 8 and 9 were significantly lower in monsoon period, so also the post-monsoon average at station 9. Stations 1 to 4, 7 and 9 showed highest seasonal average in pre-monsoon season, stations 5 and 6 in

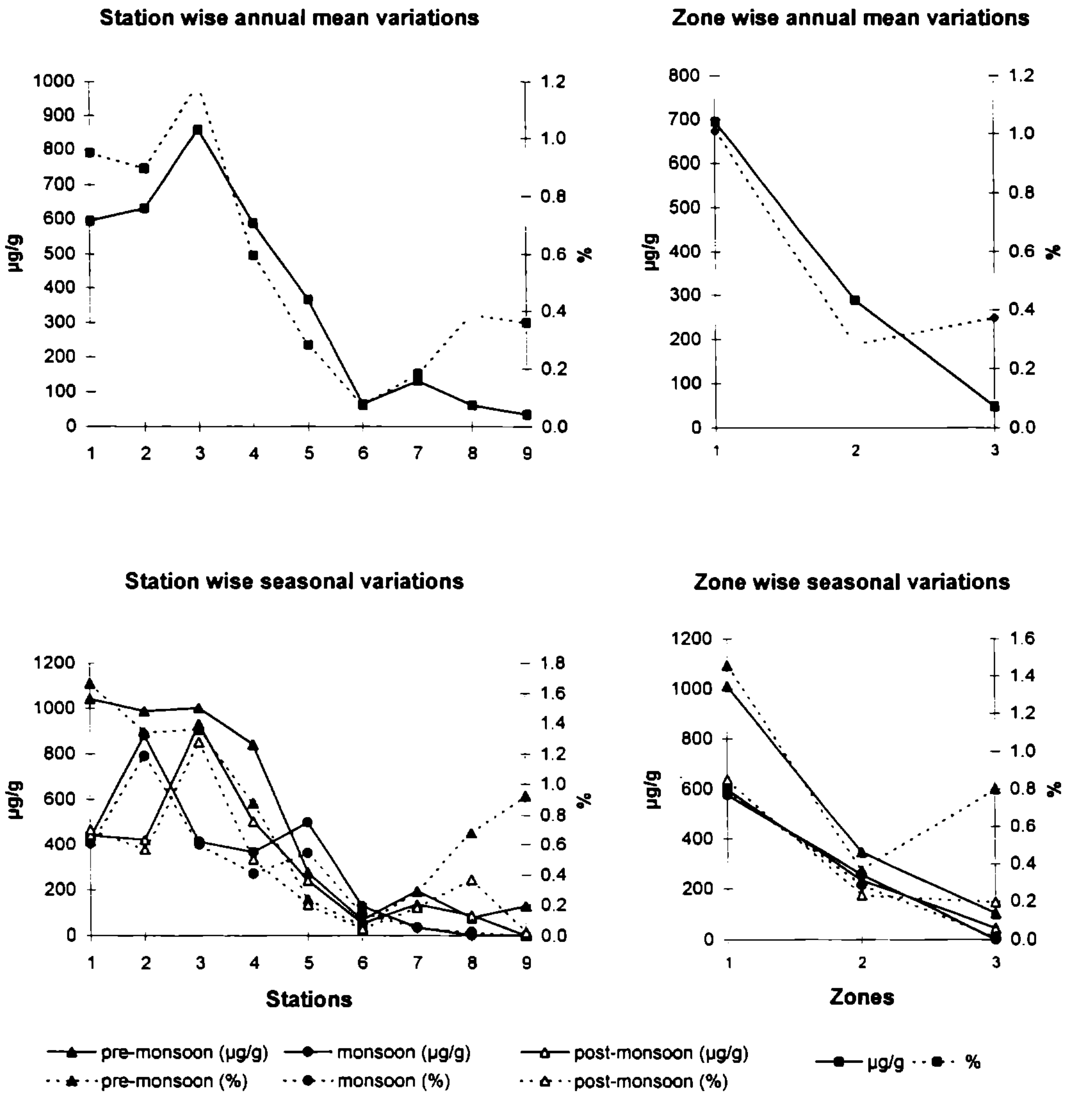


Figure 6.18 Spatial and temporal variations of exchangeable fractions of Fe (Fe_1) on absolute (µg/g) and relative (%) basis.

monsoon and station 8 in post-monsoon season. Marked variability in the concentrations of exchangeable fractions of Fe in all seasons is evident from Figure 6.18.

In the extraction procedure, the exchangeable fraction includes the iron dissolved in interstitial water as well as the iron loosely bound to adsorbing surfaces, which could be replaced by Mg ions. It has been recognized that the interstitial water contains more amounts of dissolved iron than the over lying waters (Brannon et al., 1977) and in sandy sediments the exchange of metals between the interstitial water and the overlying water will be more rapid than in clayey environments. This explains the lower concentrations of Fe_1 fraction in sediments of stations 6 to 9. The presence of high organic matter content, which mobilize iron under mildly reducing conditions explain the higher amount of Fe_1 fraction in the silty clay sediments of stations 1 to 5. The high concentrations of exchangeable fractions of iron at stations 1 to 4 during pre-monsoon period further substantiate this mobilizing character of iron. A diminishing trend in Fe_1 fractions with increasing salinity was observed by Sholkovitz (1976) and from Cochin Estuary by Nair (1992) due to the suppression of iron solubility at higher salinities. In the present study the percentage of Fe_1 fraction was found slightly higher at stations 8 and 9 especially in pre-monsoon season of higher salinities. This contrasting behaviour of the exchangeable fraction of iron could be attributed to the greater mobility of iron under a partially reducing atmosphere prevalent at these stations during the pre-monsoon season and also due to the greater acidity of the soils and sediments during the pre-monsoon season (KWBS, 1989).

The reducible fraction of iron (Fe_2)

The station wise summary statistics of Fe_2 fraction given in Table 6.8 showed that in the present survey, the concentrations varied from 1.19 to 40.02 mg/g, which in relative terms corresponds to 4.84 to 69.89 percentage of the total iron. The mean percentage value of Fe_2 fraction

(24.94 percentage) is almost comparable to that of Co_2 fraction (Table 6.2). Compared to the absolute concentrations of reducible fractions of other metals, Fe_2 fraction was the most abundant (14.53 mg/g). The station wise annual mean concentrations were found in the range 5.41 to 21.68 mg/g (Table 6.8). The lowest value and the lowest annual mean concentration were observed at station 9. Though the highest recorded value was observed at station 5 (Table 6.8), the highest annual mean concentration could be seen at station 1. The absolute values of station wise annual mean concentrations of Fe_2 fraction were found to exhibit a decreasing trend from station 1 to station 9, but the relative values, though decreased from stations 1 to 6, showed a sharp increase from stations 6 to 9 (Figure 6.19). Generally, a more or less uniform distribution pattern among the stations was observed in all the season without any appreciable seasonality (Figure 6.19). Unlike the other metals discussed, the absolute value of the reducible fraction of Fe was found about 39 times higher than the exchangeable fraction and percentage wise, about 45 times higher. These data show that a considerable amount of Fe in sediments of Kuttanad exist in the oxy-hydroxide form. The mean percentage of Fe_2 fraction observed in the present study (24.94 % of Fe_T) was much higher than the value reported by Nair (1992) from other parts of Cochin Estuary (1.34 %). But it is comparable to the values reported by Tessier et al. (1980) from St. Francois River (23.30 %), Samanidou and Fytianos, (1987) from Axios River (20.41 %), Axios Estuary (19.27 %) and Aliakmon River (27.47 %). Higher percentage of Fe_2 fractions were also reported by Tessier et al. (1980) from Yamaska River (34.10 %).

The organic cum residual fraction of iron (Fe_3)

The values of organic cum residual fractions of iron (Fe_3) ranged from a minimum of 3.85 mg/g at station 9 to a maximum of 168.47 mg/g at station 5 (Table 6.8). The percentage variation was 30.09 to 95.16 with a mean value of 74.52 percentage (Table 6.2). The mean percentage level (74.52 %) of Fe_3 fraction is comparable to that of Co_3 fraction and it is

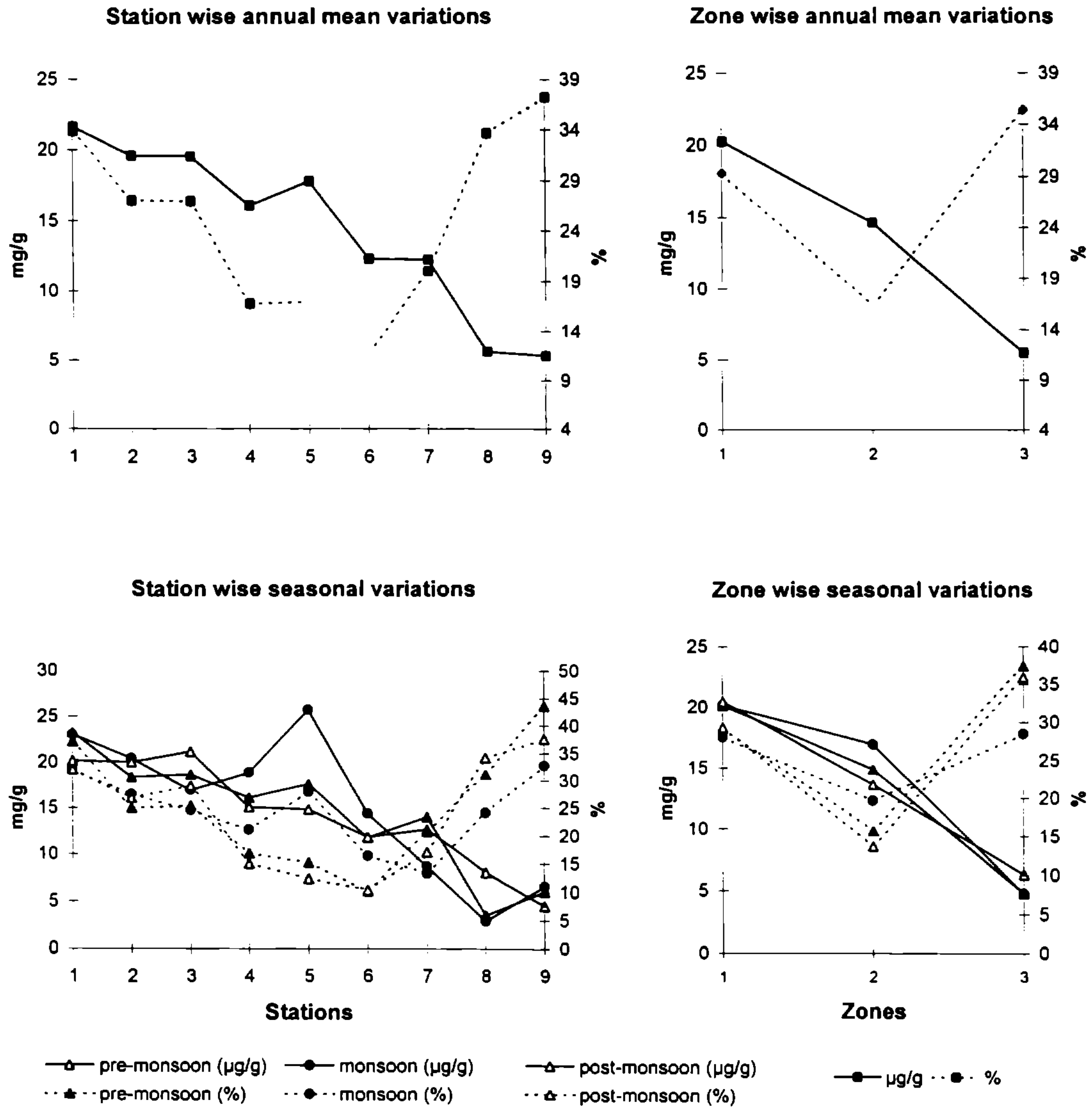


Figure 6.19 Spatial and temporal variations of reducible fractions of Fe (Fe_2) on absolute (mg/g) and relative (%) basis.

three times higher than that of the reducible fraction of iron (24.94 %). This fraction of Fe in sediments showed a minimum annual mean concentration of 8.76 mg/g at station 9, which increased to a maximum value of 97 12 mg/g at station 6 (Table 6.8). The annual mean values showed a declining trend on either sides of station 6, the decline being much higher towards station 9 than towards station 1 (Figure 6.20). As in the case of Fe_1 and Fe_2 fractions, stations 8 and 9 recorded much lower values when compared to other stations. The peak of station wise annual mean concentration graph was found in the low saline zone (zone 2) (Figure 6.20). Seasonal variations were more evident at stations 4, 5 and 6, where seasonal averages in monsoon season were found lower than the average values in pre-monsoon and post-monsoon seasons (Figure 6.20). The percentage of Fe_3 fraction observed in the present study (74.52) is more or less comparable to the values reported by Tessier et al. (1980) from Yamaska River and St. Francois River (65.80 % and 76.80 % respectively), and Samanidou and Fytianos, (1987) from Axios River, Axios Estuary, Aliakmon River and Aliakmon Estuary (79.45 %, 80.54 %, 72.29 %, and 64.51 % respectively). The Fe_3 fraction included organic fraction and residual fractions, which are associated with primary and secondary minerals and refractory organic materials (Engler et al., 1977; Tessier et al., 1979). The minimum seasonal variations observed in the case of Fe_3 fraction suggest that the major part of Fe_3 fraction was associated with the chemically inert and biologically inactive residual form. Enhanced biological activity under the influence of increasing temperature and abundant organic detritus was reported by Anirudhan (1988) during the pre-monsoon period from Cochin Estuary. This biological factor has a profound influence in controlling the organic cum residual fraction of Fe in the sediments of Kuttanad.

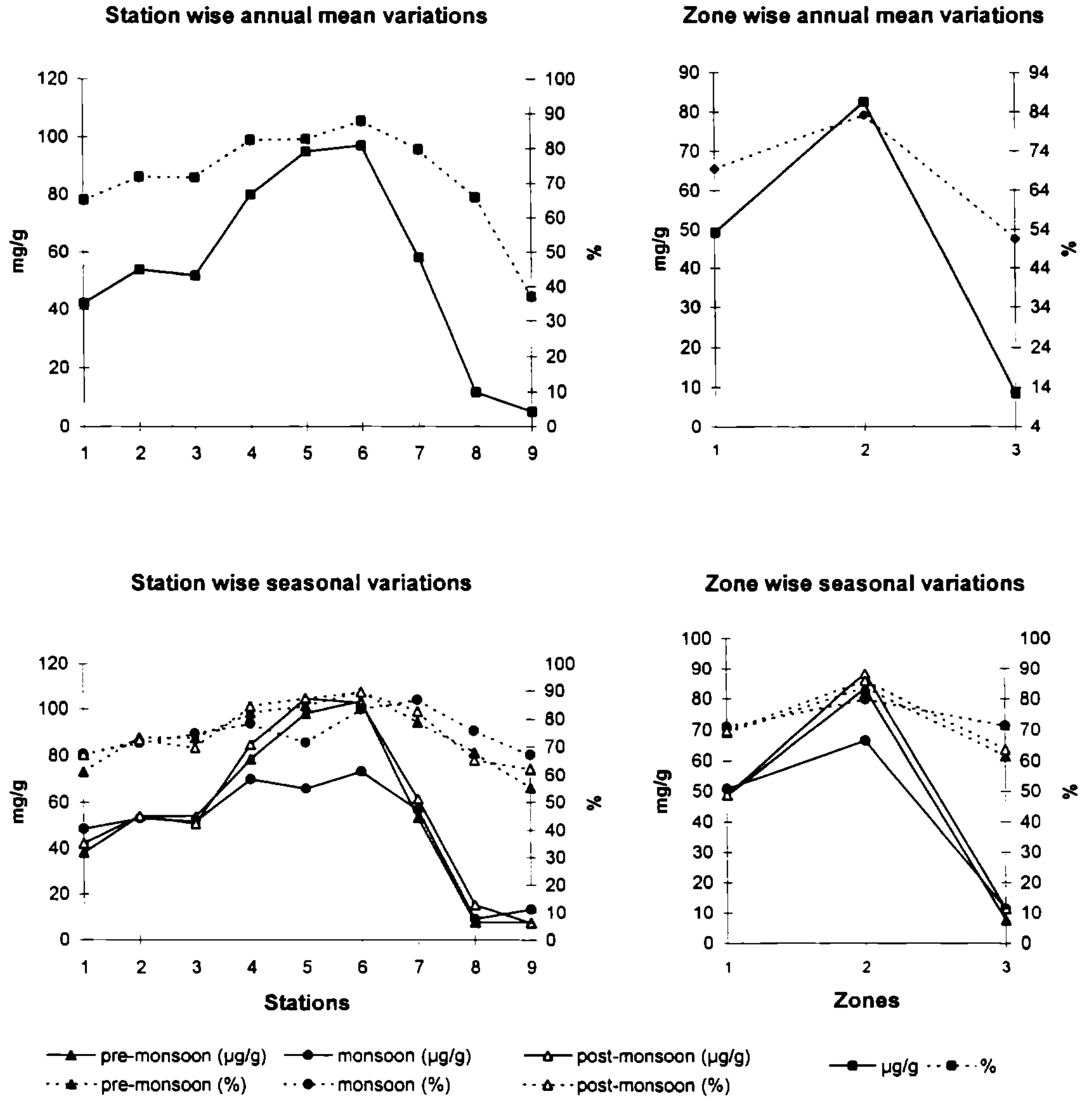


Figure 6.20 Spatial and temporal variations of organic cum residual fractions of Fe (Fe_3) on absolute (µg/g) and relative (%) basis.

MANGANESE

Total manganese in sediment (Mn_T)

Total concentrations of manganese in sediments varied from 0.07 mg/g to 1.38 mg/g (Table 6.1). As in the case of Cu, Mn also exhibited the lowest value at station 9, but the highest value was recorded at station 6 which was contrary to the behaviour of Cu. The highest annual mean concentration was also recorded at station 6 and the lowest at station 9 (Table 6.9). The annual mean concentration increased from station 1 to 6 with a slightly higher value at station 4 than at station 5, and then decreased to station 9 (Figure 6.21).

The station wise seasonal average concentration of total Mn in sediment was found to vary as given in Figure 6.21. The sediment Mn concentration was found to have maximum seasonal average in the post-monsoon season at all stations, except at stations 3 and 6, where the maximum seasonal average was found in the pre-monsoon season. Except at stations 3 and 9, the lowest seasonal values were observed in monsoon season. The spatial distribution pattern of manganese is more or less similar to that of Cd, Co, Cr and Fe. All these metals showed an increase in metal levels at zone 2 (Figure 6.21).

Manganese in the sediments of the North Sea near Belgium averaged 261 µg/g dry weights and was enriched (438 µg/g) in the clay/silt fraction (Araujo et al., 1988); the corresponding values for the Scheldt Estuary (The Netherlands) were also reported by Araujo et al. (1988) to be 117 and 434 µg/g, respectively. Comparable residues, ranging from 216 to 528 µg/g, were found in bulk samples from the Arabian Gulf (Samhan et al., 1987), whereas sediments from the Palos Verdes Shelf off the coast of Los Angeles carried manganese burdens of 273 to 403 µg/g (Stull and Baird, 1985). Much greater residues, upto 1,467 µg/g, were found in Thane

Table 6.9 Station wise summary statistics on Mn concentrations in sediments

	Stations	Min.	Max.	Mean	SD	CV
Total manganese in sediment (mg/g)	1	0.33	0.49	0.40	0.05	12.90
	2	0.29	0.55	0.46	0.08	16.47
	3	0.32	1.16	0.53	0.25	47.24
	4	0.73	0.98	0.84	0.08	8.97
	5	0.56	1.12	0.77	0.17	21.61
	6	0.55	1.38	0.90	0.25	27.66
	7	0.26	0.78	0.58	0.16	28.50
	8	0.11	0.73	0.20	0.17	83.66
	9	0.07	0.37	0.19	0.09	49.08

		Absolute concentration (µg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of manganese (µg/g)	1	98.99	241.56	164.63	45.52	27.65	26.74	51.21	40.57
	2	117.93	281.75	210.17	55.09	26.21	28.08	57.28	45.69
	3	119.72	276.22	195.79	51.26	26.18	21.37	56.02	43.64
	4	135.72	431.33	295.80	91.64	30.98	17.29	49.26	34.72
	5	105.47	394.20	231.65	82.93	35.80	14.53	55.93	31.15
	6	40.29	307.87	203.49	102.39	50.32	2.92	43.86	24.14
	7	40.93	195.98	111.52	56.36	50.54	7.51	41.87	20.65
	8	23.54	276.33	71.68	73.11	101.99	20.78	56.08	32.63
	9	2.62	66.04	40.42	21.48	53.14	3.81	54.47	23.52
Reducible fraction of manganese (µg/g)	1	51.24	178.18	116.83	41.33	35.38	13.54	43.75	28.58
	2	57.77	198.69	126.87	43.69	34.43	15.91	39.61	26.18
	3	61.41	228.03	125.47	45.30	36.10	15.92	36.36	26.11
	4	75.49	299.51	199.10	64.98	32.64	9.17	30.84	23.28
	5	109.11	305.65	177.78	66.06	37.16	13.03	36.44	22.58
	6	75.30	220.36	152.77	53.59	35.08	10.42	27.14	17.39
	7	36.09	172.12	93.19	45.02	48.31	7.83	46.73	16.60
	8	23.84	360.59	81.72	99.38	121.61	18.92	49.66	35.67
	9	22.77	289.38	94.33	75.52	80.06	26.57	77.63	44.96
Organic cum residual fraction of manganese (µg/g)	1	57.59	177.99	121.99	38.20	31.31	12.21	47.91	30.85
	2	75.83	246.35	132.30	53.37	40.34	15.45	49.73	28.13
	3	49.51	685.09	173.27	185.71	107.18	11.88	59.00	30.24
	4	240.42	541.46	351.60	105.14	29.90	24.75	65.78	42.00
	5	201.53	752.89	375.38	189.23	50.41	26.87	71.95	46.27
	6	263.76	1196.70	541.01	272.94	50.45	39.02	86.67	58.47
	7	38.64	556.25	387.37	148.66	38.38	11.40	83.66	62.76
	8	15.10	89.15	51.09	22.72	44.47	10.04	57.65	31.69
	9	2.30	211.39	59.93	59.86	99.89	1.78	68.77	31.52

(SD = standard deviation, CV = coefficient of variation)

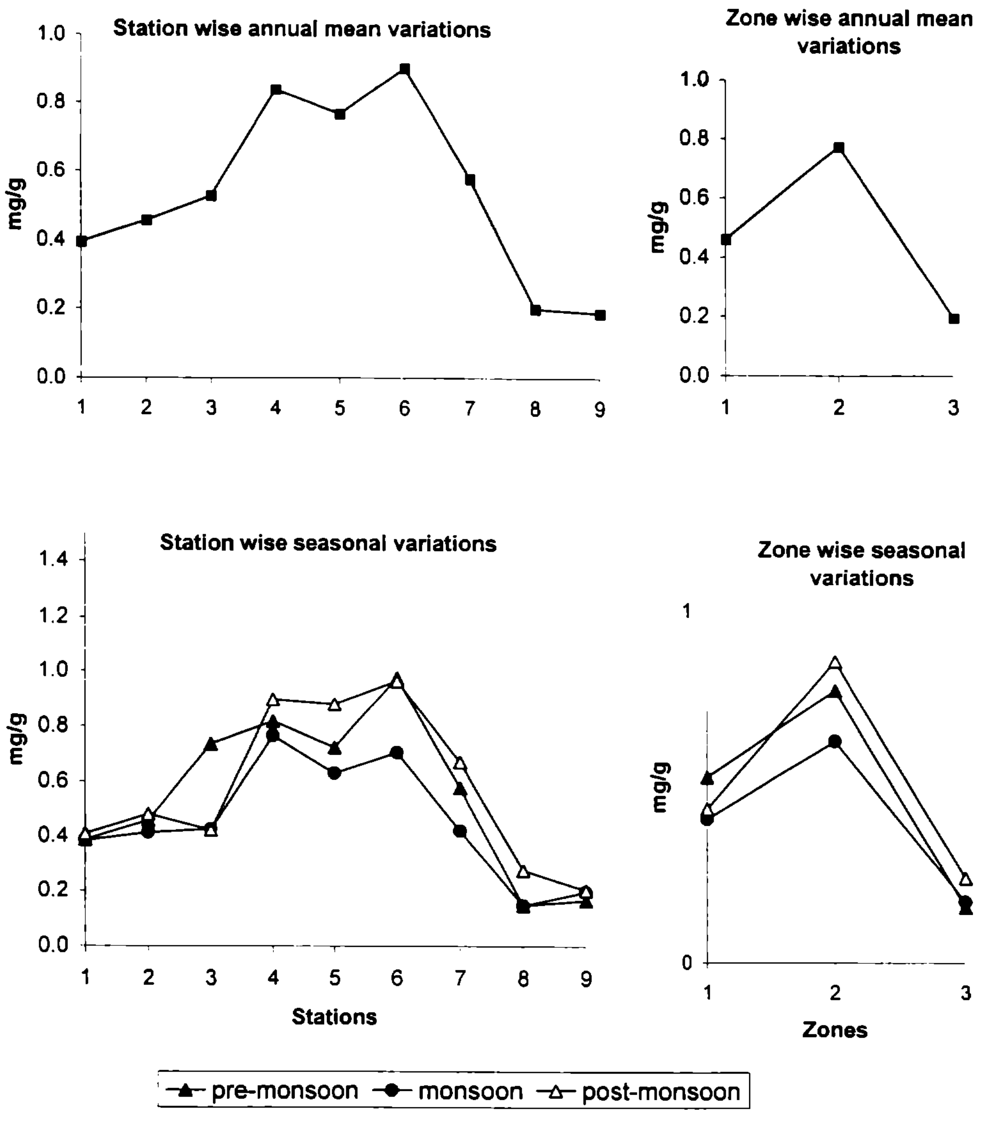


Figure 6.21 Seasonal and spatial variations of total manganese in sediments.

Creek (India), adjacent to the city of Bombay (Mohapatra, 1988). The mean value recorded by the present study (540 µg/g) is slightly lower than the Indian average of 605 µg/g (Subramanian, 1987) and also less than the world average (1050 µg/g) (Martin and Meybeck, 1979). The distribution pattern of manganese in sediments is almost similar to that of iron. As in the case of iron (zone 2), the low saline region, recorded the maximum level of manganese in all the three seasons (Figure 6.21). Higher concentration of Mn in low saline sediments was also reported by Williams et al. (1978) from Hudson Estuary and Jayasree and Nair (1995) from Cochin Estuary. The lower Mn content in the sediments of stations 8 and 9 (zone 3) is again due to the coarser sediment particles at these stations. Jayasree and Nair (1995) have reported such lowering of Mn concentration with increase in the percentage of sand in sediments from the northern part of Cochin estuarine system.

The exchangeable fraction of manganese (Mn_1)

Concentrations of exchangeable fraction of manganese in sediments varied from 2.62 to 431.33 µg/g, the lowest being at station 9 and the highest at station 4 (Table 6.9). Stations 9 and 4 were also found to record the lowest (40.42 µg/g) and highest (295.80 µg/g) of the station wise annual mean concentrations of exchangeable fraction of manganese in sediments. From stations 1 to 4, there was an increasing trend in concentration and after that the concentration slowly decreased towards station 9 (Figure 6.22). Seasonal variations were observed in the case of exchangeable fraction of Mn (Figure 6.22).

The mean concentration (173.18 µg/g) and mean percentage (32.97) of Mn_1 fraction were found to be much higher in the study area. The corresponding values reported by Nair (1992) from the northern side of Cochin Estuary was only 4.79 µg/g and 7.52 %. Values almost near to the one recorded in the present study were also reported by Tessier et al. (1980) from Yamaska River (29 %) and St. Francois River (26 %). Brannon

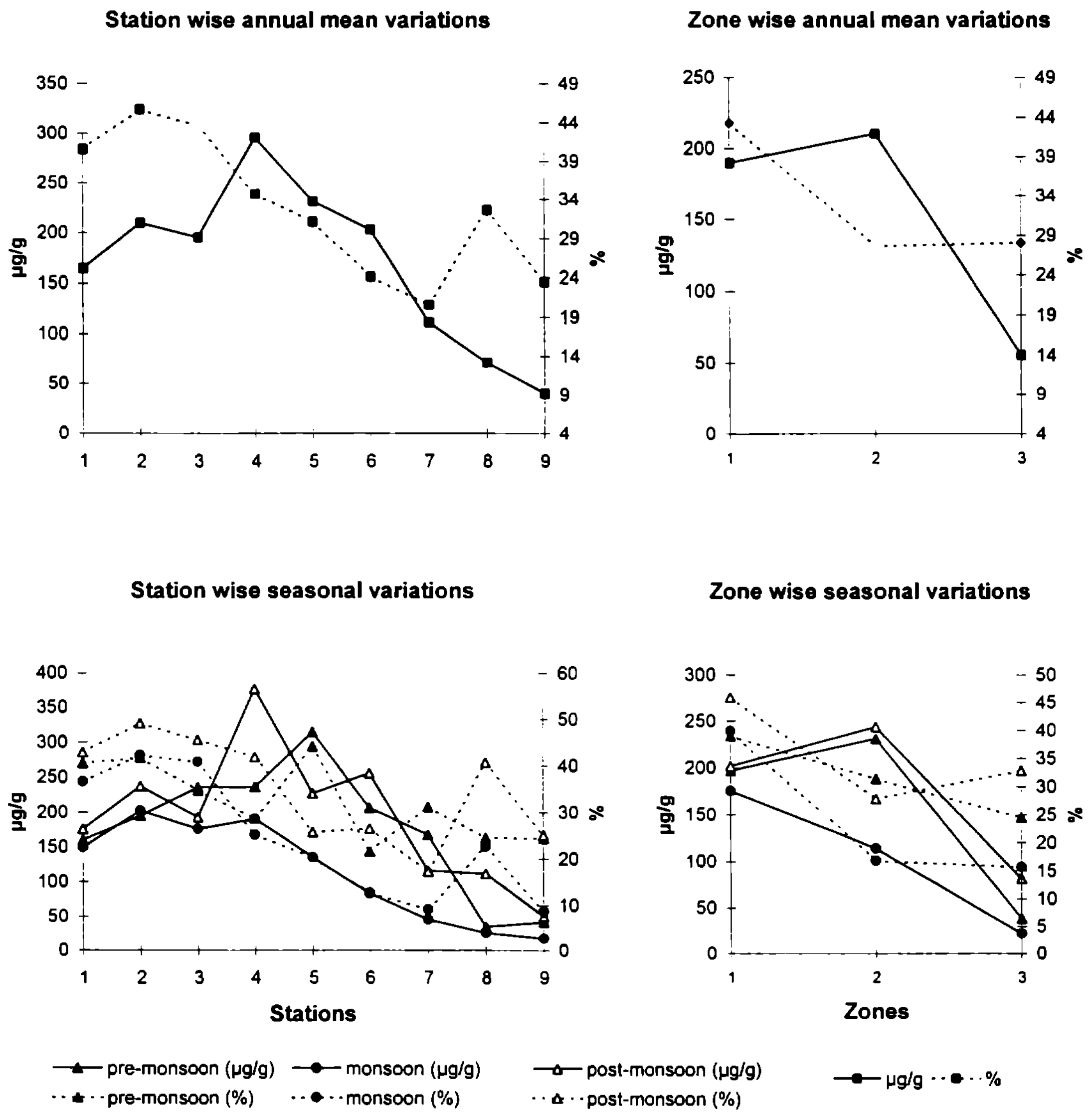


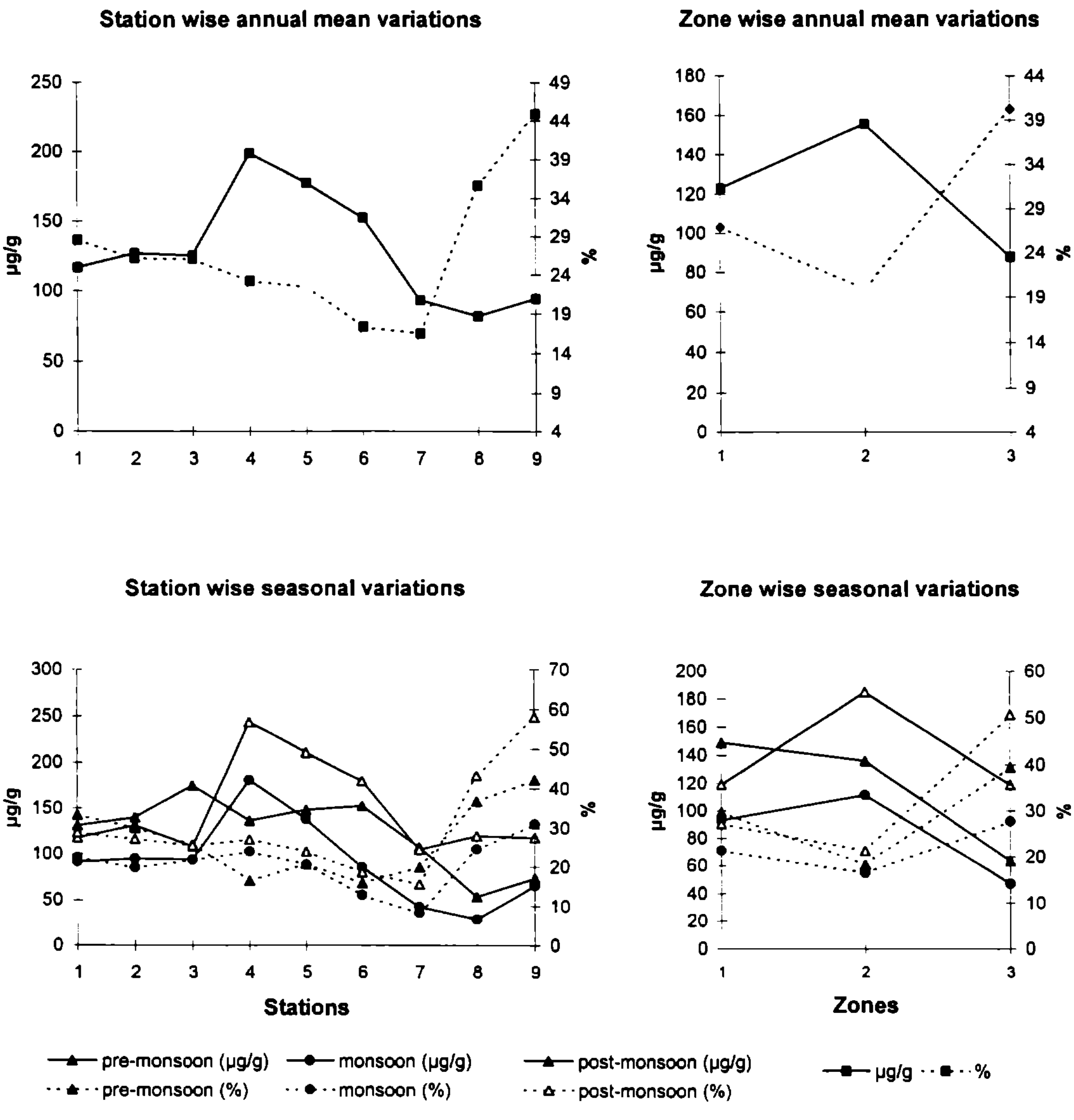
Figure 6.22 Spatial and temporal variations of exchangeable fractions of Mn (Mn_1) on absolute (µg/g) and relative (%) basis.

et al. (1977), Forstner (1982), Hong and Forstner (1983), Lee (1985) and Samanidou and Fytianos (1987) have also reported values on Mn_1 fractions from different estuaries / rivers, but they were within the range, 3.26 % to 14.93 %. One interesting feature observed in the partitioning of Mn in the sediments of Kuttanad backwaters is that compared to similar fractions of other trace metals studied, manganese exhibited the highest percentage in the exchangeable from. The higher organic carbon contents observed in the surface sediments of Kuttanad (Table 3.12, Chapter 3) may develop partial anoxic character in the sediments. This partial anoxic character of sediments will increase the mobility of Mn from sediments (Luoma, 1990).

The reducible fraction of manganese (Mn_2)

The reducible form of manganese was found to vary between 22.77 (station 9) to 360.59 µg/g (station 8) (Table 6.9) with an overall mean value of 129.79 µg/g (Table 6.2). The overall variation relative to total Mn in sediments is from 7.83 to 77.63 % with a mean value of 26.82 %. Mn was unique in the behaviour that the percentage of reducible fraction was less than that of the exchangeable fraction. The annual mean concentrations varied from a lowest value of 81.72 µg/g at station 8 to a highest value of 199.10 µg/g at station 4. Figure 6.23 shows that the annual mean concentrations at stations 4, 5 and 6 were comparatively higher. Seasonal variations were observed and can be seen from Figure 6.23. Lowest seasonal average was generally observed in monsoon season. Stations 1, 2 and 3 showed highest seasonal average in pre-monsoon seasons, whereas stations 4, 5, 6, 8 and 9 showed highest seasonal average in post-monsoon season.

Comparison of values reported by Nair (1992) on Mn_2 fractions from the middle and northern side of the Cochin Estuary (14.57 µg/g and 20.07 %) shows that the values recorded in the present study are higher (129.79 µg/g and 26.82 %), but the percentage of Mn_2 fractions


Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations

Zone wise seasonal variations

Figure 6.23 Spatial and temporal variations of reducible fractions of Mn (Mn$_2$) on absolute (mg/g) and relative (%) basis.

reported by Gibbs (1973), Brannon et al. (1977), Tessier et al. (1980), Forstner (1982), Patchineelam and Forstner (1983), Hong and Forstner (1983), Lee (1985), Samanidou and Fytianos (1987) were even higher than the values observed in the present study and were within the range 39 % to 56.06 %. One characteristic feature observed in the case of Mn partitioning in sediments of Kuttanad is that the reducible fraction was found lower than the exchangeable fraction. On probable reason for this is the conversion of the Mn (IV) to more labile Mn (II) under the partial anoxic environment (Luoma, 1990) prevailing in the sediment in presence of high organic carbon content (Table 3.11, Chapter 3).

The organic cum residual fraction of manganese (Mn_3)

The absolute values of organic cum residual fractions of manganese (Mn_3) were found to be in the range 2.30 µg/g (at station 9) to 1196.70 µg/g at station 6 (Table 6.9) with an overall mean value of 243.77 µg/g (Table 6.2). Relative to the total Mn in sediments, the values ranged from 1.78 to 86.67 percentage with a mean value of 40.21 percentage (Table 6.2). Station 6 also recorded highest annual mean concentration of Mn_3 fractions (541.01 µg/g) but the lowest was observed at station 8 (51.09 µg/g) (Table 6.9). As in the case of Fe_3 fractions, the annual mean concentrations declined on either side of station 6, stations 8 and 9 recorded the lowest of all stations and much lower than the values in other stations (Figure 6.24). The peak of annual mean concentration graph was found to be shifted more towards the estuarine region as was observed in the case of Fe_3 fractions. No definite seasonal trend in the absolute concentration of Mn_3 fractions was observed (Figure 6.24). Contrary to this, monsoon season recorded higher relative percentage of Mn_3 fractions. Zone 3 clearly recorded seasonal variations in percentage fractions with definite hike during the monsoon period and depletion during the post-monsoon season (Figure 6.24).

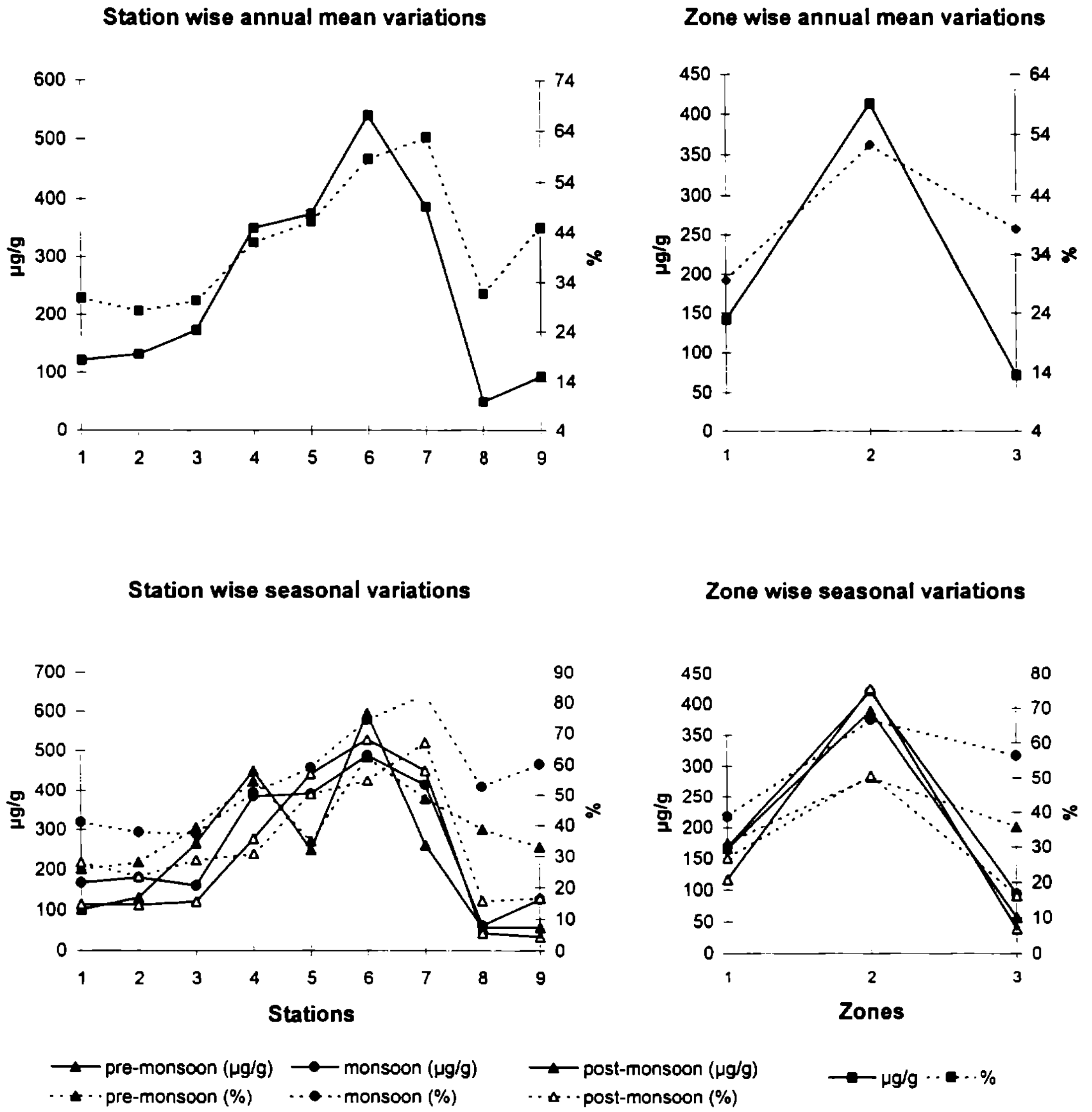


Figure 6.24 Spatial and temporal variations of organic cum residual fractions of Mn (Mn_3) on absolute (µg/g) and relative (%) basis.

Nair (1992) observed a mean value of 46.68 µg/g of Mn_3 fraction, which was 72.41 % of total Mn from the northern side of Cochin Estuary. Compared to this, the concentration of Mn_3 fraction observed in the present study was very high (243.77 µg/g) but in relative terms (40.21 %), it was less than that observed by Nair (1992). Many workers have reported values comparable to that recorded in the present study. Some of them were Gibbs (1973) (43.70 %), Brannon et al. (1977) (43.60), Hong and Forstner (1983) (44.0 %) and Samanidou and Fytianos (1987) (40.05 to 45.76 %). The higher percentage of Mn_3 fraction during monsoon period indicates the terrestrial input of this fraction of Mn. Comparing the organic cum residual fractions of all trace metals (Table 6.2), it can be seen that the lowest percentage in this fraction was recorded by Mn (40.21%). This unique behaviour of Mn shows that Mn is the most mobile metal in the aquatic environment of Kuttanad.

MOLYBDENUM

Total molybdenum in sediment (Mo_T)

Various authors have shown that molybdenum is often enriched in anoxic sediments (Gross, 1967; Bertine, 1973; Seralathan and Hartmann, 1986). The mechanism for the removal of molybdenum into sediments is not fully understood, but it is thought to involve either initial co-precipitation with iron sulphides, or adsorption onto some oxygenated phases, such as manganese oxide, which is subsequently transferred into oxygen depleted waters, where the molybdenum is released. In the underlying anoxic sediments, molybdenum may be incorporated into the sediment complex by reactions with organic materials. Because of the relatively rapid sedimentation rates of estuarine and near shore deposits compared with deep-sea sediments, molybdenum will be fairly rapidly removed in the anoxic estuarine and near shore sediments, and this is an important factor in the budget of the element. Data on molybdenum concentrations from estuarine sediments are very limited and this is the first attempt to study the levels of molybdenum in Cochin estuarine system.

The mean value of molybdenum in the present study was found to be 88.47 µg/g and the range of concentration of total molybdenum in sediments was 6.39 to 194.72 µg/g of dry sediment (Table 6.1). Station wise minimum, maximum, average, standard deviation and percentage coefficient of variation of sediment total molybdenum are given in Table 6.10. The highest value in this case was recorded at station 2 and the lowest value at station 9. The station wise annual mean concentration was in the range 16.21 to 145.98 µg/g (Table 6.10). As in the case of cadmium and cobalt, the lowest annual mean concentration of total molybdenum in sediments was observed at station 9, but the highest annual mean concentration was seen at station 2, which was contrary to the behaviour of cadmium and cobalt. The trend in the variation of station wise annual mean concentration (Figure 6.25) showed that the concentration peak is at station 2 and there is a gradual decrease in the concentration from station 2 to station 9. This trend is different from that of cadmium and cobalt, where the values increased from station 1 and the concentration peak appeared at station 6.

Seasonal variations in the concentration of total molybdenum in sediment could also be seen from Figure 6.25 but the variations were different for different stations. During the pre-monsoon season, the values ranged from 14.07 µg/g (station 8) to 137.71 µg/g (station 2) and the trend in the variation was similar to that for annual mean concentration. The monsoon and post-monsoon seasons also showed a similar trend with concentration maximum at station 2 and minimum at station 9. Thus, the seasonal distribution pattern is characterized by the post-monsoonal build up of the metal in sediments and the spatial distribution pattern is characterised by depletion of the metal concentration from the fresh water zone (zone 1) to the low saline and high saline zones (zone 2 and zone 3) (Figure 6.25). This type of a spatial distribution pattern was also observed

Table 6.10 Station wise summary statistics on Mo concentrations in sediments (µg/g)

	Stations	Min.	Max.	Mean	SD	CV
Total molybdenum in sediment	1	87.63	149.48	120.91	19.87	16.43
	2	96.57	194.72	145.98	28.28	19.37
	3	55.95	194.51	140.73	34.90	24.80
	4	97.46	149.92	125.18	16.20	12.94
	5	53.84	102.69	84.62	14.91	17.62
	6	50.20	101.64	73.36	15.93	21.72
	7	29.93	102.43	65.87	20.17	30.62
	8	10.97	77.72	23.41	17.91	76.51
	9	6.39	28.27	16.21	5.60	34.53

		Absolute concentration (µg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of molybdenum	1	1.91	2.93	2.50	0.34	13.59	1.62	2.87	2.16
	2	2.08	3.57	2.82	0.48	16.89	1.26	3.10	2.13
	3	1.61	3.53	2.56	0.58	22.84	1.17	5.68	2.10
	4	1.67	3.20	2.25	0.46	20.34	1.15	2.32	1.80
	5	1.65	2.99	2.28	0.42	18.36	1.91	3.63	2.77
	6	1.57	3.01	2.36	0.40	16.98	1.95	5.51	3.37
	7	1.10	3.22	2.26	0.64	28.48	1.51	8.10	4.05
	8	1.17	3.09	1.65	0.55	33.24	3.98	11.72	7.76
	9	0.91	2.93	1.54	0.60	38.54	5.17	27.90	11.11
Reducible fraction of molybdenum	1	7.49	11.35	9.17	1.30	14.15	5.88	10.62	7.99
	2	8.05	14.43	10.35	2.01	19.40	4.90	10.36	7.49
	3	6.42	11.79	10.16	1.61	15.85	5.32	16.74	7.95
	4	4.23	9.19	7.73	1.50	19.46	3.76	8.54	6.30
	5	5.43	10.17	7.79	1.52	19.48	6.85	11.75	9.64
	6	3.75	9.32	7.39	1.68	22.69	6.41	16.56	10.64
	7	3.45	10.45	7.21	2.04	28.33	4.76	22.85	12.28
	8	2.42	13.94	4.48	3.43	76.60	12.60	22.25	18.06
	9	2.07	5.92	3.62	1.11	30.68	14.55	37.16	23.13
Organic cum residual fraction of molybdenum	1	76.78	137.15	105.55	19.01	18.01	86.79	92.50	89.85
	2	83.66	182.55	129.25	29.43	22.77	86.63	93.75	90.37
	3	43.41	180.79	126.73	37.13	29.30	77.59	93.16	89.95
	4	88.50	141.28	114.69	17.69	15.43	89.36	94.76	91.90
	5	46.46	93.25	71.75	13.70	19.10	85.78	90.80	87.60
	6	39.78	91.73	62.54	16.44	26.28	79.25	90.90	85.99
	7	20.66	91.66	56.17	21.92	39.03	69.05	93.73	83.67
	8	7.34	60.69	19.13	15.29	79.94	66.88	81.31	74.17
	9	2.54	21.85	11.55	5.59	48.43	39.77	80.28	65.76

(SD = standard deviation, CV = coefficient of variation)

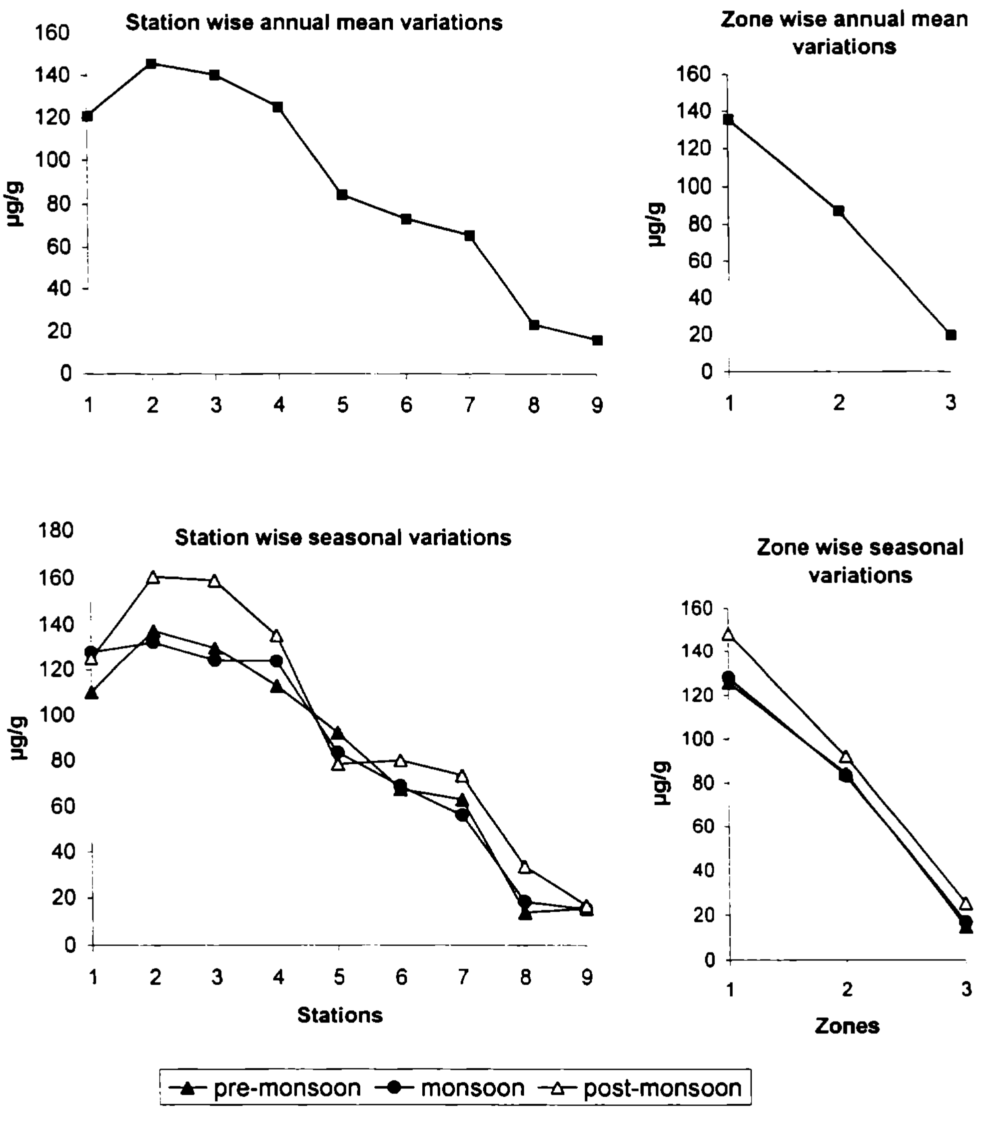


Figure 6.25 Seasonal and spatial variations of total molybdenum in sediments.

for copper (Figure 6.13). Both the metals showed high values in the fresh water region of zone 1 and low values at zone 3. This means that both copper and molybdenum have a common source of input in the estuary and the fate and transport of these metals in this part of the Cochin Estuary are identical. Seralathan and Hartmann (1986) reported molybdenum concentrations in the range <1 to 10 µg/g from the sediment cores of African continental margin.

The exchangeable fraction of molybdenum (Mo_1)

The mean values of exchangeable fraction of molybdenum (Mo_1) were found to be 2.25 µg/g in the range 0.91 to 3.57 µg/g (Table 6.2). Relatively, a mean percentage of 4.14 of the total Mo, in the range 1.15 to 27.90 % was observed (Table 6.2). In this case, station 2 showed highest recorded value and the lowest, as in the case of most of the other elements was observed at station 9 (Table 6.10). The range of station wise annual mean concentrations was 1.54 to 2.82 µg/g (Table 6.10). Stations which recorded lowest and highest values also recorded lowest and highest annual mean concentrations. The overall trend (Figure 6.26) had a decreasing tendency from station 1 to station 9, or in other words the riverine zone showed higher values than the estuarine zone. Variations in the station wise seasonal average values are also represented in Figure 6.26. Any specific seasonal variations could not be found from graph. One unique feature observed was the considerable increase in the percentage of the Mo_1 fraction at zone 3 during all the seasons. The trend in the station wise annual mean concentrations suggests that the sediments in the fresh water zone have more ion-exchangeable manganese than sediments in the low saline region. Another possible reason for the observed decreasing trend in station wise annual mean concentration towards zone 3 may be the greater percentage of coarser particles in the sediments of this region.

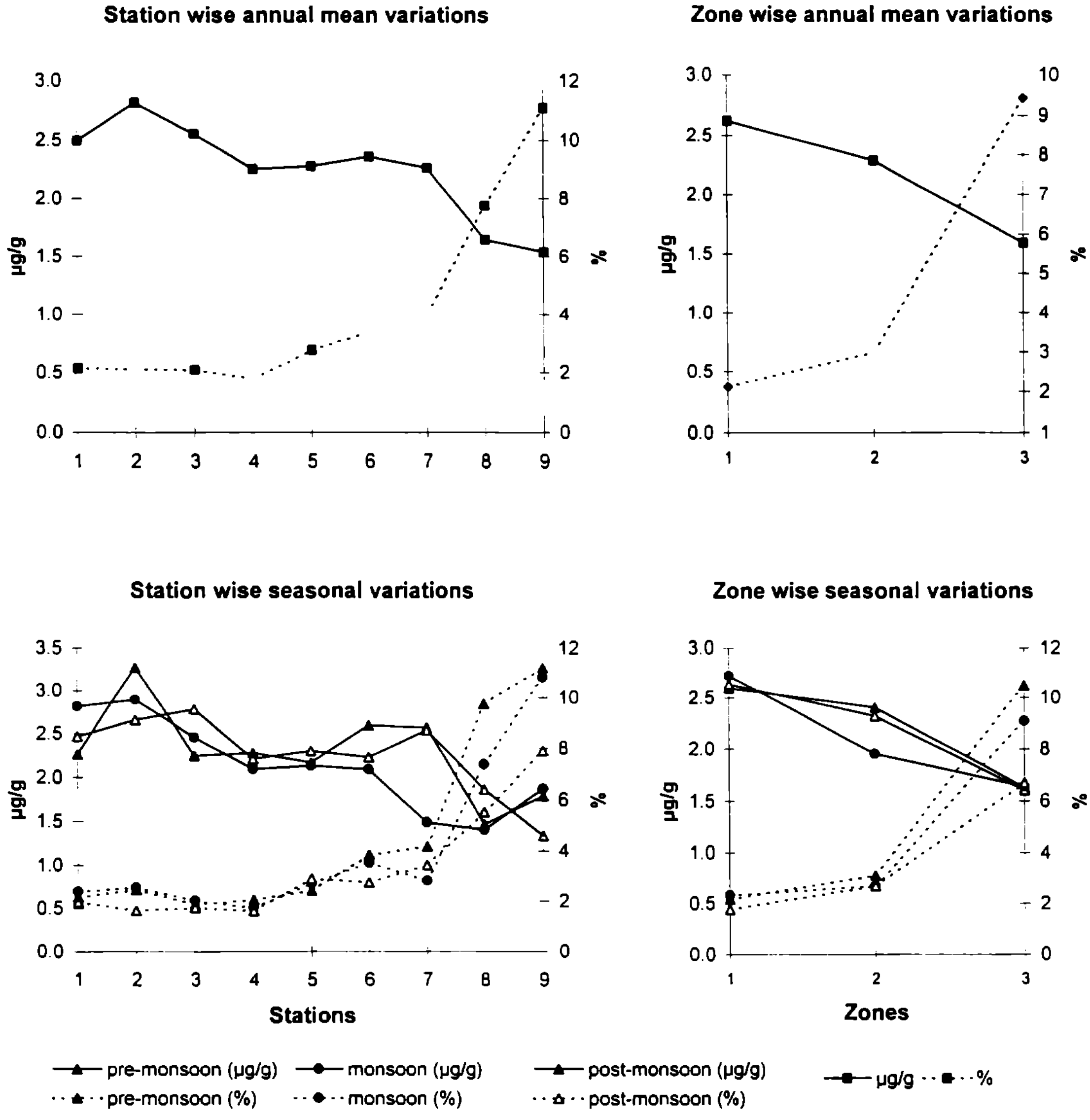


Figure 6.26 Spatial and temporal variations of exchangeable fractions of Mo (Mo_1) on absolute (µg/g) and relative (%) basis.

The reducible fraction of molybdenum (Mo_2)

The station wise summary statistics on reducible fraction of molybdenum (Mo_2) is given in Table 6.10. As in most other cases, lowest value (2.07 µg/g) and lowest annual mean concentration (3.62 µg/g) were observed at station 9. Similarly, highest value (14.43 µg/g) and highest annual mean concentration (10.35 µg/g) were recorded at station 2. Maximum scatter of values was observed at station 8 with a coefficient of variation 76.60 (Table 6.10). The mean relative proportion of the Mo_2 fraction is 11.50 percentage of Mo_T (Table 6.2), which was comparable to the value observed for Cr_2. Only Cu_2 fraction exhibited lower percentage than this. Figure 6.27 shows that the station wise annual mean concentrations had a decreasing trend from station 2 to 9. Seasonally, monsoon period recorded lower values in most of the stations (Figure 6.27). Percentage wise, the Mo_2 fraction of total molybdenum was higher at zone 3 as observed in the Mo_1 fraction. Similar behaviour was also observed for Mn_2, Fe_2, Cr_2 and Co_2 fractions. Molybdenum enrichment by adsorption onto Mn oxides was reported by Calvert and Price (1977). Seralathan and Hartmann (1986) have also reported the influence of manganese oxide phase in controlling the biogeochemistry of Mo in the oxic, suboxic and anoxic sediments.

The organic cum residual fraction of molybdenum (Mo_3)

The study on the partitioning of molybdenum in the Kuttanad sediments showed that the mean percentage of organic cum residual fraction of molybdenum (Mo_3) (84.36 %) is comparable to that of Cr_3 fraction (85.74 %) (Table 6.2). The concentration range was found in between 2.54 to 182.55 µg/g with a relative variation of 39.77 to 94.76 percentage of the total Mo. The overall mean percentage (84.36) of Mo_3 is about 20 times that of the exchangeable fraction and 7 times that of the reducible fraction. The station wise annual mean concentrations were in the range 11.55 to 129.25 µg/g (Table 6.10). Station 9 recorded the lowest

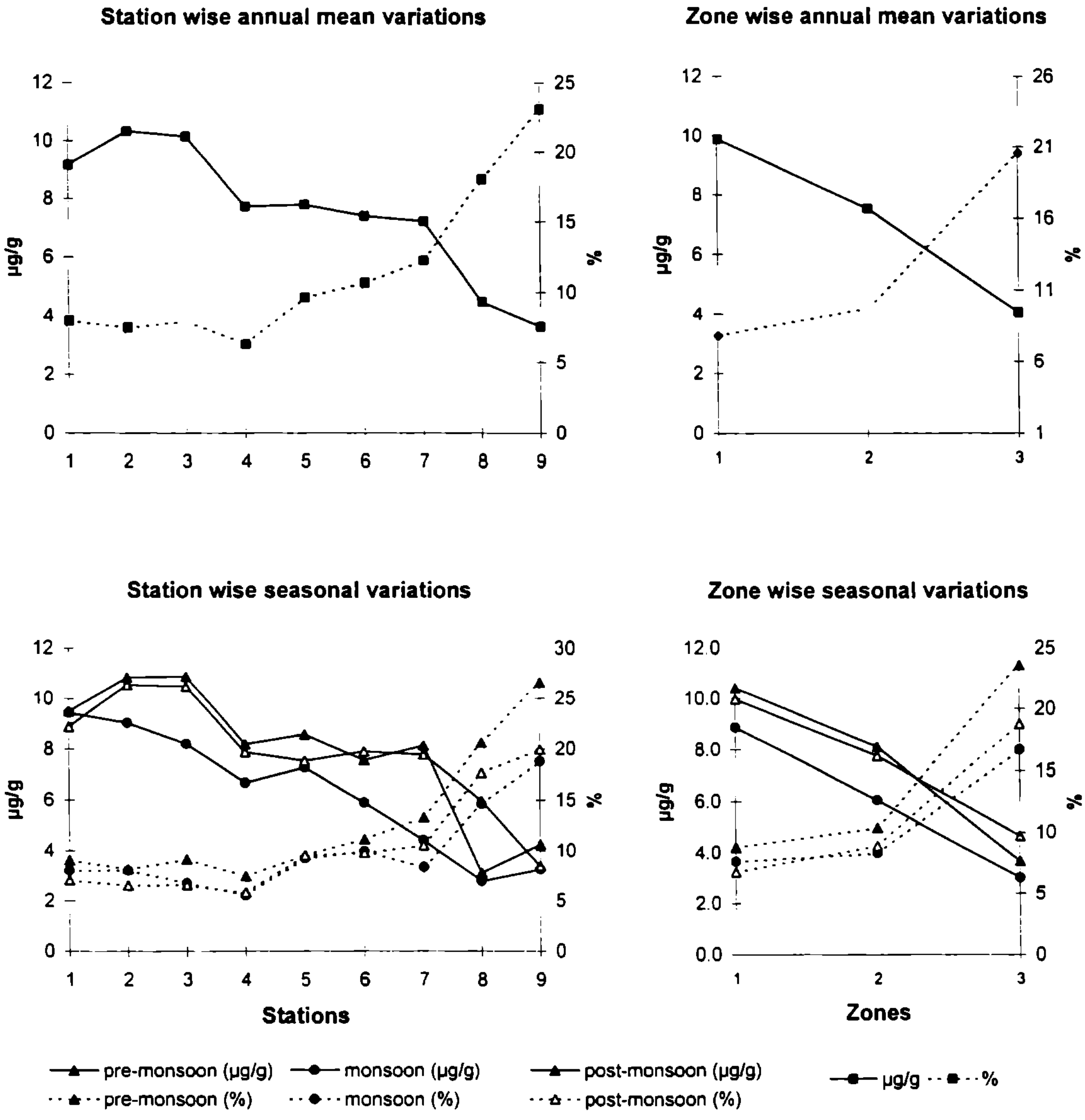


Figure 6.27 Spatial and temporal variations of reducible fractions of Mo (Mo_2). on absolute (µg/g) and relative (%) basis.

value as well as lowest annual mean concentration, whereas the highest value and the highest annual mean concentration were observed at station 2. The station wise annual mean concentration graph (Figure 6.28) showed a peak at station 2 and a gradual decreasing trend was observed from station 2 to station 9. Unlike Fe_3 and Mn_3 fractions, the peak of the concentration graph was found in the riverine stations. The post-monsoon season showed comparatively higher seasonal concentrations in most of the stations, whereas the concentrations in monsoon and pre-monsoon seasons did not differ much (Figure 6.28). The percentage wise fraction of Mo_3, as in the case of Cr_3 fractions, showed least variations among the seasons. The trace element Mo behaves conservatively in sea water (Head and Burton, 1970) but is strongly enriched in reducing sediments (Crusius et al., 1996). The potential for authigenic enrichment of molybdenum above crustal concentrations is greater than for many other elements, due to the high ratio of $(\text{metal})_{sw}/(\text{metal})_{crust}$ (Crusius et al., 1996). The comparatively higher percentage of Mo_3 (84.36 %) fraction implies that major portion of molybdenum in the sediments of Kuttanad is associated with organic matter and with the less mobile residual form. Seralathan and Hartmann (1986) had reported that occurrence of Mo in the sediments from suboxic or anoxic conditions was strongly associated with organic matter and / or its diagenetic products (sulphides, and partly phosphates).

NICKEL

Total nickel in sediment (Ni_T)

Concentrations of Ni_T in sediments were in the range 8.89 µg/g (station 9) to 91.55 µg/g (station 2) (Table 6.11). The station wise annual mean concentrations of total nickel in sediments varied from 15.03 to 73.90 µg/g. The lowest value was observed at station 9 and the highest at station 4. The values showed an increasing trend from station 1 to station 4 and then decreased towards station 9 with the concentration maxim at station 4 (Figure 6.29). The annual mean concentrations observed at station 8

Table 6.11 Station wise summary statistics on Ni concentrations in sediments (μg/g)

	Stations	Min.	Max.	Mean	SD	CV
Total nickel in sediment	1	58.00	79.31	67.25	7.15	10.64
	2	30.04	91.55	69.13	20.37	29.47
	3	56.41	81.97	72.29	9.44	13.06
	4	66.15	80.10	73.90	4.20	5.68
	5	38.18	67.37	57.97	8.36	14.42
	6	47.71	65.86	56.06	6.53	11.64
	7	23.90	61.78	43.93	10.44	23.76
	8	8.95	57.55	18.86	13.22	70.11
	9	8.89	27.31	15.03	4.66	31.02

		Absolute concentration (μg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of nickel	1	0.89	10.52	4.58	2.58	56.39	1.42	15.22	6.97
	2	3.35	9.55	5.92	2.22	37.45	4.11	14.16	8.28
	3	3.16	10.38	6.51	2.49	38.33	4.92	18.17	9.40
	4	1.77	8.01	4.59	2.15	46.84	2.24	11.10	6.18
	5	1.98	9.04	3.67	2.02	55.00	2.95	13.75	6.67
	6	1.74	8.01	3.98	2.05	51.42	3.61	15.08	7.51
	7	1.83	6.57	3.58	1.43	39.87	3.81	22.53	8.89
	8	1.24	5.85	2.85	1.48	51.74	6.03	34.43	18.66
	9	0.89	2.95	1.82	0.80	43.77	6.64	20.98	13.20
Reducible fraction of nickel	1	14.37	26.02	19.64	4.12	21.00	20.40	36.87	29.16
	2	17.73	28.82	20.95	3.09	14.73	20.39	33.41	27.68
	3	10.07	25.16	19.64	4.41	22.45	14.30	33.96	26.98
	4	14.54	25.54	18.20	3.55	19.51	19.81	32.63	24.33
	5	11.22	21.13	16.64	2.96	17.80	18.43	40.24	29.68
	6	7.60	21.39	15.87	4.18	26.36	15.77	42.38	29.15
	7	7.88	19.74	14.30	3.90	27.25	16.78	45.04	32.48
	8	6.03	29.83	10.44	7.00	67.06	38.70	76.80	57.69
	9	6.43	14.65	9.58	2.53	26.41	47.64	75.92	65.08
Organic cum residual fraction of nickel	1	32.14	56.33	43.45	7.75	17.83	54.89	73.02	63.86
	2	32.60	68.01	49.63	11.57	23.31	53.98	75.50	64.03
	3	28.19	60.03	46.96	9.34	19.89	49.36	78.16	63.62
	4	45.39	60.36	51.92	4.81	9.27	57.98	76.45	69.49
	5	18.60	48.78	36.65	8.64	23.57	48.71	78.11	63.64
	6	24.89	45.95	34.62	6.85	19.79	49.32	80.62	63.34
	7	9.45	48.10	27.42	10.38	37.86	32.43	79.33	58.63
	8	0.13	24.25	5.35	7.22	134.94	1.08	49.03	23.66
	9	0.61	9.70	3.59	3.06	85.33	5.00	45.72	21.72

(SD = standard deviation, CV = coefficient of variation)

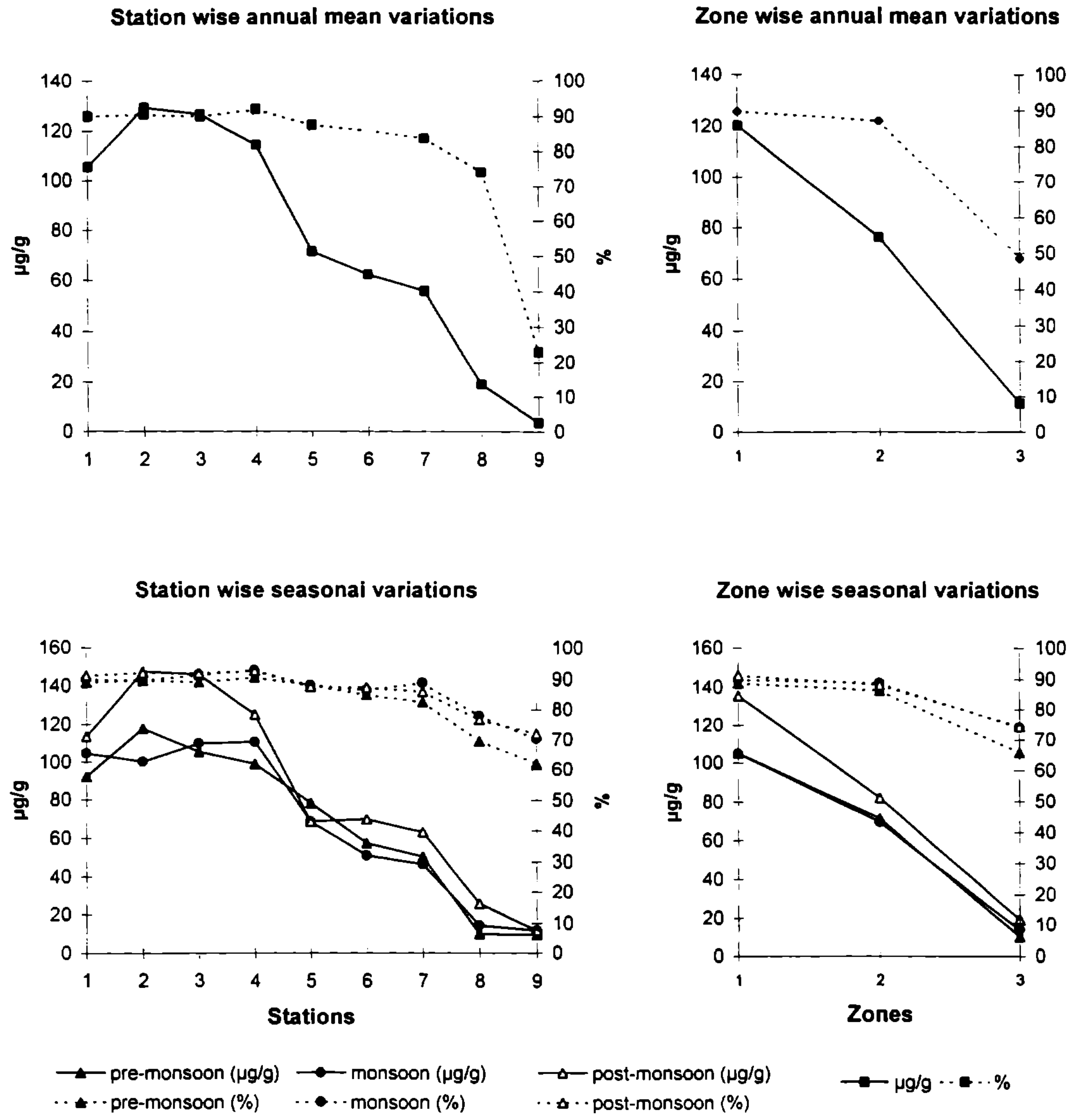


Figure 6.28 Spatial and temporal variations of organic cum residual fractions of Mo (Mo_3) on absolute (µg/g) and relative (%) basis.

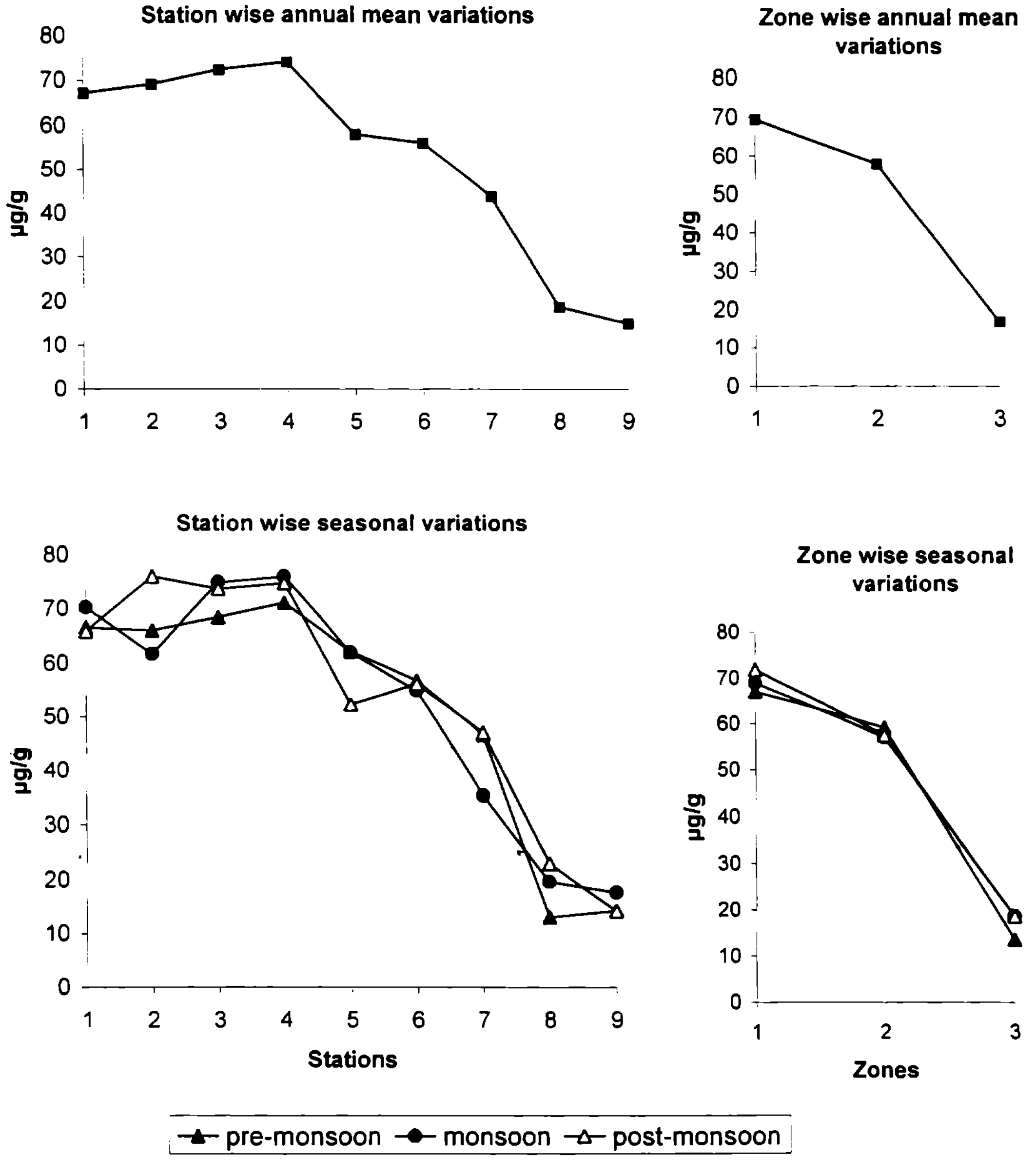


Figure 6.29 Seasonal and spatial variations of total nickel in sediments.

(18.86 µg/g) and station 9 (15.03 µg/g) were much less when compared to the values in the other stations (in the range 43.93 to 73.93 µg/g).

Seasonal variations were observed (Figure 6.29), but they were not uniform throughout the stations. The upper and lower limit of the range of values in monsoon and post-monsoon seasons were slightly shifted towards the higher side than that in pre-monsoon season. The lowest seasonal average in monsoon and post-monsoon seasons were at station 9, whereas in the pre-monsoon season, it was at station 8. The highest seasonal average was observed at station 4 in all the three seasons. The trend observed in the variation of seasonal average concentrations of total nickel was more or less similar to that observed in the case of annual mean concentration, i.e., after an initial increase from station 1 to station 4 the values showed a decreasing trend from station 4 to station 9 with the concentration maxima at station 4.

Total nickel residues in sediments typically range upto 100 µg/g dry weight, but may fall below 1µg/g in some unpolluted coastal waters. Maximum residues are typically associated with nickel-bearing geologic formations and with the discharge of industrial and municipal wastes. Enrichment factors (concentration in sediments/concentration in earth's crust) typically range from 1 to 12 (Sinex and Wright, 1988). The overall annual mean concentration of nickel in the surficial sediments of Kuttanad area was found to be 52.71 µg/g (Table 6.1). Biksham and Subramanian (1988) also have reported a mean comparable value (52 µg/g) from the Godavari River basin. The Indian average of Ni_T in river bed sediments is only 37 µg/g (Subramanian, 1987). But the value recorded in the present study is higher than the values reported from Cochin estuary by Jayasree and Nair (1995) and Nair et al. (1990), which were 3 µg/g and 26.67 µg/g respectively. This may be due to the difference in the sampling locations and the partially flushed nature of the water body of Kuttanad. Thus, in the case of nickel also, there is enrichment of the metal in the southern upstream part of the Cochin Estuary. The zone wise distribution pattern of nickel is found to be different from that of Cd, Co, Cr, Fe and Mn and is more or less similar to that of Mo (Figure 6.25). In the case of nickel, the highest value was recorded at the fresh water zone and the lowest at zone 3. The higher values observed at zone 1 shows that river is the major source of input of nickel in the aquatic system of Kuttanad. The lower values observed at zone 3 when compared to that of zones 1 and 2 are attributed to the difference in the texture of sediments, zone 1 and zone 2 being richer in fine particles of sediment and sediments of zone 3 being richer in coarse sandy particles (Figure 3.17 in Chapter 3). Unlike that of metals like Cd, Co, Cr, Fe and Mn, the sediments of the low saline region of zone 2 are not found enriched in nickel content.

The exchangeable fraction of nickel (Ni_1)

The mean value of exchangeable fraction of Ni (Ni_1) recorded in the study area was 4.29 µg/g, within the range 0.89 to 10.52 µg/g (Table 6.2). The relative values varied from 1.42 to 34.43 percentage of total Ni with a mean value of 9.53 % (Table 6.2). Data on the station wise annual mean concentration, minimum, maximum and standard deviations of nickel determined in the exchangeable fraction of sediments are furnished in Table 6.11. The lowest (0.89 µg/g) and highest concentrations (10.52 µg/g) were observed at stations 9 and 1 respectively. The maximum and minimum annual mean concentrations (station wise) were recorded at stations 3 and 9 respectively. Figure 6.30 gives the trend of station wise variation of annual mean concentrations. Initially, the values showed an increasing trend from station 1 to station 3 and then showed a decreasing trend towards station 9. It could be seen that generally higher values were recorded in post-monsoon and pre-monsoon seasons.

The mean value and the mean percentage of Ni_1 fraction observed in the present study were found higher than that reported by Nair (1992) from Cochin Estuary (0.23 µg/g and 1.45 %) and were also found

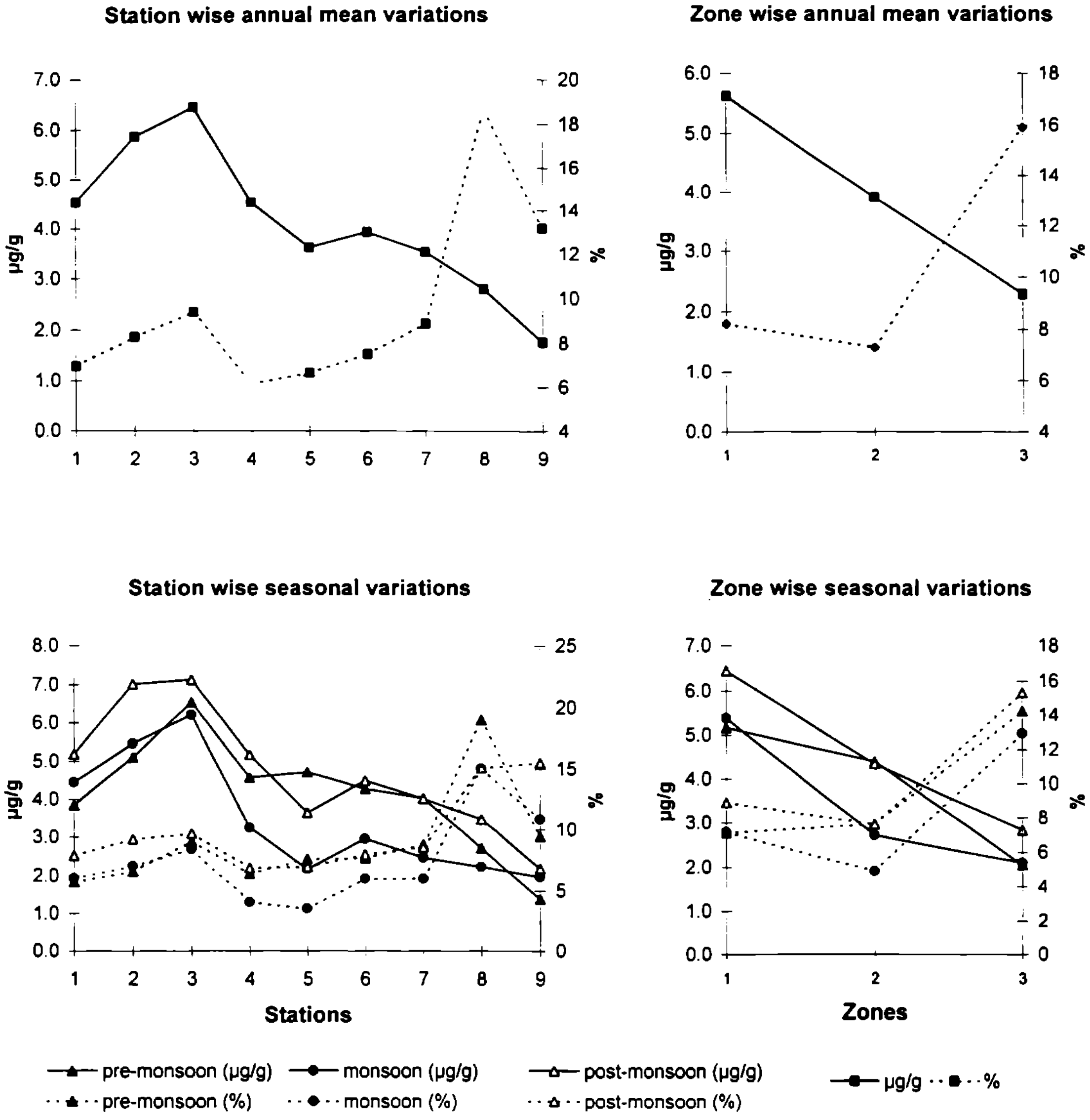


Figure 6.30 Spatial and temporal variations of exchangeable fractions of Ni (Ni_1) on absolute (µg/g) and relative (%) basis.

higher than the values reported from other water bodies by Gibbs (1973), Brannon et al. (1977), Tessier et al. (1980) and Pardo et al. (1990). Among the exchangeable fractions of the 10 metals studied, Ni ranks third in abundance (in absolute value) after Fe and Mn. The distribution pattern indicated higher contribution of the exchangeable fraction of Ni in the sediments of the riverine regions of the estuary (zone I). The most important factor determining the distribution of Ni between solid and solution phases is the pH (Anderson and Christensen (1983). The higher percentage of exchangeable fraction of Ni at zone 3 may, therefore, be due to the greater mobility of Ni from sediments of this zone due to the lowering of pH of the sediments (KWBS, 1989) under a partial reducing environment prevailing in this zone.

The reducible fraction of nickel (Ni_2)

In the present study, the reducible fraction of nickel (Ni_2) was found to vary from 6.03 to 29.83 µg/g, with a mean value of 16.14 µg/g (Table 6.2), both the lowest and highest values were observed at station 8 (Table 6.11). The whole range of values on a relative basis varied from 14.30 to 76.80 percentage of Ni_T, with an overall mean of 35.80 % of total Ni (Table 6.2). Among the reducible fractions of the ten metals studied, Ni ranks second in abundance in absolute concentration (first being Cr) after Fe and Mn. Percentage wise, Ni_2 recorded the highest percentage of the total (35.80), though in relative terms, this comes to only about 4 times that of the exchangeable fraction as observed in the case of Cd and Zn. The annual mean concentrations ranged from a lowest value of 9.58 µg/g at station 9 to a highest value of 20.95 µg/g at station 2. Maximum scatter in values was seen at station 8 (coefficient of variation = 67). After a slight increase from station 1 to station 2, the annual mean concentrations showed a gradual decreasing trend towards station 9 (Figure 6.31). Generally, a slight increase in concentration could be seen during post-monsoon season. The same trend was observed in the percentage wise distribution also, but one notable difference observed was that sediments at

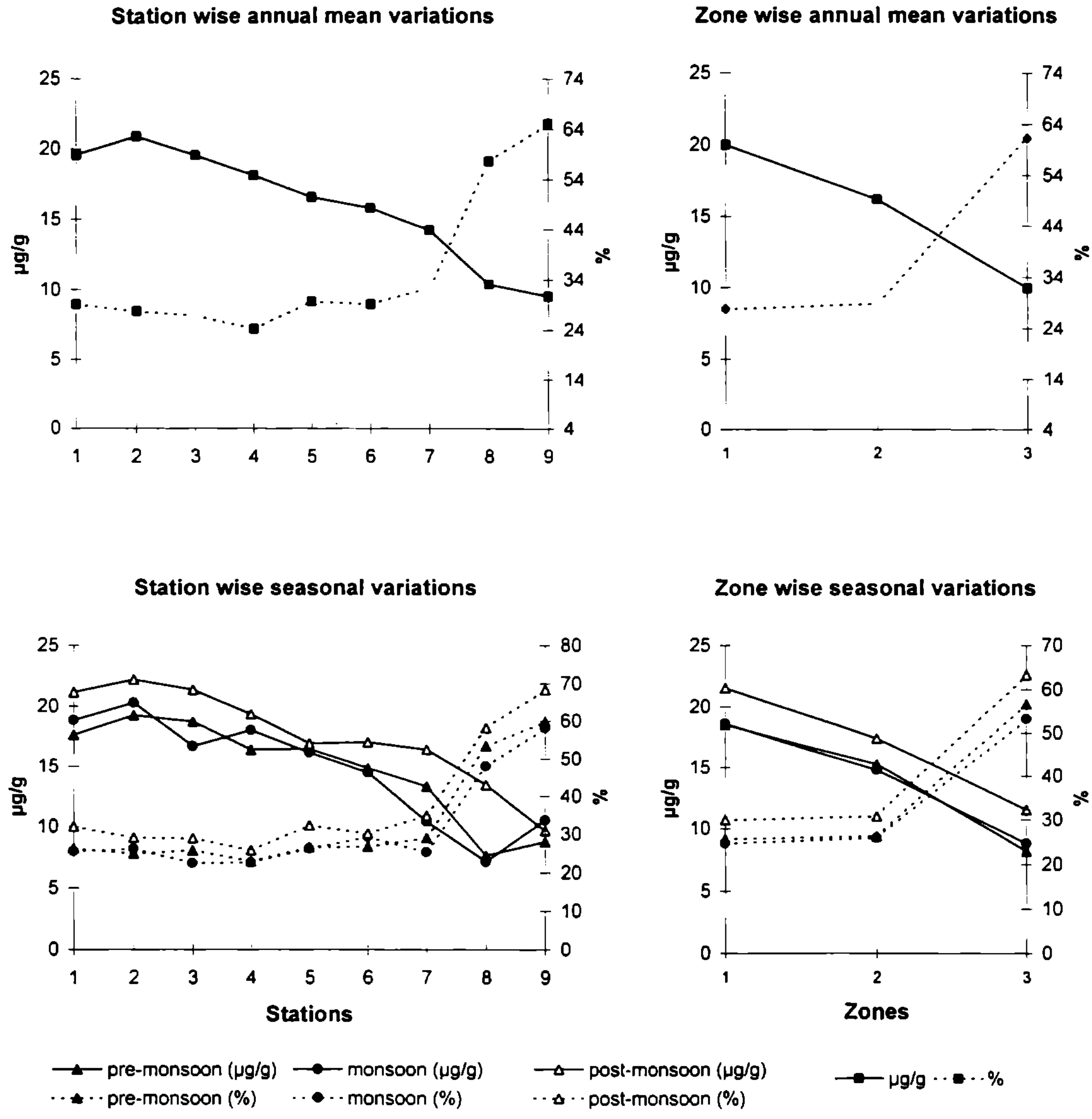


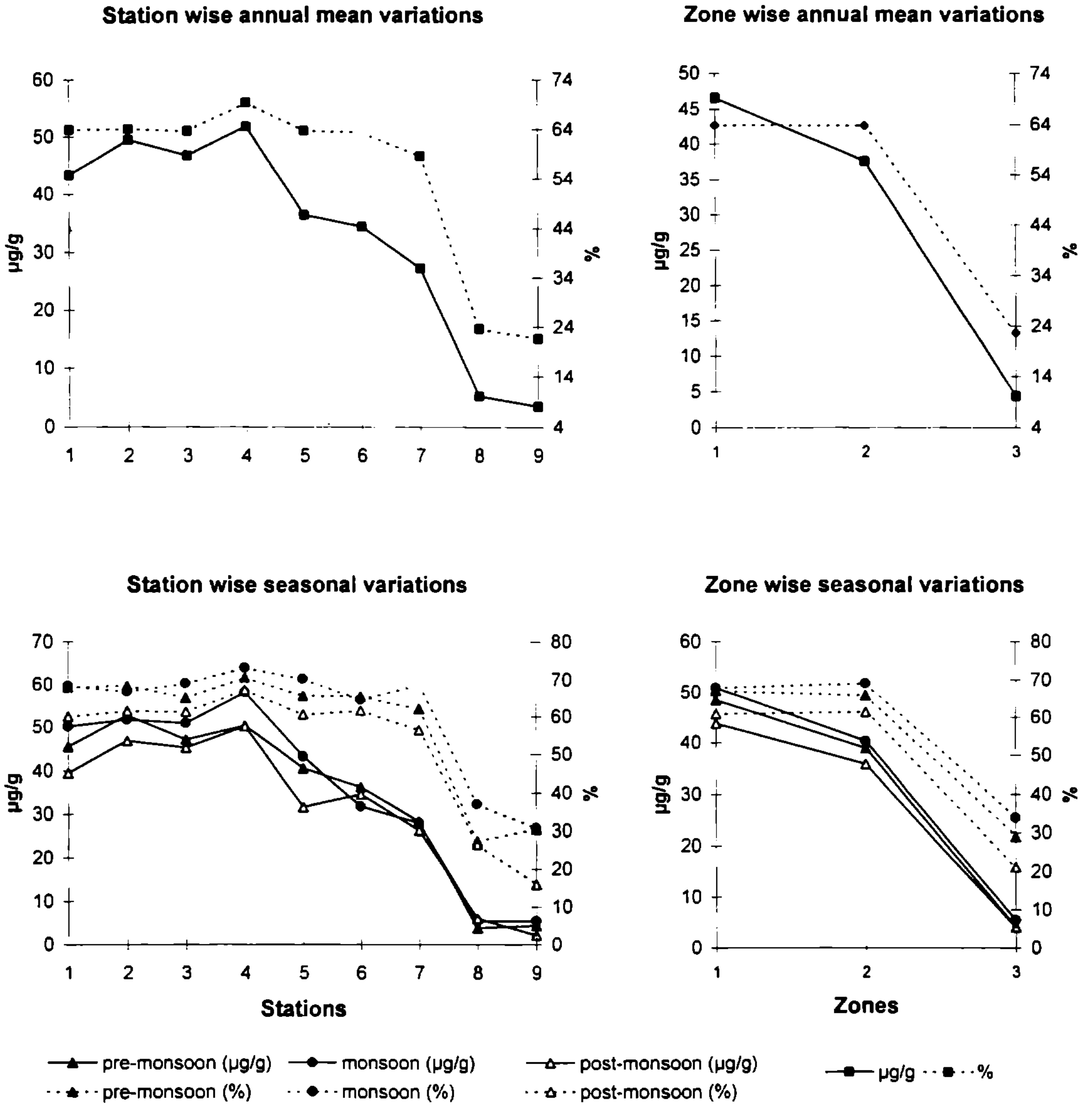
Figure 6.31 Spatial and temporal variations of reducible fractions of Ni (Ni_2) on absolute (µg/g) and relative (%) basis.

stations of zone 3 which were sandy in nature also recorded higher percentage of Ni_2 fractions than observed at zones 1 and 2 during all seasons (Figure 6.31). Nair (1992) also recorded higher percentage of Ni_2 fraction from the riverine side of other parts of Cochin Estuary where the percentage of sand was comparatively higher. Though the mean concentration and the mean percentage of Ni_2 fraction in this study (16.14 µg/g and 35.80 % respectively) was much higher than the values reported by Nair (1992) from other parts of Cochin Estuary (0.57 µg/g and 3.38 % of total Ni respectively), it was almost comparable to the values reported by Pardo et al. (1990) from Pisuerga River (30.50 %) and Tessier et al. (1980) from St. Francois River (27.80 %). Gibbs (1973) reported even higher percentage of Ni_2 fraction (47.8 %) from Yukon River. Lower values were also recorded in literature. Some of them are Brannon et al. (1977) from Mobile Bay, Ashtabula and bridge port (2 % each), Tessier et al. (1980) from Yamaska River (17.9 %) and Lee (1985) from Keum Estuary (18.9 %) etc. All these values indicate that the behaviour of nickel in different estuaries is different, without any universal pattern of distribution, and Ni is highly susceptible to leaching from the sediments of Kuttanad backwaters. The spatial variation of the reducible fraction of Ni was in unison with similar fraction of Fe and Mn. One probable reason for this behaviour is, therefore, the adsorption/coprecipitation of Ni along with Fe/Mn oxy-hydroxides.

The organic cum residual fraction of nickel (Ni_3)

The mean absolute value of Ni_3 fraction in the surficial sediments of Kuttanad backwaters was found to be 33.29 µg/g (Table 6.2) and varied from a minimum value of 0.13 µg/g at station 8 to a maximum value of 68.01 µg/g at station 2 (Table 6.11). Relative to the total nickel concentration in sediments, variations were found to be in the range 1.08 to 80.62 % with a mean value 54.67 % (Table 6.2). Highest annual mean concentration (51.92 µg/g) was observed at station 4, whereas the lowest annual mean concentration (3.59 µg/g) was found at station 9 (Table 6.11).

In general, there was an increasing trend from station 1 to station 4 and a declining trend from station 4 to station 9 (Figure 6.32). In the case of Ni_3 fraction also, stations 8 and 9 showed considerably lower values (5.35 and 3.59 µg/g respectively) when compared to the values at other stations (27.42 to 51.92 µg/g). The station wise seasonal average values did not show any marked variability in seasons (Figure 6.32). But the percentage wise variations showed slight increase during monsoon, and a small depletion during post-monsoon period. Another notable feature in the spatial distribution pattern was that the zone 3 recorded lower concentrations as well as lower percentage values, unlike the distribution pattern of Ni_1 and Ni_2 fractions, which showed an increase in percentage of Ni_1 and Ni_2 fractions at zone 3 (Figure 6.32). The sum of the percentage of organic cum residual fraction observed in the present study (54.67 %) was almost comparable to the values reported by Gibbs (1973) from Yukon River (47 %) and Elliot et al. (1990) from Pennsylvania sludge (55. 5 %). Many other workers reported very high percentage of Ni_3 fractions, for e.g., Brannon et al. (1977) found 97 % of Ni_3 fraction in Mobile Bay sediments, 75 % in Ashtabula sediments and 95 % from bridge port sediments; Tessier et al. (1980) reported 81.4 % and 72.2 % respectively in Yamaska River and St. Francois River. Lee (1985) observed 80.2 % of Ni_3 fraction in Keum estuarine sediments. Nair (1992) in a study of the northern side of the Cochin estuarine system found that 95.17 % of Ni was associated with organic and residual fraction. All these data indicate that a major portion of Ni is associated with the more environmentally mobile phases of sediment in the southern upstream part of Cochin estuarine system. Any slight decrease in pH or change in redox condition of the system can mobilise an appreciable amount of Ni from the sediments to the water column and such a situation is highly detrimental to the water quality of the area.



Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations

Zone wise seasonal variations

Figure 6.32 Spatial and temporal variations of organic cum residual fractions of Ni (Ni_3) on absolute (µg/g) and relative (%) basis.

LEAD

Total lead in sediment (Pb_T)

Total concentration of lead in sediments in the present study was in the range 5.08 to 103.85 µg/g, the lowest being at station 9 and the highest at station 2 (Table 6.12). The station wise annual mean concentration of total lead in sediments was found to be within the range 22.23 to 70.58 µg/g (Table 6.12). The lowest value, as in the case of most of the other elements, was at station 9 and the highest at station 3. The values showed an increasing trend from station 1 to station 3 and then decreased gradually from station 4 to station 9 (Figure 6.33). Here also, the annual mean concentrations at stations 8 and 9 were considerably lower than the values recorded at other stations.

The station wise seasonal average values showed variations (Figure 6.33) from stations 1 to 4. From stations 5 to 9, the seasonal differences were not very significant. From stations 1 to 4, the pre-monsoon season recorded the lowest seasonal average values among the seasons. In these stations, the seasonal average values did not differ much during monsoon and post-monsoon seasons. The lowest seasonal average was observed at station 9 for all the three seasons. During the monsoon and post-monsoon seasons, the fresh water zone (zone 1) recorded the highest value and the lowest was observed at zone 3. In the pre-monsoon season, zones 1 and 2 recorded nearly equal values but zone 3 recorded the lowest average.

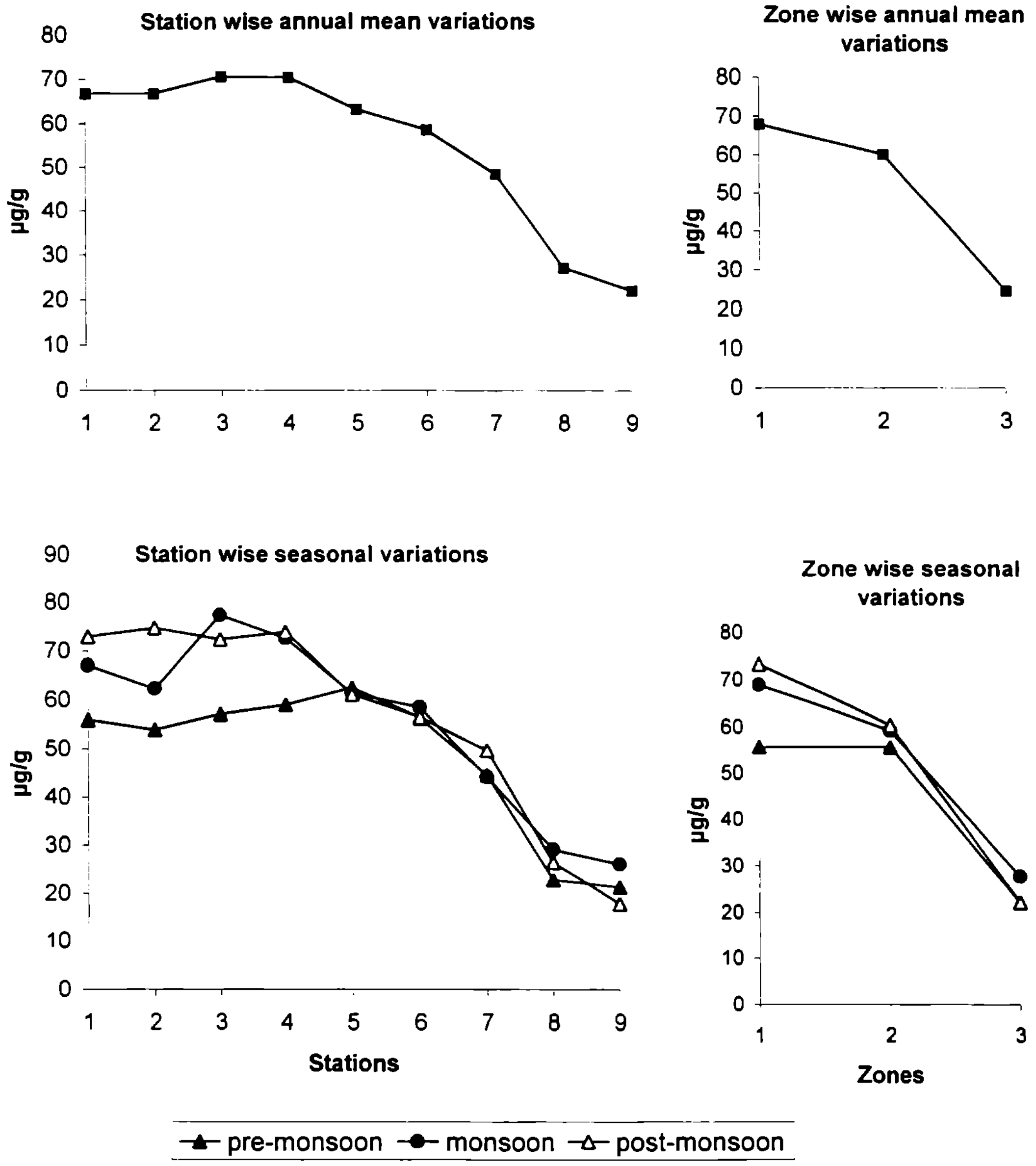
Approximately, 99% of the lead entering the oceans with the suspended load of rivers is deposited in the sediments of estuaries and continental shelves (Craig, 1980). Residues in the 15-50 µg/g dry weight range were frequently reported for coastal/estuarine sediments (Samhan et al., 1987; Araujo et al., 1988; Subramanian et al., 1988), and may exceed 400 µg/g near waste outfalls (Stull and Baird, 1985; Stull et al., 1986;

Table 6.12 Station wise summary statistics on Pb concentrations in sediments (µg/g)

	Stations	Min.	Max.	Mean	SD	CV
Total lead in sediment	1	53.54	102.58	66.79	13.58	20.33
	2	34.50	103.85	66.81	19.73	29.53
	3	51.16	93.71	70.58	13.42	19.01
	4	50.13	89.85	70.42	12.70	18.03
	5	36.10	85.82	63.22	15.05	23.81
	6	39.29	76.58	58.66	10.79	18.39
	7	11.41	71.73	48.64	16.26	33.43
	8	12.36	73.91	27.25	18.38	67.46
	9	5.08	39.40	22.23	12.11	54.50

		Absolute concentration (µg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of lead	1	0.34	7.37	3.85	3.24	84.16	0.51	12.11	5.16
	2	0.20	8.74	3.99	3.41	85.33	0.32	12.88	5.38
	3	0.27	10.27	4.27	3.68	86.30	0.41	13.22	5.39
	4	0.26	9.25	3.53	3.16	89.49	0.47	12.09	4.17
	5	0.03	8.06	3.26	3.06	93.66	0.04	15.52	4.70
	6	0.07	6.87	3.33	2.94	88.39	0.14	11.05	4.94
	7	0.26	8.42	3.04	2.81	92.23	0.47	16.94	5.85
	8	0.07	7.35	2.50	2.40	96.04	0.18	35.65	11.11
	9	0.18	4.70	1.99	1.83	91.80	0.74	31.44	10.39
Reducible fraction of lead	1	11.86	23.45	17.27	3.54	20.53	16.00	32.13	25.75
	2	8.60	31.02	18.38	6.26	34.08	10.52	33.92	25.29
	3	7.86	28.52	17.91	5.84	32.62	9.96	35.85	25.36
	4	5.20	20.13	13.88	4.58	32.99	6.11	30.95	19.48
	5	6.94	19.68	12.67	4.11	32.41	8.22	30.43	19.60
	6	3.55	18.44	11.77	4.54	38.59	4.85	33.79	19.87
	7	4.70	20.96	10.97	4.77	43.47	6.55	32.55	21.40
	8	2.28	30.02	7.62	8.06	105.78	5.99	50.14	28.99
	9	1.90	10.03	5.84	2.57	43.95	5.61	61.46	30.09
Organic cum residual fraction of lead	1	34.95	81.95	47.89	14.24	29.73	56.72	81.88	69.09
	2	27.44	72.39	51.01	12.52	24.54	55.75	88.63	69.33
	3	32.76	70.18	49.62	12.30	24.79	56.49	88.99	69.25
	4	43.16	79.56	56.25	12.65	22.49	65.20	93.36	76.35
	5	30.53	76.92	51.03	14.86	29.12	58.80	91.12	75.70
	6	28.99	69.22	46.14	12.04	26.10	64.36	94.60	75.19
	7	25.12	66.65	38.79	13.13	33.85	59.93	92.92	72.74
	8	2.66	41.55	19.37	15.08	77.85	19.70	93.01	59.90
	9	0.82	31.71	16.27	11.90	73.13	7.10	93.52	59.52

(SD = standard deviation, CV = coefficient of variation)


Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations

Zone wise seasonal variations

Figure 6.33 Seasonal and spatial variations of total lead in sediments.

Luoma and Philips, 1988). Extremely high concentrations of lead are periodically reported for fresh water sediments receiving industrial or municipal wastes. In one example, residues in the sediments of two lakes in the Sudbury mining district (Canada) were as high as 250-350 µg/g in the upper 10cm of cores, falling to 50 µg/g below 15 cm (Nriagu and Rao, 1987). Mudroch et al. (1988), reviewing a number of studies on lead in the deposition basins of the Great Lakes, found that surface residues were upto 13 times greater than background levels. Jones (1986) reported that lead in the River Rheidol (Wales) was extremely high (upto 2,00 µg/g) in surficial sediments, due to discharge from a lead-zinc mine. Lead is found to be enriched in the southern upstream part of Cochin Estuary (present study) which is evident from the mean lead level (54.96 µg/g) in the sediments of this area as against the mean lead content reported by Nair et al. (1990) and Jayasree and Nair (1995) from Cochin Estuary which were 2.7 µg/g and 10.43 µg/g respectively. Lead concentrations in the range 10 to 190 µg/g were reported in another study of the Cochin Estuary by Ouseph (1987). The study sites included industrial effluent discharge sites also. The spatial distribution pattern of Pb bears some similarity with Cu, Mo and Ni such that these elements have higher levels in the sediments of the fresh water region (zone 1) and lowest concentration in the sediments of zone 3 (Figures 6.13, 6.25 & 6.29). This means that the major source of input of Cu, Mo, Ni and Pb into environment of Kuttanad is the rivers. This is further substantiated by the higher levels of Pb in the fresh water zone during monsoon and post-monsoon seasons when the river flow is maximum. The comparatively higher values in sediments of zones 1 and 2 than that of zone 3 may also be due to the fine texture of sediments in this area.

The exchangeable fraction of lead (Pb_1)

The exchangeable fraction of lead (Pb_1) varied from 0.03 to 10.27 µg/g with a mean value of 3.08 µg/g (Table 6.2). With respect to the total lead, the values ranged from 0.04 to 35.65 percentage with a mean of

6.34 percentage (Table 6.2). The relative abundance of the Pb_1 fraction was slightly less than that of the similar fraction of Ni and Cd but higher than that of Co, Cr, Cu, Fe and Mo (Table 6.2). The lowest value was observed at station 5 and the highest at station 3 (Table 6.12). Station 9 recorded lowest annual mean concentration of 1.99 µg/g and station 3 recorded the highest annual mean concentration of 4.27 µg/g (Figure 6.34). The trend in the variation of annual mean concentrations of lead (Figure 6.34) was similar to that for nickel, i.e., the values showed a decreasing trend from station 3 to station 9 after an initial increase from station 1 to station 3. All stations recorded lowest seasonal average in pre-monsoon season (0.25 to 1.20 µg/g), and post-monsoon season recorded the highest seasonal average at all stations. Generally, seasonal averages in post-monsoon (2.29 to 4.76 µg/g) and monsoon seasons (1.92 to 4.82 µg/g) were appreciably higher than the values in pre-monsoon season. Though the absolute concentrations of Pb_1 fraction showed a decreasing trend in the order zone 1 > zone 2 > zone 3 in the annual mean as well as seasonal variations, the percentage of this fraction with reference to the total Ni showed appreciable increase at zone 3 in the annual mean and seasonal variations.

The mean concentration (3.08 µg/g) and percentage (6.34) of Pb_1 fraction observed in the present study was higher than the mean concentration (0.37 µg/g) and the mean percentage (2.86) reported by Nair (1992) from northern parts of Cochin Estuary and also higher than the values reported by Forstner (1982), Calmano and Forstner (1983), Hong and Forstner (1983), Samanidou and Fytianos (1987), Elliot et al. (1990) and Pardo et al. (1990) which were in the range 0.23 % to 4.20 %. The higher percentage of Pb_1 fraction in the study area again indicates the higher solubility and exchangeability of sediment associated Pb in the area. The higher concentrations of Pb_1 fraction at zones 1 and 2 can be attributed to the silty clay nature of sediments, which have high adsorption sites to hold lead ions.

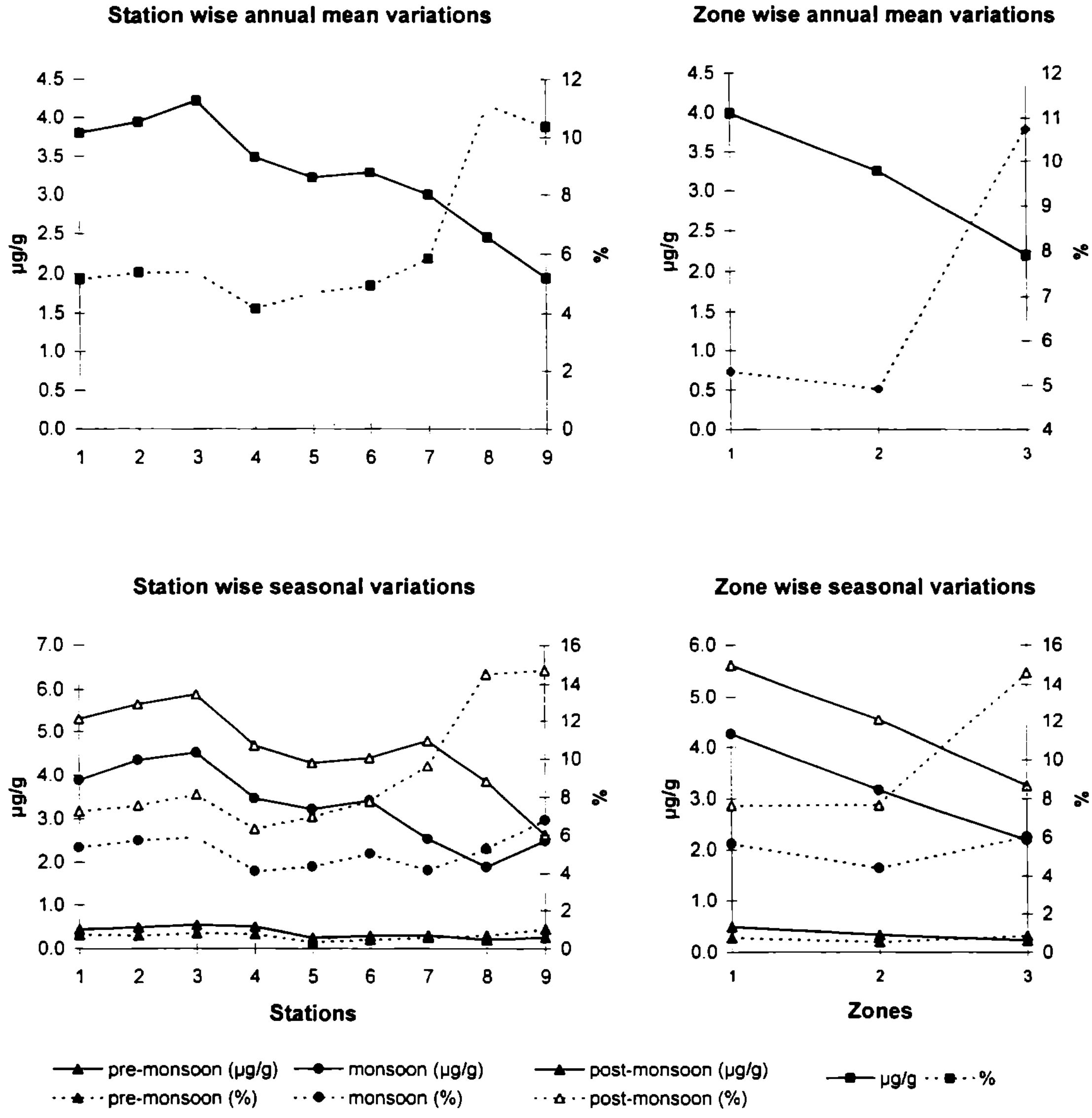


Figure 6.34 Spatial and temporal variations of exchangeable fractions of Pb (Pb_1) on absolute (µg/g) and relative (%) basis.

The reducible fraction of lead (Pb_2)

The reducible fraction of lead (Pb_2) was found to vary from 1.90 to 31.02 µg/g, the lowest being at station 9 and the highest at station 2 (Table 6.12), with a mean value of 12.92 µg/g (Table 6.2). With respect to the total Ni, the values varied from 4.85 to 61.46 % of Pb_T. The mean percentage of Pb_2 fraction (23.98 %) was about 4 times higher than that of the exchangeable fraction (Table 6.2). As observed in the case of Cd, stations 9 and 2 also recorded the lowest and highest annual mean concentrations, the values being 5.84 µg/g and 18.38 µg/g respectively (Figure 6.35). The trend in the variations of the annual mean concentrations (Figure 6.35) of Pb_2 was almost similar to that of Ni_2 fraction (Figure 6.31). The concentrations showed a slight increase from station 1 to station 2 and then decreased gradually towards station 9. The absolute as well as percentage of Pb_1 fraction showed enhanced values during post-monsoon and lower values during monsoon seasons. During post-monsoon season, stations of zone 3 recorded considerable hike in the percentage of Pb_2 fraction (Figure 6.35).

Unlike the exchangeable fraction (Pb_1), the percentage of reducible fraction of lead (Pb_2) recorded in the present study (23.98 %) was found less than many of the earlier reported values from different parts of the world, but at the same time higher than the value (10.0 %) observed by Nair (1992) from other locations of Cochin Estuary. The values reported by Tessier et al. (1980), Calmano and Forstner (1983), Lee (1985), Samanidou and Fytianos (1987) and Pardo et al. (1990) from different rivers/estuaries fall within the range 31.4 to 67.0 %. Low percentage were also reported from Rhine River (0.80 %) by Forstner (1982) and from Waser Estuary (2 %) by Calmano and Forstner (1983).

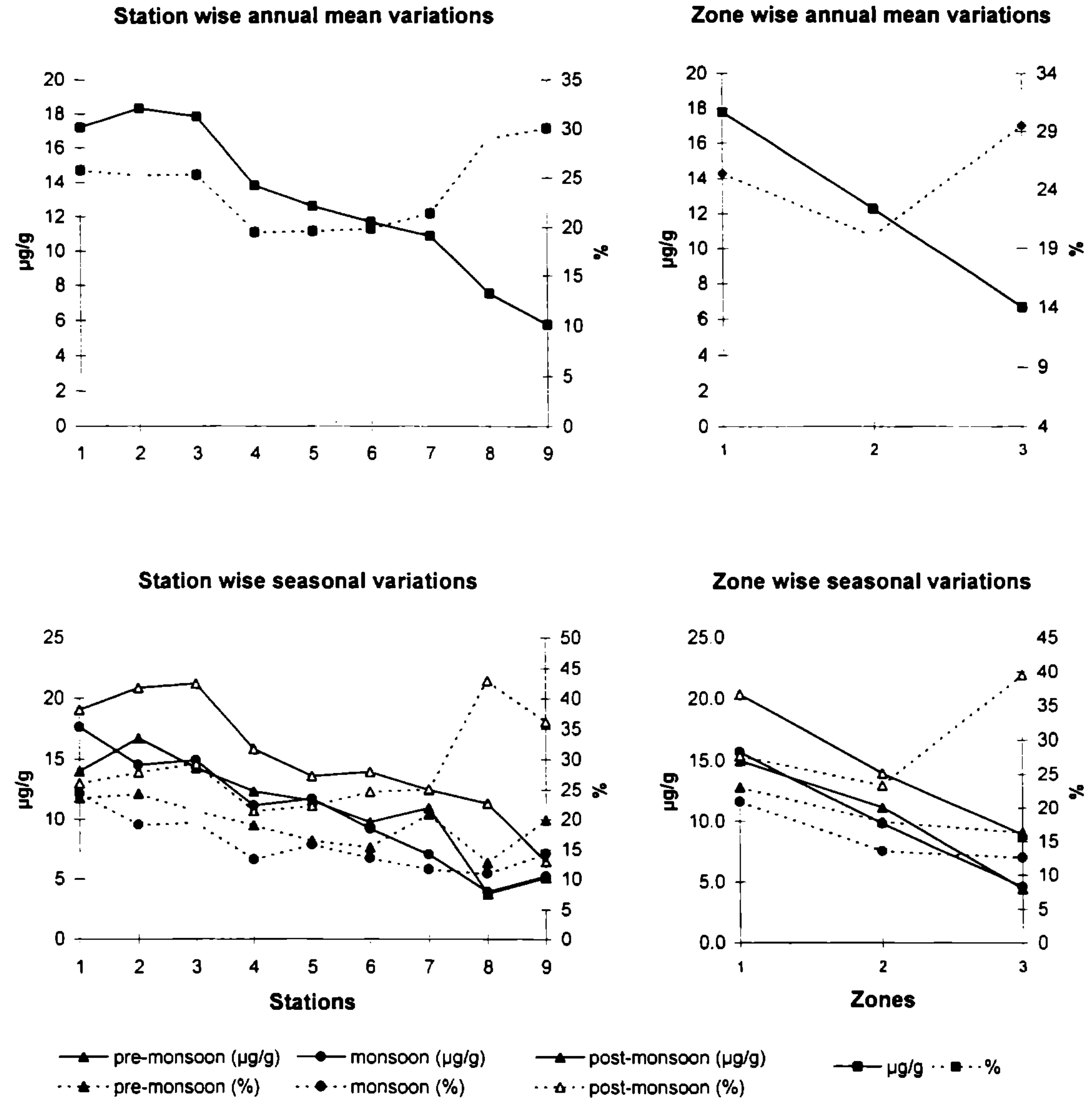
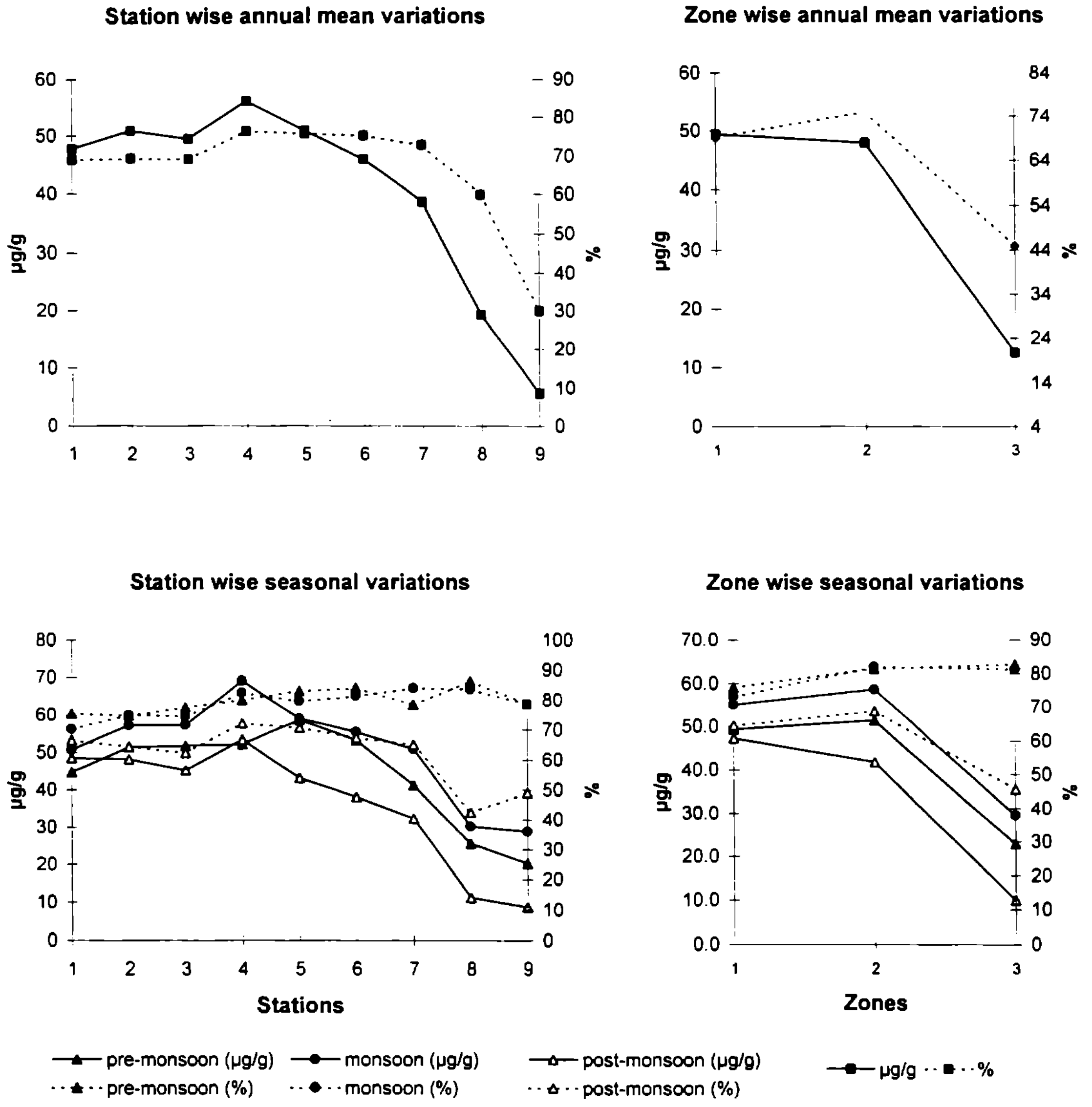


Figure 6.35 Spatial and temporal variations of reducible fractions of Pb (Pb_2) on absolute (µg/g) and relative (%) basis.

The organic cum residual fraction of lead (Pb_3)

The mean percentage of organic cum residual fraction of lead (69.68 %) was about three times that of reducible fraction and 11 times that of exchangeable fraction of lead and was found in the range 7 10 to 94.60 % (Table 6.2). This study has revealed that Pb_3 fraction showed spatial and temporal variations, the value varying within the range 0.82 µg/g at station 9 to 81.95 µg/g at station 1 (Table 6.12). Station 9 also recorded lowest annual mean concentration (16.27 µg/g), but the highest annual mean concentration (56.25 µg/g) was observed at station 4. Figure 6.36 showed that annual mean values of Pb_3 decreased gradually from station 4 to station 7, followed by a sudden decrease at stations 8 and 9. The values at stations 1, 2 and 3 were almost comparable and were less than that of station 4 (Figure 6.36). Station wise seasonal average values showed comparatively enhanced values in monsoon season (Figure 6.36) in all stations and generally, depletion in the concentration of Pb_3 fraction was observed in post-monsoon season. No distinguishable variations in the percentage of Pb_3 fraction were observed during monsoon and pre-monsoon seasons, but post-monsoon season recorded considerable depletion in the percentage. Stations 8 and 9 showed considerable decrease in values especially in post-monsoon season.

Lee (1985) reported 68.6 % of total Pb in the organic and residual form, which was in agreement with the mean percentage of Pb_3 recorded in the present study (69.87 %). Values higher than this were observed by Calmano and Forstner (1983) from Neckar River (76 %), Elliot et al. (1990) from Pennsylvania sludge (85.0 %) and by Nair (1992) from the northern side of Cochin estuarine system (87.15 %). But many workers like Tessier et al. (1980), Forstner (1982), Samanidou and Fytianos (1987) and Pardo et al. (1990) also reported lower values in the range 33 % to 61.76 %.


Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations

Zone wise seasonal variations

Figure 6.36 Spatial and temporal variations of organic cum residual fractions of Pb (Pb_3) on absolute (µg/g) and relative (%) basis.

ZINC

Total zinc in sediment (Zn_T)

Total zinc concentrations in the sediments were found to vary within the range 21.06 to 276.55 µg/g (Table 6.1). The minimum annual mean concentration was found at station 9, but the maximum annual mean concentration was observed at station 4 (Table 6.13). The trend in station wise annual mean concentration showed a gradual increase from station 1 to 4 and then decreased gradually to station 9, barring a slight increase at station 6 (Figure 6.37). Thus, the maximum of station wise total zinc concentration was observed at station 4, while in the case of copper it was at station 3.

The station wise seasonal variations of Zn in sediments are also given in Figure 6.37 All stations, except station 7, recorded highest seasonal averages in monsoon, and the lowest seasonal average recorded was in pre-monsoon season in all the stations. Seasonal average concentrations of total zinc in the pre-monsoon, monsoon and post-monsoon seasons were 52.08 to 150.29 µg/g, 101.72 to 190.35 µg/g and 77.62 to 182.92 µg/g in the respective order. From the ranges of values, it could be seen that the lower and upper limit of the ranges had considerably increased in the monsoon and post-monsoon seasons when compared to the range in pre-monsoon season. The lowest seasonal average in pre-monsoon and post-monsoon seasons was at station 9, while in monsoon season, it was at station 8. Station 4 recorded the highest seasonal average in pre-monsoon and post-monsoon seasons, while in monsoon season, it was at station 3.

Sediments are primary sink for zinc. Residues in excess of 1,000 µg/g dry weight have been found in the vicinity of mines and smelters (Poulton, 1987). Relatively high concentrations can also be found near major municipalities and coal-burning power stations. Poulton (1987), for

Table 6.13 Station wise summary statistics on Zn concentrations in sediments (µg/g)

	Stations	Min.	Max.	Mean	SD	CV
Total zinc in sediment	1	86.50	228.38	146.36	40.84	27.91
	2	52.38	276.55	151.39	55.95	36.95
	3	88.64	267.01	161.14	48.38	30.03
	4	115.79	272.01	173.87	46.66	26.83
	5	108.02	220.13	156.57	36.40	23.25
	6	95.84	204.52	158.70	36.48	22.98
	7	79.29	250.09	138.58	48.08	34.70
	8	22.51	242.45	84.95	57.96	68.23
	9	21.06	187.05	77.70	49.91	64.24

		Absolute concentration (µg/g)					Relative concentration (%)		
		Min.	Max.	Mean	SD	CV	Min.	Max.	Mean
Exchangeable fraction of zinc	1	0.24	7.48	2.07	2.62	126.95	0.17	4.69	1.42
	2	0.56	4.26	2.17	1.20	55.44	0.45	3.79	1.50
	3	0.60	8.08	3.11	2.87	92.28	0.43	4.78	1.87
	4	0.36	2.58	1.01	0.57	57.09	0.26	1.50	0.59
	5	0.39	3.60	0.87	0.92	105.39	0.22	2.17	0.57
	6	0.10	1.89	0.59	0.48	81.94	0.07	1.09	0.37
	7	0.17	1.59	0.57	0.41	71.84	0.13	1.17	0.45
	8	0.13	0.48	0.29	0.12	41.29	0.14	1.01	0.45
	9	0.07	0.38	0.19	0.10	52.44	0.05	1.04	0.40
Reducible fraction of zinc	1	12.36	30.60	20.59	6.18	29.99	8.15	26.03	14.67
	2	14.87	34.32	23.83	5.93	24.90	9.32	27.54	15.84
	3	14.30	30.50	22.97	4.74	20.65	8.45	29.94	15.30
	4	12.78	25.39	18.02	4.47	24.80	6.04	21.03	10.80
	5	8.10	23.36	15.43	5.12	33.17	5.62	18.44	9.99
	6	7.67	19.99	14.56	4.10	28.19	4.37	15.52	9.33
	7	6.27	20.12	12.77	4.56	35.70	3.69	18.26	9.59
	8	2.67	27.79	7.29	7.38	101.19	4.03	24.20	9.07
	9	1.88	12.13	5.56	3.04	54.69	2.39	32.97	10.30
Organic cum residual fraction of zinc	1	67.25	196.74	126.14	39.30	31.15	72.49	89.40	83.90
	2	73.15	239.62	134.72	48.95	36.33	68.67	88.95	82.66
	3	61.40	229.13	135.58	45.21	33.35	69.27	87.64	82.83
	4	94.48	250.07	160.02	47.88	29.92	78.24	93.45	88.61
	5	93.13	196.12	144.49	35.49	24.56	81.15	94.10	89.44
	6	80.63	187.11	148.35	35.10	23.66	84.12	95.18	90.30
	7	66.25	229.39	133.24	47.70	35.80	80.58	95.91	89.96
	8	20.60	214.20	79.51	52.67	66.24	74.80	95.61	90.48
	9	16.16	180.33	72.52	49.52	68.28	66.00	97.49	89.30

(SD = standard deviation, CV = coefficient of variation)

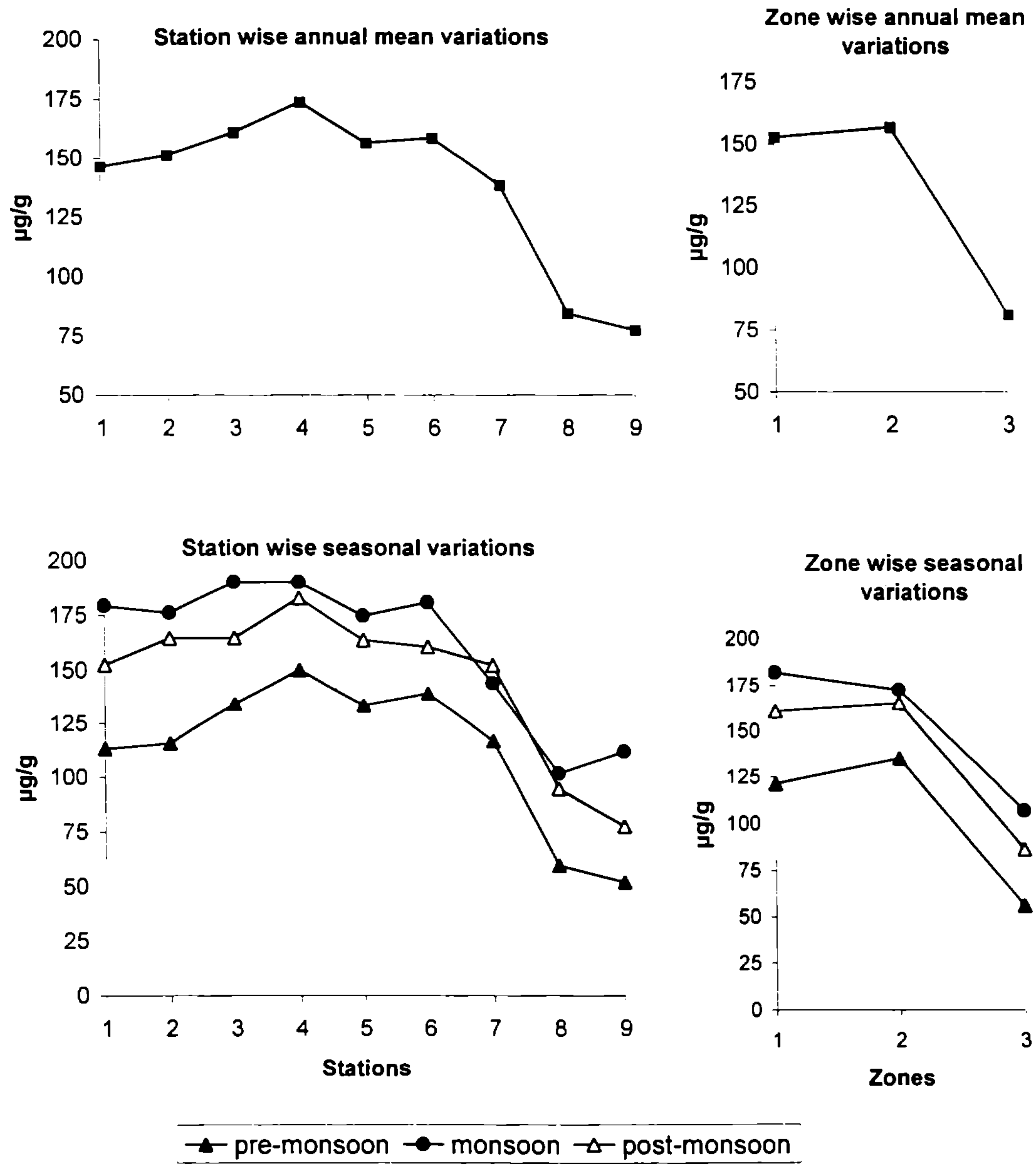


Figure 6.37 Seasonal and spatial variations of total zinc in sediments.

example, reported that a core sample from Hamilton Harbour (a major steel-producing region in Canada) contained 5,700 µg/g of zinc. By comparison, sediments from uncontaminated waters typically contain residues of 5 to 50 µg/g. The average Zn concentration recorded in the present study is 138.81 µg/g (Table 6.1). This is comparable to the mean value of 125 µg/g of Zn reported from the Mahanadi River basins (Chakrapani and Subramanian, 1990). However, the value is comparatively higher than the values of Zn reported from other parts of Cochin Estuary. Jayasree and Nair (1995) observed a mean value of 14 µg/g and Nair et al. (1990) reported an average value of 64.29 µg/g from Cochin Estuary. As observed in the case of Cd, Co, Cr, Fe and Mn, Zn also showed slight enrichment in zone 2, but the mean value did not differ appreciably from that of zone 1 (Figure 6.37). The slight enrichment of total zinc in sediments at zone 2 may be due to the proximity of this zone to the vast area of agricultural land, where pesticides like Mancozeb (which contains approximately 20 % Mn and 5% Zn) are excessively used. Sediment grain size is another important factor, which determines the spatial distribution of Zn in this region. This is evident from the low Zn level in sediments of zone 3, which contain high percentage of sediment particles, which are above 63 µm particle size and the higher content of zinc in the sediments of zones 1 and 2, which are either silty-clay or clayey-silt.

The exchangeable fraction of zinc (Zn_1)

The relative abundance of the exchangeable fraction of zinc (0.85 percentage of total Zn) was very small and was comparable to that of Cu_1 and Fe_1, which were 0.37 and 0.55 percentages respectively (Table 6.2). The values ranged between 0.05 to 4.78 percentages. This fraction of Zn showed high variability in the values, which is evident from the high coefficient of variation of 134 (Table 6.2). Such a high variability was also shown by similar fraction of Cd, Cr, Fe and Pb. The spatial and seasonal variations of Zn_1 fractions were represented in Figure 6.38. From a lowest concentration of 0.07 µg/g at station 9, the values increased to a maximum

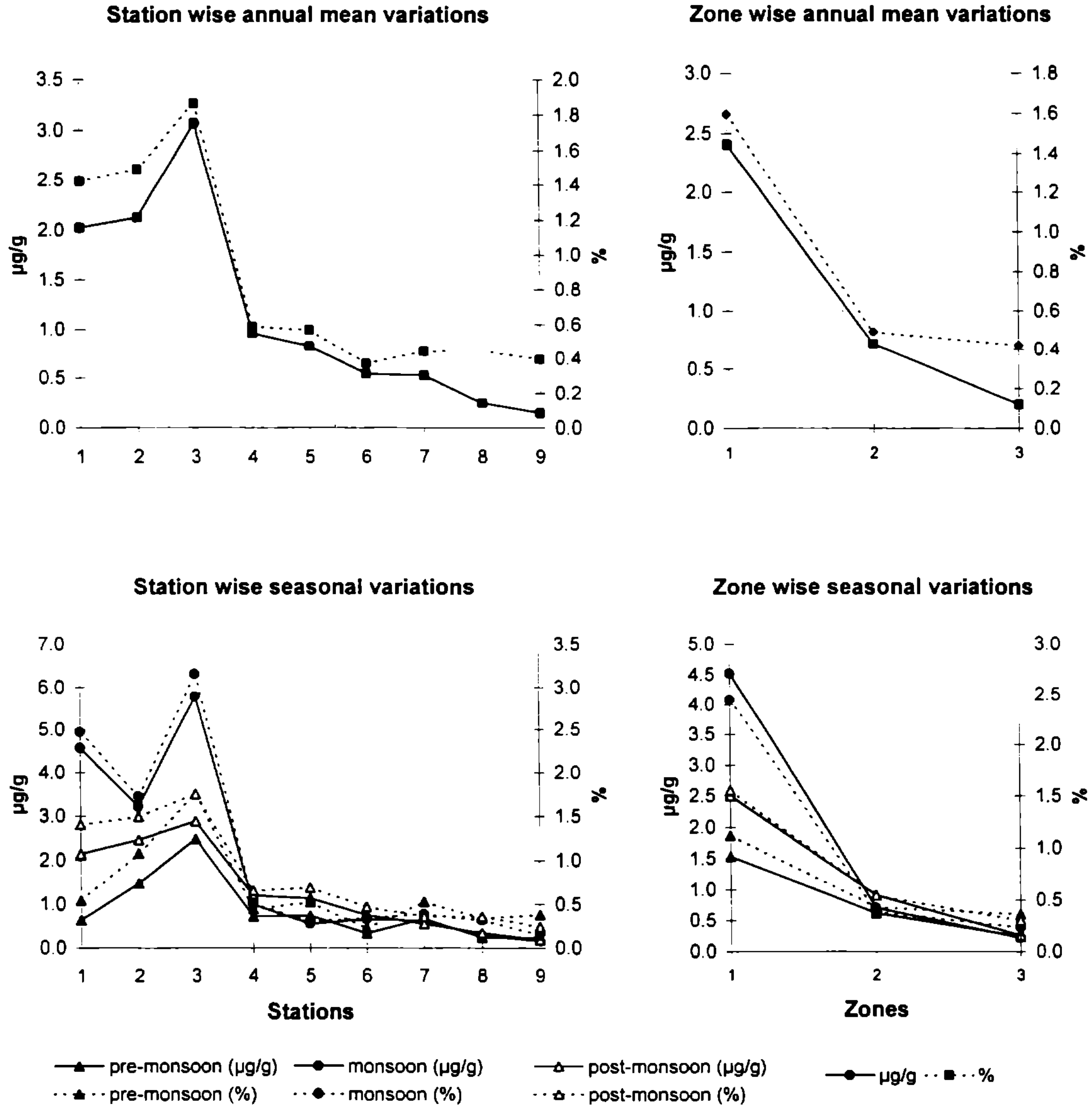


Figure 6.38 Spatial and temporal variations of exchangeable fractions of Zn (Zn_1) on absolute (μg/g) and relative (%) basis.

of 8.08 µg/g at station 3. The stations 3 and 9 also recorded highest and lowest annual mean concentrations, which were 3.11 µg/g and 0.19 µg/g respectively. The trend in annual mean concentration (Figure 6.38) was similar to that observed for lead and nickel i.e., after an initial increase from station 1 to station 3, the concentration showed a decreasing trend from station 3 to station 9. The annual mean concentrations at stations 4 to 9 (range 0.19 to 1.01 µg/g) were found to be appreciably lower than that observed at stations 1 to 3 (range 2.07 to 3.11 µg/g). The trend in the variations of station wise seasonal average values is also given in Figure 6.38. Exchangeable fraction of zinc was found to be high in absolute concentration as well as in percentage at zone 1, and only the stations in this zone showed some variations in seasonal concentrations. The trend in seasonal variations at this riverine zone was such that the period of maximum land runoff (monsoon) recorded highest concentration as well as percentage, and the period of low discharge (pre-monsoon) recorded low concentrations as well as percentage.

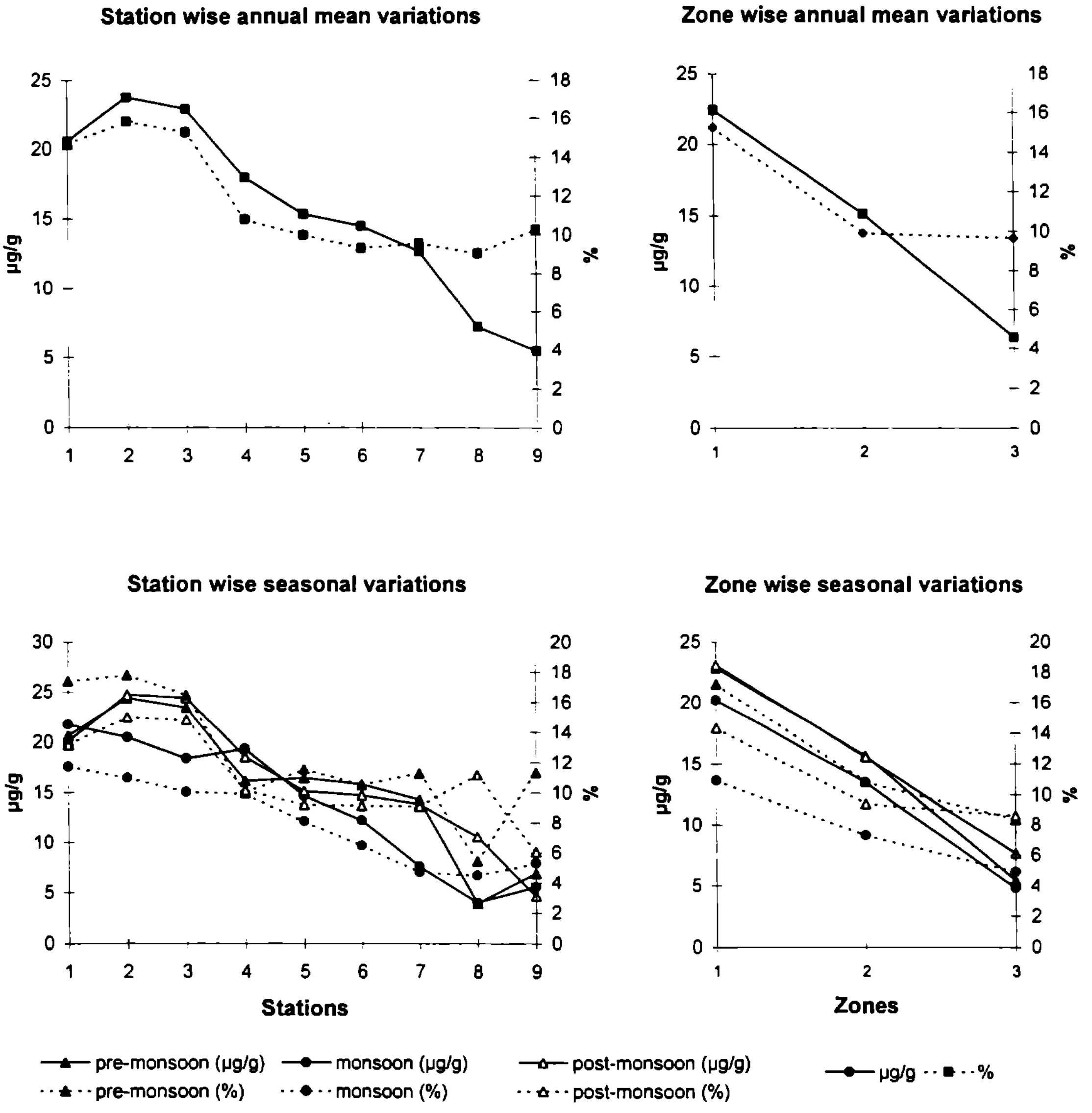
The absolute as well as the relative concentrations of Zn_1 fraction observed in the present study (1.28 µg/g and 0.85 % respectively) were comparable to many of the earlier reported values from other water bodies. For e.g., the values reported from Yamaska River (0.9 %) by Tessier et al. (1980), Axios River and Estuary (0.76 % and 0.99 % respectively) by Samanidou and Fytianos (1987) and Pisuerga River (1.06 %) by Pardo et al. (1990) are comparable to the present study. Nair (1992) reported 1.75 % of Zn_1 fraction from other parts of Cochin Estuary, which receives industrial effluents. The higher concentration and percentage of Zn_1 fraction in the riverine zone (zone 1) indicate that the major source of labile form of Zn in the study area was riverine input.

The reducible fraction of zinc (Zn_2)

Investigation into the reducible fraction of zinc in the sediments of Kuttanad area showed variations from the lowest value, 1.88

µg/g to the highest value of 34.32 µg/g, with a mean value of 15.67 µg/g (Table 6.2). With respect to total Zn, the relative values ranged from 2.39 to 32.97 percentage (Table 6.2). The mean percentage of Zn_2 fraction (11.66 %) was more than 10 times higher than that of Zn_1 fraction and was comparable to the percentage of Mo_2 and Cr_2 fractions (Table 6.2). Wide scatter in values at station 8 was evident from the highest coefficient of variation of 101.19. The station wise annual mean concentrations varied in a similar way as that of lead and nickel i.e., the values showed a regular decrease from station 2 to station 9 after a small increase from station 1 to station 2 (Figure 6.39). Generally, pre-monsoon and post monsoon seasons showed higher concentrations and higher percentage of the fraction (Figure 6.39).

Nair (1992) reported 14.94 µg/g of Zn_2 fraction (15.80 % of total Zn) from the downstream part of Cochin Estuary. The absolute concentration was comparable with the result of the present study (15.67 µg/g) but the relative concentration is slightly lower (11.66 %) than that reported by Nair (1992). Samanidou and Fytianos (1987) also had reported percentage of Zn_2 fraction comparable to this study from Aliakmon River (17.17 %) and Aliakmon Estuary (17.87 %). Compared to the values reported by Tessier et al. (1980), Forstner (1982), Calmano and Forstner (1983), Lee (1985) and Pardo et al. (1990) for the Zn_2 fraction (range 24.5 % to 63 %), the percentage of Zn_2 fraction observed in this study was lower. But it was also observed that very low percentages of Zn_2 fractions were also reported from Mobile bay (4.15 %) by Brannon et al. (1977), from the unpolluted area of Subae River (9.6 %) by Patchineelam and Forstner (1983) and from Yellow River (3 %) by Hong and Forstner (1987). This fraction of Zn, which was associated with Fe-Mn oxi-hydroxide, showed some similarity with the seasonal variation of Mn_2 fraction, which also showed lower concentrations and lower percentage during monsoon and higher concentrations and percentage during pre-monsoon and post-monsoon seasons. This indicated the predominant role of Mn over Fe in



Station wise annual mean variations

Zone wise annual mean variations

Station wise seasonal variations

Zone wise seasonal variations

Figure 6.39 Spatial and temporal variations of reducible fractions of Zn (Zn_2) on absolute (µg/g) and relative (%) basis.

scavenging Zn from the water column and also in determining the fractionation of Zn in the sediments.

The organic cum residual fraction of zinc (Zn_3)

The mean percentage of the organic cum residual fraction of zinc was 87.50 % in the range 66.00 to 97.49 percentage (Table 6.2). This was around 100 times higher than that of Zn_1 fraction and 8 times higher than that of Zn_2 fraction. In absolute concentration, the values varied from 16.16 µg/g to 250.07 µg/g with a mean value of 126.07 µg/g. Station 9 and station 4 recorded the lowest and highest annual mean concentrations (72.52 and 160.02 µg/g respectively) (Figure 6.40). The values recorded at stations 8 and 9 were much lower (79.51 and 72.52 µg/g respectively) than the values of other stations (in the range 126.14 to 160.02 µg/g). Like that of Cd_3 fractions, definite seasonal variations were also observed in the case of Zn_3 fractions, which was evident from Figure 6.40. Similar to that of Cd_3 fractions, Zn_3 fractions also showed highest seasonal average values in monsoon period in all stations. But unlike that of Cd_3 fraction, which showed lowest seasonal average in the post-monsoon season, the lowest seasonal average of Zn_3 fraction was observed in pre-monsoon season. One unique feature observed was in the percentage wise distribution pattern which showed an increasing trend from zone 1 to zone 3 during pre-monsoon and monsoon seasons (Figure 6.40). A similar trend was observed in the distribution of percentage fraction of Cd_3 and Pb_3 during monsoon and pre-monsoon seasons.

The residual fraction of Zn, which is associated with Zn_3 fraction, is generally considered as an inert fraction being detrital and lattice origin (Salomons and Forstner, 1980) and is usually less susceptible to seasonal changes. Thus, the seasonal changes observed in Zn_3 fractions were mainly attributed to the organic fraction associated with this. Hodgson et al. (1966) reported that 60-75 % of soluble Zn in terrestrial soils was present as organic chelates, and rainwater draining the soil might be

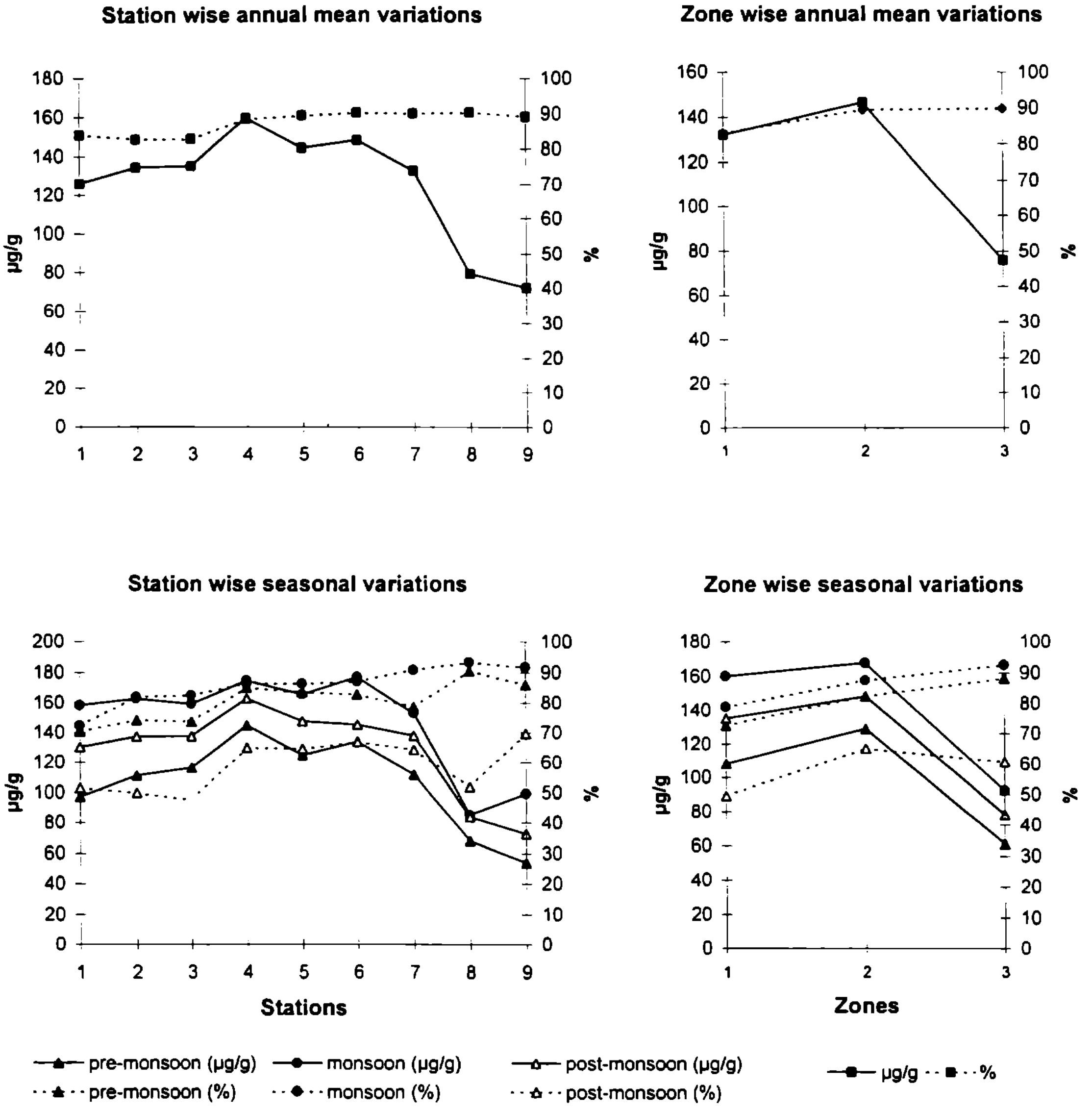


Figure 6.40 Spatial and temporal variations of organic cum residual fractions of Zn (Zn$_3$) on absolute (μg/g) and relative (%) basis.

containing appreciable amounts of Zn in this form. Shibu et al. (1990) has reported high content of organically bound Zn in the waters of Cochin Estuary. The high content of organic Zn in river water would get flocculated and sedimented, contributing an appreciable percentage to total zinc (87.5 %), which was the highest percentage of similar fractions of the 10 metals studied after Cu_3. The increasing trend in the percentage of Zn_3 fractions from zone 1 to zone 3 indicated that the input of organically bound zinc from the paddy fields around zone 2 and zone 3 are predominant over the riverine input which is evident from the comparatively low percentage of Zn_3 fractions in the riverine zone (zone 1). Nair (1992) in a study of the northern side of Cochin estuarine system observed 82.50 % of Zn_3 fraction which was almost comparable to the value obtained in the present study (87.5 %), at the same time the absolute concentration (126.07 µg/g) recorded in the present study was higher than that reported by Nair (1992). Almost comparable values were also reported by Samanidou and Fytianos (1987) from Aliakmon River (81.08 %) and Aliakmon Estuary (80.38 %).

Correlation between variables

A correlation study was attempted to find out the relationship between the distribution pattern of various metals, to find out the relationship between sediment total metal and sediment characteristics like moisture, grain size and organic carbon and also to find out the relationship between the distribution of metals and hydrographic parameters like bottom water salinity, pH and dissolved oxygen. The Pearson correlation coefficient 'r' was used to establish the relationship among the variables. The 'r' values for the pairs of variables are given in Table 6.14. None of the metals showed significant correlation with pH, but all metals showed significant negative correlation with salinity. The significance of this negative correlation of sedimented trace metals with salinity lies in the fact that stations 8 and 9, which recorded maximum salinity during the period of survey in the pre-monsoon season, also recorded the maximum

Table 6.14 Correlation values(r) between pairs of parameters compared (n = 108)

Parameter	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
DO	0.28	0.12	0.14	0.07	0.14	0.13	0.02	0.15	0.21	0.30
SPM	-0.18	-0.05	-0.12	-0.07	-0.10	-0.10	-0.08	-0.08	-0.06	-0.24
Salinity	-0.27	-0.34	-0.49	-0.42	-0.43	-0.35	-0.47	-0.49	-0.43	-0.47
pH	0.10	-0.15	0.09	0.14	-0.01	-0.03	0.08	0.07	0.14	0.20
Sand	-0.35	-0.69	-0.79	-0.81	-0.65	-0.55	-0.82	-0.88	-0.81	-0.74
Silt	0.20	0.79	0.87	0.74	0.77	0.71	0.78	0.87	0.81	0.75
Clay	0.42	0.43	0.54	0.70	0.39	0.27	0.68	0.70	0.62	0.57
OC	0.23	0.55	0.75	0.78	0.55	0.42	0.73	0.87	0.72	0.54
Zn	0.67	0.54	0.69	0.56	0.58	0.47	0.46	0.67	0.76	
Pb	0.45	0.63	0.83	0.80	0.65	0.47	0.67	0.86		
Ni	0.28	0.65	0.89	0.91	0.69	0.51	0.85			
Mo	0.01	0.42	0.72	0.86	0.47	0.31				
Mn	0.14	0.89	0.77	0.22	0.88					
Fe	0.22	0.91	0.90	0.44						
Cu	0.19	0.42	0.74							
Cr	0.22	0.84								
Co	0.23									

(DO = Dissolved oxygen, SPM = Suspended particualte matter, OC = Organic carbon) percentage of sand in the sediments and in the present study it was seen that sediments containing higher percentage of sand are impoverished in the concentration of trace metals. Therefore, the above points suggest that pH and salinity are not alone the decisive factors that determine the distributional characteristics of trace metals in the estuarine sediments. It is the combined effect of various other factors that influence the distribution of trace metals in the sediments of the area. Almost all trace metals, and to a lesser extent Cd, exhibited highly significant correlation with the silt and clay fractions (less that 63 µm size fraction). This feature implies that grain size of the sediments has a major role in the distribution of trace metals in sediments. Except Cd and Cu, all other metals were found to be having significant correlation with Fe and Mn. Cu showed significant correlation only with Fe. The correlation of Cd with Fe and Mn was not found very significant. The above facts suggest that Fe and Mn oxides play a major role on the distribution of almost all trace metals studied except Cd. Iron and manganese are extremely important elements in aquatic geochemical processes because their various oxides and hydroxide species act as scavengers for a variety of trace metals (de Groot, 1976). Except Cd, all other nine metals studied were found to have strong correlation with organic carbon content of sediment. Estuaries are environments of generally high biological productivity. Aquatic organisms are well known for their ability to take up trace elements from solution and particulates (Bowen, 1966; Riley and Chester, 1971). Earlier, productivity studies in the area have indicated that phytoplankton production far exceeds the zooplankton production (Qasim, 1970). Correspondingly, the underlying sediments are rich in organic matter content (Murty and Veerayya, 1972). It is, therefore, possible that the elements are incorporated into the sediments in association with organic matter to a certain extent. While this is broadly so, Cr, Cu, Mo, Ni and Pb seem to have stronger relationship with organic matter in these sediments than Cd, Co, Fe, Mn and Zn. Some metals show highly significant correlations to each other. They are Cd/Zn, Co/Pb, Co/Ni, Co/Cr, Cr/Zn, Cr/Pb, Cr/Ni, Cr/Mo, Cr/Cu, Cu/Pb, Cu/Ni, Cu/Mo, Mo/Pb, Mo/Ni, Ni/Zn, Ni/Pb and Pb/Zn. The high correlation between metals indicates that they are introduced from similar sources and behave similarly chemically. Most other studies of metal distributions in intertidal and subtidal sediments have also found high inter metal correlations (Santschi et al., 1984; Zwolsman et al., 1996; Basaham and El-Sayed, 1998).

Conclusively, the distribution pattern of Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn in the sediments of the aquatic system of Kuttanad have revealed that

* Elemental concentrations follow closely the texture of the sediments
* Sands contain very low concentration of all elements
* Elemental concentration increases with decrease in grain size
* Except Cd, all the other 9 elements bear significant relationship with organic carbon
* Almost all the ten trace elements studied were found enriched in the sediments of the southern upstream part of Cochin estuarine system.

The enrichment of trace metals in the sediments of the region can be due to

* Their association with organic matter of the sediments
* Their association with ferric and manganese hydroxides through adsorption and co-precipitation
* Lack of proper exchange of trace elements between sediments and water as the tidal effect through the Cochin barmouth is practically restricted by the salinity barrier at Thanneermukkam
* The increased rate of settling of suspended solids in the comparatively calm and shallow water body
* Settling of the suspended load carried by the four rivers in the fresh water zone itself, especially in the pre-monsoon season, before

being carried to the estuary, due to the restricted flow of water in this season.

- The sediments are largely organic-rich clayey-silts or silty-clay in which metal concentrations exceed background levels, and which attain peak values in the upper and middle reaches of the estuary.

Correlations among similar fractions of trace metals in the sediments are given in Table 6.15. When the exchangeable fraction of cadmium showed highly significant correlation ($p << 0.001$) with similar fraction of cobalt, chromium, copper and lead, the exchangeable fraction of cobalt was well correlated with similar fraction of all other trace metals studied. Similarly, significant correlations were found among exchangeable fractions of chromium, lead, copper, cobalt and cadmium. The exchangeable fraction of Fe (Fe_1) showed significant correlation with only Co_1 and Mo_1, whereas exchangeable Mn (Mn_1) was found well correlated with Co_1, Mo_1 and Ni_1. Mo_1/Ni_1 and Ni_1/Zn_1 pairs were also found significantly correlated. Unlike the exchangeable fractions, the reducible fractions of all trace metals were significantly correlated among each other, except Mn_2/Cr_2, Mn_2/Cu2 and Mn_2/Fe_2 pairs. Similarly, many of the trace metal fractions in the organic cum residual fractions were also found significantly correlated. But in the case of Cd, poor correlation was found with similar fractions of other trace metals except with Zn_3 and Pb_3. Co_3/Mo_3, Co_3/Cu_3, Cu_3/Mn_3, Cu_3/Fe_3, Mn_3/Pb_3, Mn_3/Ni_3 and Mn_3/Mo_3 pairs were also not found to exhibit any significant correlations between them.

In terms of absolute concentrations, all trace metals studied were found to be enriched in suspended particulate matter (Table 6.16) with respect to the bulk sediments. The annual mean values at each station showed that (Table 6.16) the enrichment factor (ratio of concentration in suspended particulate matter to concentration in bulk sediment) was maximum for manganese. Particulate manganese was enriched by a factor of 26 to 158 times. Compared to other trace metals, Cr was least enriched in particulate phase, average being 2.78. On an average basis, the order of

Table 6.15 Correlation between similar fractions of trace metals in sediments (n = 90)

	Cd_1	Co_1	Cr_1	Cu_1	Fe_1	Mn_1	Mo_1	Ni_1	Pb_1
Zn_1	0.140	0.772	0.147	0.658	0.266	0.198	0.180	0.460	0.141
Pb_1	0.992	0.544	0.966	0.617	-0.024	0.247	0.287	0.296	
Ni_1	0.310	0.516	0.325	0.450	0.256	0.449	0.480		
Mo_1	0.269	0.352	0.306	0.296	0.392	0.423			
Mn_1	0.257	0.497	0.261	0.276	0.322				
Fe_1	-0.059	0.413	-0.008	0.150					
Cu_1	0.617	0.819	0.616						
Cr_1	0.967	0.548							
Co_1	0.535								

	Cd_2	Co_2	Cr_2	Cu_2	Fe_2	Mn_2	Mo_2	Ni_2	Pb_2
Zn_2	0.833	0.928	0.933	0.682	0.553	0.361	0.919	0.856	0.893
Pb_2	0.917	0.866	0.869	0.603	0.571	0.389	0.882	0.888	
Ni_2	0.864	0.869	0.838	0.576	0.679	0.489	0.865		
Mo_2	0.850	0.883	0.891	0.579	0.602	0.378			
Mn_2	0.469	0.476	0.298	0.157	0.267				
Fe_2	0.486	0.655	0.632	0.468					
Cu_2	0.402	0.600	0.630						
Cr_2	0.802	0.930							
Co_2	0.843								

	Cd_3	Co_3	Cr_3	Cu_3	Fe_3	Mn_3	Mo_3	Ni_3	Pb_3
Zn_3	0.557	0.464	0.625	0.431	0.535	0.357	0.363	0.569	0.640
Pb_3	0.552	0.519	0.719	0.662	0.558	0.276	0.568	0.805	
Ni_3	0.217	0.499	0.843	0.890	0.553	0.204	0.863		
Mo_3	-0.161	0.248	0.726	0.913	0.356	-0.006			
Mn_3	0.136	0.836	0.580	-0.089	0.765				
Fe_3	0.168	0.884	0.862	0.281					
Cu_3	0.065	0.223	0.663						
Cr_3	0.119	0.772							
Co_3	0.206								

Table 6.16 Enrichment factor for trace metals in suspended particulate matter with respect to bulk sediments (conc. in SPM / conc. in bulk sediments)

Stations	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
1	15.17	3.34	1.27	5.03	1.92	60.84	1.31	2.97	7.11	6.67
2	18.19	3.07	1.55	5.68	2.34	55.30	1.14	3.78	7.92	7.33
3	11.46	2.27	0.96	2.96	1.86	39.65	1.25	2.25	4.89	5.31
4	13.24	1.98	1.12	4.81	1.30	26.93	1.30	3.16	7.95	5.52
5	9.91	1.49	1.26	8.25	1.12	26.02	2.04	3.77	9.24	5.61
6	11.06	2.08	1.13	7.97	1.01	42.80	1.46	4.84	8.27	7.47
7	17.99	2.91	2.64	12.84	1.84	48.55	2.46	5.82	16.62	6.67
8	16.43	7.68	6.32	30.62	6.43	158.62	9.87	15.05	17.26	14.87
9	17.55	9.23	8.80	28.25	7.80	98.04	10.55	12.77	27.05	13.81
Average	14.56	3.78	2.78	11.82	2.85	61.86	3.49	6.05	11.81	8.14

(SPM = suspended particulate matter)

enrichment of particulate trace metals is Cr < Fe < Mo < Co < Ni < Zn < Pb = Cu < Cd < Mn. As the suspended sediments are finer and richer in multiple hydroxide coatings, organic and heavy metal scavenging clays, they carry high heavy metals (Forstner and Wittmann, 1983; Singh, 1999). Varying levels of enrichment of heavy metals in suspended sediments have been reported by many workers (Gibbs, 1977; Borole et al., 1982; Ramesh et al., 1990; Biksham et al., 1991). A general trend observed from the values (Table 6.16) is that there was an increase in the enrichment factor for all the trace metals at zone 3. This was not unexpected as the bulk sediments at zone 3 were depleted in total trace metals due to the sandy nature of sediments at these stations.

CHAPTER 7

MODELLING OF THE SYSTEM – A STEADY STATE APPROACH

INTRODUCTION

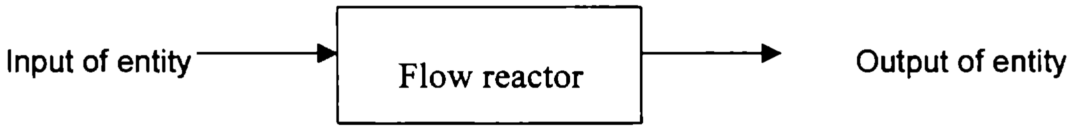
The definition of a system is generally done by taking into account the various processes and system characteristics. Models are used to define a process or a system. Of the different models available, the concept of analytical models is used here. Analytical models are mathematical expressions of a system or process which can be either explanatory or predictive. Even though computer simulation is the next step of the analytical modelling, it is not attended here.

In the modelling of environmental system, the various approaches used so far can be broadly seen in two headings

1. Mass balance (Sillen, 1961)
2. Steady state approximation (Schindler, 1991)

The conservation of mass is the basic concept of the mass balance and generally works on the equilibrium conditions. This can be applied to individual processes and can give more or less reliable predictions. But at the same time in a multivariant system where different processes operate simultaneously, the mass balance models can only very rarely advantageous. In the steady state, the individual processes are considered to be in a dynamic steady state, i.e. the process need not be in equilibrium but the change in concentration of the interacting species is taken as negligible. It is so possible to take the sum of the processes to explain the total character of the system. This is generally used for defining the environmental systems where simultaneous operation of the different contributing processes will be taking place.

Environmental systems like Kuttanad water can be better represented by the flow reactor model which can be given in a general form as:



In a simple flow reaction scheme, the reaction characteristics can be assessed by monitoring the velocity of the flow and change in concentration of the chemical entity. When the reactions and the reactants are specified, the extent of reaction or the reactivity can be worked out by simple kinetic equations or by a phenomenological reaction (Haefner, 1996) like,

$$\frac{dx}{dt} = \Sigma \text{ inflows} - \Sigma \text{ outflows}, \quad \text{for the extent of reaction}$$

$$\text{and} \qquad m = \frac{\Sigma \text{ outflows}}{\Sigma \text{ inflows}} \qquad \text{for the reactivity.}$$

In the aquatic system, a direct quantification in terms of the actual load transferred to the reactor or the actual load released from the reactor is always an impossible task. The character of the reactants and the reactivity of the system are considerably complex also. The normal kinetic equations thus cannot be used here.

Definition of the present system – Kuttanad waters

As discussed in the materials and methods (Chapter 2) the region is split into 3 zones based on hydrographic parameters. This requires a little more explanation. The different processes and the behaviour of the zones are re-examined here. Zone 1 is the source of materials of the zone 2. Zone 2 contains significant contributions as lateral entry from the surrounding area due to the various processes operating there. Zone 1 has contributions from land, weathering of rocks and river bed and many of the anthropogenic sources. The individual contributions, except in modifying, the magnitude or quantum of the materials, is considered to have insignificant role in defining the mixing compartment i.e. zone 2. Zone 3 represents the discharge zone of the zone 2. As in the case of zone 1, the various processes like further mixing, geochemical reactions etc. present in the zone 3 can in no way modify the processes present in zone 2. Zone 2 is considered as a reaction cell and the various processes in this zone are precipitation/dissolution, adsorption/desorption, sedimentation/resuspension, mineralization and other diagenetic processes. This zone is shallow in character with a depth ranging from 1.5 to 3.0 M. The conceptual framework of the different processes operating in the system can be given as a flow chart (Figure 7 1).

Assumptions

The possibilities of the different processes that can contribute to the behaviour and concentration of the trace metals in the system points to the requirement of a multivariable model to define the system. Though the scope of geochemical transformations in zone 1 is very limited, zone 2 and zone 3 represent highly complex and geochemically reactive regions. A compartmental process based approach is essential to diagnose the

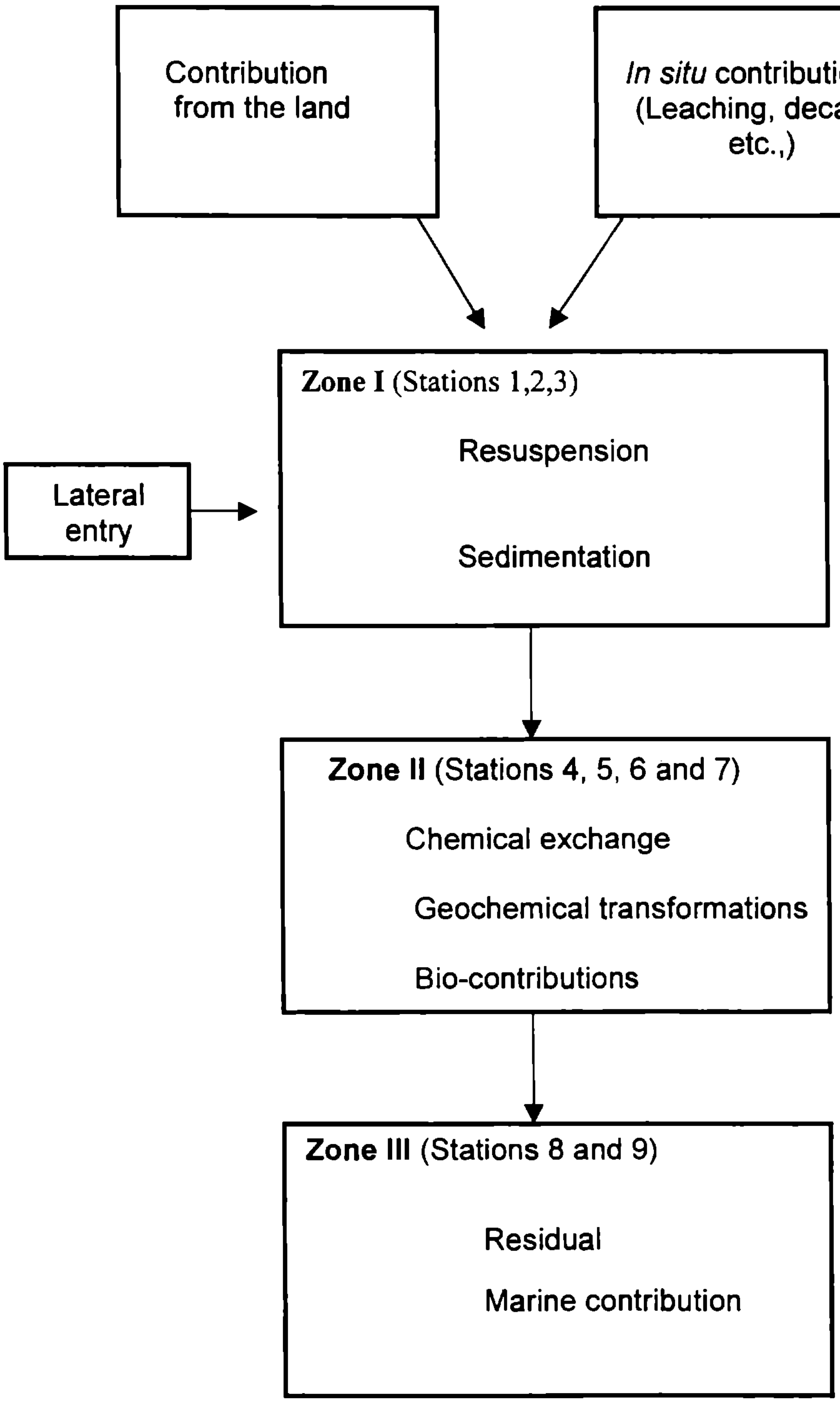


Figure 7.1 Flow chart for different processes operating in the system

character of zones 2 and 3. As sediment, water and particulate constitute the media which support the different geochemical processes, all the processes operating in the system is viewed separately in three compartments viz, sedimentary, dissolved and particulate. The net reactivity and contribution to the system can be obtained by taking the sum of the inflows and outflows of the metal.

The following basic assumptions form the foundation of this treatment.

1. The quantification of the inflows and outflows are restricted to the concentration of the metal in each compartment as the concentration will be a reflection of the movement of the species between the compartments.

2. Though the system will not be in equilibrium, a steady state is a general feature. No high accumulation or removal of the metal in the system or any of the compartments at any stage is envisaged.

3. The net rate of accumulation or the net rate of transport in any of the compartment at any stage will be near to zero.

4. Except the general geochemical processes, no auxiliary factors will have significant contribution to the concentration of the metal in any compartment. This may not be true for all the metals but the exception can be considered separately.

5. In the sedimentary compartment the contributors are:

(a) Inflow Exchange, sorption, precipitation, complexation with the dissolved species.
Sedimentation of particulate matter.

(b) Out flow – Exchange, desorption, dissolution – with water
- Resuspension of sediments
- Storage to deeper sediments

6. The processes in the dissolved compartment are

(a) Inflow – discharge from previous zone (upstream)
- Dissolution from particulate
- Lateral entry, human activity, if any
- Release from sediment

(c) Outflow – Discharge to next zone (down stream)
Particulate adsorption
Sedimentary sorption

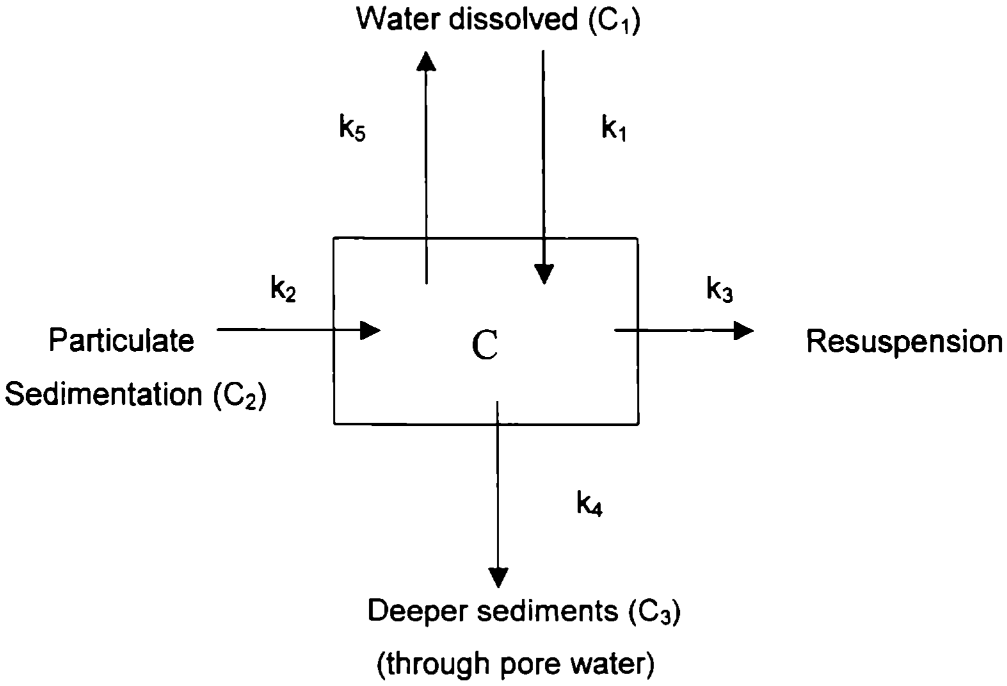
7 In the particulate compartment, the processes are

(a) Inflow – discharge from upstream
- Adsorption from water
- Resuspension of sediment
- Lateral entry, if any

Mathematical basis of the Model.

Zone 2 can be considered as a 3 compartment system, the compartments being dissolved, particulate and sediment. Though there is definite exchange of chemical species between these compartments, for a better understanding of the processes, these compartments are treated separately and integrated at a later stage.

Sedimentary compartment



The net change in concentration of the metal in the sedimentary compartment thus can be given as

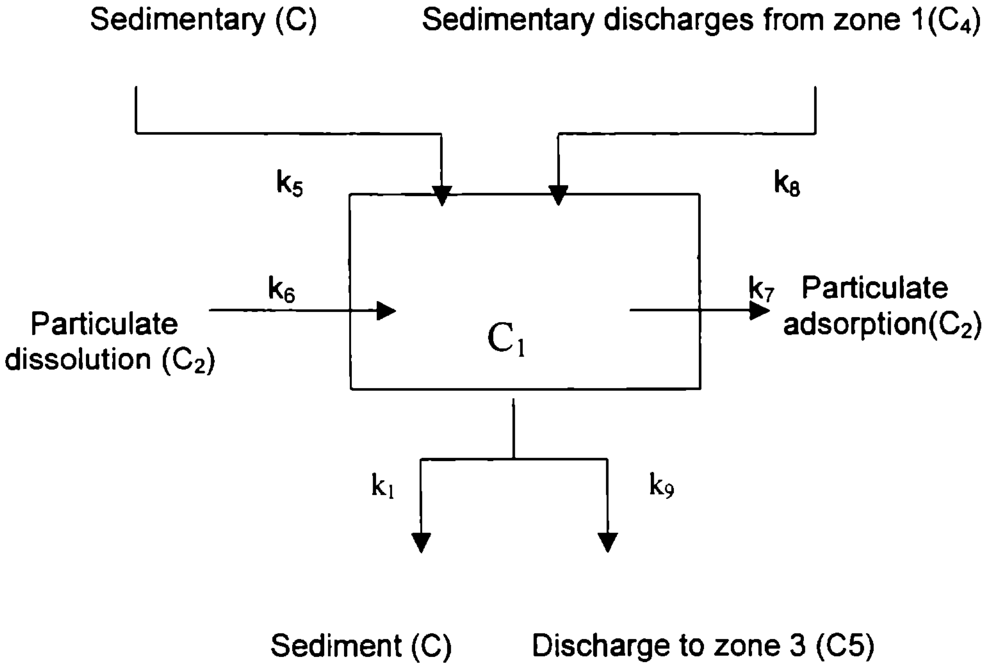
$$dC/dt = k_1C_1 + k_2C_2 - k_3C - k_4C - k_5C \quad \text{------(1)}$$

From the steady state approximation,

$$dC/dt = 0$$

$$\text{i.e,} \quad k_1C_1 + k_2C_2 = C(k_3 + k_4 + k_5) \quad \text{-------(2)}$$

Dissolved compartment



The net rate of change of dissolved metal in the compartment can be given as:

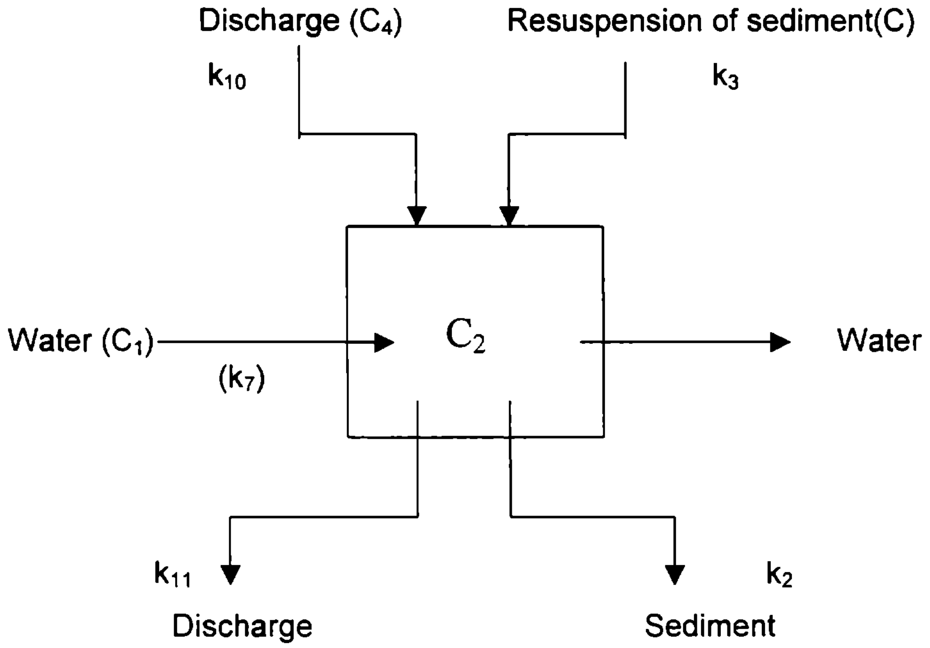
$$dC_1/dt = k_5C + k_8C_4 + k_6C_2 - k_1C_1 - k_9C_1 - k_7C_1 \quad \text{----------} (3)$$

Applying steady approximation,

$$dC_1/dt = 0$$

i.e, $$k_5C + k_8C_4 + k_6C_2 = C_1(k_1 + k_7 + k_9) \quad \text{----------} (4)$$

Particulate compartment



The rate of change of concentration of the metal in the particulate compartment is given by

$$dC_2/dt = k_{10}C_4 + k_3C + k_7C_1 - k_6C_2 - k_{11}C_2 - k_2C_2 \quad \text{---------}(5)$$

Applying for

$$dC_2/dt = 0$$

i.e, $k_3C + k_{10}C_4 + k_7C_1 = C_2(k_2 + k_6 + k_7)$ ---------(6)

Integration of the compartment and development of the model

The integration of the model is done based on two basic considerations viz. (a) The dynamic processes equilibrium which is the basis of the steady state treatment is not affected by the magnitude of the input or output but depend only on the effective concentration available in the system and (b) The dispersive character of the particulate will always result in proportionality between the concentration of the metal in the dissolved and particulate phases and the sedimentation and resuspension process will not affect this proportionality (Schindler, 1991).

As per the above assumptions, $C_2 \propto C_1$

Or $C_2 = mC_1$ -----------------(a)

where m is the distribution coefficient of the metal between the particulate matter and water.

So equation changes to

$$(k_1 + k_2 m)\, C_1 = C(k_3 + k_4 + k_5)$$

or, $C_1 = KC$ -----------------(b)

where $K = \dfrac{(k_3 + k_4 + k_5)}{(k_1 + k_2 m)}$ K, thus, represents the partition coefficient of the distribution of metal between the dissolved and sediment.

The model

The main objectives of the modelling are:

(1) To identify and if possible quantify the lateral additions.

(2) To quantify the role of geochemical reactivity in the distribution of the metals.

The major problem in adopting the flow reactor model in the present system is the lateral addition of chemical entities including some of the trace metals to the zone 2 by the agricultural and other human activities prevailing in this zone. A direct quantification of the lateral additions impossible due to the diversity of the source as well as the addition modality. In this study, the results obtained, while attempting to correlate the various geochemical processes operating in the system, are

(a) dissolved metal ion concentration in a zone always maintains a constant proportionality with the concentration of the metal in particulate and sediment compartments.

(b) The particulate load in water remains at almost steady value.
The change in concentration of the metal ion in the particulate fraction
In the different zones thus can be considered as the index of the
geochemical processes.

In the present treatment, the distribution coefficient of the particulate to dissolved metal concentration is used to determine the possible amount of metal ion that has reached the system. The difference between the calculated and observed is considered as the lateral addition.

In order to have a better clarity of the above argument, the system is re-examined below.

When sinking of particulate matter in all the zones to form part of the sediment is negligible, as is the case in the present study, and when there is no geochemical process which modify the chemical environment of the system, the concentration of the metal in the particulate compartment as well as its ratio with the concentration in dissolved compartment should have been same. But if the geochemical reactivity of the zones are different, both the metal concentration in the particulate compartment and the ratio to the dissolved will change. The ratio of the particulate to the dissolved observed at the reactive zone computed along with the actual concentration available in the particulate at the zone 1 can give a picture about the geochemical reactivity of the zone. The ratio between the particulate and dissolved is taken as a state variable and is used to get the auxiliary variables which are indicative of the geochemical reactivity.

Computation of the variables

Variables identified are:

(1) Concentration of metal (dissolved) in zone 1 = C_{11}

(2) Concentration of metal (dissolved) in zone 2 = C_{12}

(3) Concentration of metal (dissolved) in zone 3 = C_{13}

(4) Concentration of metal (particulate) in zone 1 = C_{21}

(5) Concentration of metal (particulate) in zone 2 = C_{22}

(6) Concentration of metal (particulate) in zone 3 = C_{23}

(7) Concentration of metal (sediment) in zone 1 = C_{31}

(8) Concentration of metal (sediment) in zone 2 = C_{32}

(9) Concentration of metal (sediment) in zone 3 = C_{33}

(10) Particulate to dissolved ratio in zone 1 = m_1

(11) Particulate to dissolved ratio in zone 2 = m_2

(12) Particulate to dissolved ratio in zone 3 = m_3

Auxilliary variables are:

(1) Contribution of zone 1 if the reactivity of zone is equal to zone 2

$$A = m_2 \times C_{21}$$

(2) Lateral addition, $B = C_{12} - A$

(3) Magnitude of lateral addition if the reactivity of zone 2 is equal to zone 1

$$C = B \times m_1$$

Based on the above considerations, the model parameters, ie, reactivity and partition coefficient, are calculated from the variables and auxiliary variables as

Model Parameters:

(1) Reactivity of zone 2, $R_1 = \dfrac{C_{12}}{C + C_{11}}$

(2) Reactivity of zone 3, $R_2 = \dfrac{C_{13}}{C_{12}}$

(3) Partition coefficient K of metal between the sediment and water in zone 1

$$= \frac{C_{11}}{C_{12}}$$

(4) Partition coefficient K of metal between the sediment and water in zone 2

$$= \frac{C + C_{11}}{C_{32}}$$

(5) Partition coefficient K of metal between the sediment and water in zone 3

$$= \frac{C_{13}}{C_{33}}$$

The data obtained for the different model parameters are given in Table 7.1. The following are the results:

The definition of reactivity in the present model argument will represent a positive one (+1) as the state of dynamic equilibrium where no change in concentration between the zones will take place. The values beyond positive one represent processes which will facilitate addition of trace metal and less than one indicates removal of the metal. In the present study, significant positive values beyond one is observed in zone 2 only with Fe and in zone 3 for Cd, Fe and Mn. The difference in behaviour of Cd and Mn at zone 2 and zone 3 can only be due to the increase in salinity structure. It is also to be noted that in all the zones the sediment is almost in a reducing environment, as is evident from the pH values, and the depth of the water column is about 1.5 to 10.0 m. The low pH generally facilitates the release of Fe and Mn and removal of Cu. The high negative value obtained for Cu clearly supports the removal of Cu to sediment. The difference in the reactivity observed between Fe and Mn confirms with the earlier observation of precipitation and removal of Mn from the dissolved phase in the oxygenated surface waters (Forstner and Wittmann, 1983). The high value of Fe thus can only be due to lateral addition. The higher reactivity of Cd in zone 3 and the values observed in the particulate and sedimentary phases may be due the formation and dissolution of chloro-complexes in saline waters. The values of the partition coefficient separates Cu & Mn from other three metals. These two metals exhibited a decrease in the partition coefficient from zone1 to zone 2. The removal of Cu & Mn from the dissolved phase is evident from these trend. Fe exhibited significant increase in the partition coefficient in zone 2 compared to zone 1 indicating the dissolution of Fe from sediment. In the zone 3 for all the metals examined, the partition coefficient was very low. The sandy character of the sediment restricting the accumulation and retention of metals may be the reason. In short, the partition coefficient values support the arguments made earlier.

Table 7.1 Values of different model parameters (on annual and zonal basis)

Metal	Zones	C_1(µg/l)	C_2(µg/g)	C_3(µg/g)	m	A	B	C	Reactivity	K
Cd	1	2.16	28.73	2.02	13.33	2.54	0.14	1.91		0.94
	2	2.68	30.36	2.42	11.32				0.66	0.90
	3	3.11	21.85	1.72	7.03				1.16	0.55
Co	1	0.82	174.86	60.39	212.48	0.98	-0.04	-7.52		73.39
	2	0.94	168.53	83.36	178.86				-0.14	88.47
	3	0.92	116.35	16.34	127.10				0.97	17.85
Cu	1	2.27	220.52	50.87	97.31	2.30	-0.03	-3.11		22.45
	2	2.27	217.45	29.12	96.00				-2.70	12.86
	3	2.22	222.95	8.24	100.42				0.98	3.71
Fe	1	69.48	135.30	67.67	1.95	86.78	-12.49	-24.33		0.97
	2	74.28	115.82	94.06	1.56				1.65	1.27
	3	86.69	98.12	15.95	1.13				1.17	0.18
Mn	1	0.41	22.44	0.46	55.29	2.47	0.56	30.86		1.13
	2	3.03	27.51	0.75	9.09				0.10	0.25
	3	4.79	19.80	0.19	4.13				1.58	0.04

Validation of the model

The basic consideration in the development of the model is the steady state behaviour of the zones and the definite relationship between the concentrations of the metals in the different phases.

The correlations between the metal concentrations in the dissolved, particulate and sediment compartment are given in Table 7.2. The significant correlations obtained are indicative of the validity of the assumption considered for the integration of the model.

The correlation analysis of the data for the relation between the dissolved metal concentration and the sedimentary metal concentration and the particulate and sediment metal concentrations agrees with the integration process validating the model.

Table 7.2 Correlation coefficients between metal concentrations in the dissolved, particulate and sediment compartments.

Metal	Zones	Dissolved Vs particulate			Dissolved Vs sediment			Particulate vs sediment		
		Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
Cd	1	-0.354	-0.570	-0.590	-0.324	-0.044	-0.431	0.104	0.268	0.643
	2	0.684	-0.304	-0.146	0.214	0.093	-0.574	0.380	0.283	0.179
	3	0.768	0.392	-0.612	-0.317	0.725	-0.822	-0.119	0.055	0.618
Co	1	0.295	-0.027	0.014	-0.451	-0.092	0.525	-0.021	-0.288	-0.005
	2	-0.260	0.068	-0.164	-0.102	0.253	0.318	0.123	0.347	-0.321
	3	-0.825	-0.062	0.243	0.044	-0.536	0.508	0.175	-0.231	0.425
Cu	1	0.598	0.513	-0.206	0.432	0.065	0.405	0.665	-0.063	-0.291
	2	-0.423	-0.377	-0.164	-0.242	-0.443	0.279	0.252	0.361	0.082
	3	-0.317	-0.237	0.147	-0.412	-0.555	0.603	-0.213	0.536	0.325
Fe	1	0.273	-0.804	0.479	-0.354	-0.570	-0.590	0.020	-0.359	0.634
	2	0.674	-0.670	-0.199	0.684	-0.304	-0.146	0.107	0.323	-0.132
	3	0.467	-0.025	-0.837	0.768	0.392	-0.612	-0.056	0.185	0.410
Mn	1	0.663	-0.451	0.612	-0.631	-0.236	-0.080	-0.310	-0.180	-0.244
	2	0.428	-0.362	0.803	-0.036	-0.325	-0.090	0.487	0.496	-0.177
	3	-0.081	-0.534	0.071	-0.286	0.876	-0.310	-0.041	-0.733	0.171

(For pre-monsoon, n = 36; monsoon, n = 27; post-monsoon, n = 45)

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Not referred to in original

Annexure - 1. Station wise monthly data of general hydrographical parameters and sedimental characteristics

Parameter	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
TEMPERATUE (°C)	Surface water	1	31.0	30.0	29.5	32.0	32.0	32.5	31.0	30.0	27.5	27.5	28.5	29.2
		2	30.5	30.0	29.5	32.0	32.5	32.0	31.0	31.0	28.0	27.0	28.5	29.5
		3	30.4	28.5	29.0	31.5	32.0	31.5	31.0	31.0	28.0	28.0	28.7	29.0
		4	31.0	29.0	28.5	32.0	31.8	31.0	31.5	31.0	28.0	28.5	29.0	29.5
		5	30.7	28.0	29.0	32.0	32.0	32.0	32.0	30.7	27.8	28.0	29.0	29.0
		6	30.6	28.5	29.3	32.0	32.0	32.0	33.0	30.2	27.2	28.5	30.0	29.5
		7	29.5	28.0	29.4	30.5	30.5	32.0	32.0	30.0	27.0	28.7	29.5	28.3
		8	29.4	28.5	29.0	32.0	31.5	31.0	32.0	30.0	27.0	28.0	29.3	28.0
		9	29.6	28.8	29.2	31.5	31.5	31.0	32.0	30.0	27.0	28.0	29.3	28.0
	Bottom water	1	30.0	29.2	29.0	30.0	31.0	32.0	30.5	29.5	27.2	27.0	28.0	28.7
		2	30.0	29.2	28.5	30.0	32.0	31.5	30.5	30.5	27.5	27.0	28.0	28.5
		3	29.5	28.0	28.0	31.0	31.0	31.0	30.5	30.5	27.8	27.5	28.3	28.0
		4	30.2	29.0	28.0	32.0	31.0	30.7	31.0	31.0	27.8	28.0	28.5	29.0
		5	29.8	27.7	28.2	32.0	31.5	31.5	32.0	30.4	27.5	28.0	29.0	29.0
		6	30.0	28.3	28.5	32.5	31.5	31.5	33.0	30.0	27.0	28.5	29.5	29.0
		7	29.2	27.1	29.0	30.0	30.0	31.5	32.0	30.0	27.0	28.4	29.5	28.0
		8	29.2	28.3	28.5	31.5	31.0	31.0	31.5	30.0	27.0	28.0	29.0	28.0
		9	29.4	28.6	28.7	31.0	31.0	30.5	31.5	30.0	27.0	28.0	29.0	28.0
DEPTH (m)		1	10.0	10.0	10.0	9.0	9.0	10.0	9.0	10.0	10.0	10.0	10.0	9.0
		2	9.8	9.5	9.3	9.0	9.0	9.0	9.0	10.0	10.0	10.0	9.8	9.7
		3	9.0	9.0	10.0	8.0	6.0	8.0	7.5	9.5	9.5	9.0	8.0	7.0
		4	2.5	3.0	2.5	2.5	2.0	2.0	2.0	1.5	2.0	2.0	3.0	2.0
		5	2.5	3.0	3.0	2.0	1.5	1.0	2.0	1.0	3.0	2.0	2.0	1.0
		6	3.0	3.5	3.0	1.5	2.5	3.0	3.0	3.0	4.0	3.0	4.5	3.0
		7	1.5	3.0	2.5	2.0	1.5	1.5	1.5	1.5	2.0	1.5	2.5	2.0
		8	1.5	2.0	2.0	1.5	1.5	2.0	2.0	2.0	1.5	1.0	2.0	2.0
		9	1.5	2.0	2.0	2.0	2.0	2.0	1.5	1.5	1.5	1.5	1.5	2.0

Annexure - 1(Contd...).

Parameter	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
pH	Surface water	1	7.4	6.9	7.4	8.0	7.5	7.0	6.9	6.6	6.8	6.6	7.4	6.6
		2	7.1	6.9	7.4	7.7	7.4	6.9	6.9	6.6	6.6	6.6	6.8	6.9
		3	7.1	6.9	7.3	7.2	6.7	7.1	7.2	6.8	6.6	6.4	6.6	6.7
		4	7.2	6.8	7.3	6.8	6.7	6.5	6.5	6.7	6.6	6.4	6.6	6.2
		5	6.9	7.1	7.1	6.9	6.9	6.6	6.7	6.7	6.7	6.4	6.4	6.8
		6	7.1	6.7	6.9	6.6	5.7	6.5	6.7	6.8	6.9	6.7	6.6	6.9
		7	6.9	6.7	6.3	6.7	4.7	4.3	6.6	6.8	7.0	6.6	6.3	7.2
		8	6.9	6.7	7.2	6.8	6.2	6.7	6.2	6.7	6.9	7.0	6.8	7.0
		9	6.7	6.6	6.8	6.0	6.0	5.9	5.9	6.9	7.0	7.0	6.9	6.9
	Bottom water	1	6.9	6.8	7.2	6.2	6.2	6.1	7.4	6.7	6.9	6.6	6.9	6.5
		2	6.9	6.9	7.1	6.2	6.2	6.9	6.9	6.7	6.5	6.4	6.6	6.7
		3	6.8	6.7	6.9	6.9	6.4	6.2	7.1	6.9	6.5	6.4	6.4	6.4
		4	7.1	6.9	7.2	6.2	6.7	6.2	6.6	6.8	6.6	6.4	6.4	6.1
		5	6.9	7.0	7.1	6.7	6.9	6.5	6.6	6.8	6.6	6.4	6.4	6.6
		6	7.1	6.7	7.0	6.2	5.7	6.4	6.7	6.9	6.4	6.3	6.4	6.6
		7	6.9	6.6	6.3	6.7	4.7	4.5	6.5	6.9	6.9	6.2	6.3	7.0
		8	6.8	6.8	6.8	6.2	6.1	6.2	6.2	6.8	6.9	7.0	6.9	6.9
		9	6.7	6.6	6.9	6.1	6.1	6.2	5.9	7.0	7.0	7.1	7.1	6.9
DISSOLVED OXYGEN (mll^{-1})	Surface water	1	5.13	4.28	5.25	6.93	4.8	6.88	4.82	4.33	4.33	4.32	4.89	4.96
		2	5.26	3.64	5.25	5.67	4.59	5.42	3.77	4.75	4.68	4.60	3.82	5.03
		3	5.24	4.70	4.62	4.98	5.42	6.88	4.61	4.97	4.98	4.98	4.89	5.20
		4	5.79	5.56	5.25	6.09	4.80	5.21	4.82	5.40	5.41	5.42	5.61	5.26
		5	4.70	3.85	3.78	7.55	4.80	7.09	4.61	5.40	5.35	5.30	5.23	3.74
		6	4.70	5.77	7.14	4.41	4.38	6.05	4.61	5.19	5.20	5.20	4.53	6.66
		7	3.52	6.20	5.88	4.20	4.38	5.00	4.40	4.97	4.95	4.92	4.18	3.33
		8	4.44	6.41	5.46	3.78	4.59	5.47	4.19	5.40	5.07	4.73	5.61	4.03
		9	4.39	7.06	4.20	5.04	4.38	5.42	4.61	4.75	5.03	5.30	5.63	5.39
	Bottom water	1	4.42	5.35	4.83	5.46	4.38	2.81	5.87	4.97	4.96	4.95	6.62	6.48
		2	4.31	5.77	4.20	5.46	2.50	1.88	3.98	4.97	4.91	4.85	5.73	4.21
		3	4.61	4.70	4.62	4.40	4.17	3.54	4.40	4.97	4.98	4.98	4.59	4.38
		4	4.70	7.69	7.14	5.46	4.59	4.38	5.03	5.19	5.20	5.20	4.71	4.50
		5	4.52	2.99	4.41	5.04	4.80	6.05	5.61	4.97	4.99	5.00	4.47	3.51
		6	4.09	4.92	4.62	4.83	4.17	4.38	4.82	5.19	5.20	5.20	4.00	3.91
		7	4.35	5.99	5.88	4.62	4.59	6.67	5.45	5.19	5.16	5.13	5.19	5.73
		8	4.35	5.56	4.62	3.57	4.17	5.18	3.98	4.75	5.03	5.30	5.91	4.03
		9	4.31	4.70	3.57	3.36	4.17	3.34	4.40	5.40	5.07	4.73	5.40	5.21

Annexure - 1(Contd...).

Parameter	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
SALINITY X 10^{-3}	Surface water	1	0.08	0.09	0.07	0.10	0.17	2.15	1.43	0.09	0.07	0.08	0.07	0.13
		2	0.05	0.06	0.05	0.10	0.10	0.59	0.53	0.08	0.05	0.06	0.05	0.07
		3	0.05	0.12	0.05	0.11	0.52	0.07	0.31	0.09	0.05	0.06	0.05	0.05
		4	0.05	0.08	0.07	0.12	0.53	1.14	1.77	0.26	0.07	0.07	0.07	0.08
		5	0.05	0.09	0.07	0.22	1.28	1.30	1.63	0.20	0.08	0.07	0.07	0.08
		6	0.08	0.09	0.32	0.67	2.19	1.67	2.96	0.43	0.08	0.08	0.07	0.08
		7	0.10	0.10	0.86	2.62	7.98	2.95	4.49	0.59	0.08	0.08	0.07	0.08
		8	0.08	3.24	3.56	3.52	7.27	8.08	10.36	0.17	0.12	0.12	0.07	0.12
		9	0.50	4.28	4.21	9.73	12.08	11.03	10.11	0.23	0.10	0.09	0.08	0.13
	Bottom water	1	0.08	0.09	0.07	0.08	0.35	4.57	1.49	0.14	0.07	0.07	0.24	0.12
		2	0.05	0.07	0.05	0.08	0.20	1.35	0.54	0.08	0.05	0.05	0.05	0.07
		3	0.06	0.07	0.05	0.12	0.53	0.27	0.38	0.08	0.05	0.05	0.07	0.07
		4	0.07	0.08	0.07	0.13	0.53	1.31	1.76	0.25	0.07	0.07	0.07	0.08
		5	0.07	0.09	0.07	0.30	1.25	1.43	1.91	0.19	0.09	0.07	0.07	0.07
		6	0.08	0.10	0.32	0.67	2.38	1.71	2.98	0.49	0.09	0.08	0.07	0.09
		7	0.08	0.09	1.03	2.69	8.22	2.99	5.03	0.61	0.09	0.10	0.07	0.23
		8	0.08	3.27	5.43	6.58	7.42	8.81	9.89	0.19	0.14	0.05	0.05	0.12
		9	0.10	4.78	4.71	10.21	12.34	11.29	10.30	0.19	0.13	0.09	0.06	0.11
SUSPENDED PARTICULATE MATTER (mgl^{-1})	Surface water	1	2.53	9.75	7.46	26.48	92.92	2.84	3.1	1.79	5.16	1.78	4.37	8.14
		2	7.04	14.21	7.15	17.15	2.12	1.66	2.27	1.2	3.16	1.66	5.59	3.52
		3	9.81	22.17	5.68	8.50	4.31	2.36	1.59	3.067	4.67	2.88	8.29	8.8
		4	6.03	7.99	10.91	15.08	14.61	5.76	3.82	2.15	1.93	1.23	4.56	3.57
		5	4.41	8.57	7.79	14.2	9.88	6.28	4.83	1.04	4.98	1.23	6.76	3.88
		6	2.99	4.38	5.86	14.69	12.39	2.27	2.64	7.02	7.34	1.18	3.51	4.27
		7	1.50	7.84	5.97	23.21	95.05	1.44	1.95	1.17	12.43	13.07	6.08	4.05
		8	3.77	6.85	4.5	11.55	88.66	2.74	9.14	3.1	5.88	4.92	6.56	5.55
		9	6.01	8.97	6.41	10.41	97.64	4.39	4.23	7.01	11.61	2.58	6.17	6.57
	Bottom water	1	16.87	18.62	12.07	14.10	109.9	5.15	4.59	2.06	11.46	3.04	12.22	20.13
		2	8.33	48.90	5.37	20.22	27.0	4.51	5.26	1.67	10.23	3.82	11.77	30.0
		3	11.73	16.64	7.21	11.21	20.0	14.06	55.38	7.43	43.33	59.93	19.3	22.27
		4	1.17	13.38	14.64	25.37	26.46	26.24	13.19	2.87	9.83	11.45	52.83	10.17
		5	1.59	5.70	8.97	29.31	18.67	11.08	17.00	13.79	19.94	17.48	32.38	20.34
		6	1.95	7.89	9.06	17.92	15.27	10.74	15.09	14.16	62.61	4.67	21.3	52.4
		7	4.56	24.75	10.94	47.22	100.58	35.51	45.66	5.87	9.58	1.21	21.89	6.60
		8	14.82	22.88	8.49	23.10	100.16	5.13	44.15	9.21	9.56	4.65	10.39	14.44
		9	8.90	22.54	19.52	14.13	7.59	6.53	7.69	5.54	13.23	5.7	15.35	11.97

Annexure - 1(Contd...).

Parameter	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
MAGNESIUM (mgl^{-1})	Surface water	1	2.17	3.32	2.81	4.58	7.92	94.6	54.6	4.32	1.81	1.86	1.71	4.07
		2	1.13	2.8	2.92	3.66	7.02	24.9	18.6	2.56	1.35	1.15	1.22	1.96
		3	1.08	3.32	1.99	4.21	10.4	9.55	12.3	3.44	1.4	1.19	1.22	1.34
		4	1.57	3.16	4.65	6.61	22.4	55.8	69.5	10.6	2.1	1.81	1.52	4.91
		5	2.73	4.57	4.62	10.6	21.7	53.9	66.2	7.71	2.71	1.58	1.3	2.81
		6	2.7	5.03	15.2	34.8	54.6	64.2	108	13.7	2.37	2.17	1.87	3.64
		7	2.51	4.44	33.6	126	113	128	179	24.1	2.17	1.38	1.66	3.23
		8	2.46	158	179	325	312	326	477	5.96	3.85	3.07	1.64	4.34
		9	2.48	250	291	349	520	447	479	7.29	3.72	2.21	1.82	4.44
	Bottom water	1	2.13	2.85	3.62	4.66	14	226	55	4.23	1.84	1.7	7.49	3.68
		2	1.16	2.89	1.88	3.82	9.68	62	19.3	2.73	1.1	1.1	1.2	1.5
		3	1.07	3.01	2.03	4.34	9.73	10.4	12.9	3.19	1.26	1.17	1.26	1.45
		4	1.87	3.27	4.03	7.08	22.7	60	69	10.4	1.96	1.71	1.55	4.66
		5	1.95	3.09	5.01	13.4	22	55	77.4	7.68	2.87	1.48	1.27	2.87
		6	2.95	5.15	14.8	35.9	54.3	64.8	116	16.6	2.85	2.08	1.77	3.78
		7	2.53	4.4	33.4	128	89.3	135	211	24.5	2.66	1.55	1.67	8.19
		8	2.38	177	301	389	366	339	460	6.51	4.35	3.22	1.75	4.42
		9	2.52	277	297	436	509	462	473	8.1	3.93	2.49	1.79	4.18
CALCIUM (mgl^{-1})	Surface water	1	2.65	3.49	3.43	4.83	7.35	33.40	22.10	4.35	2.36	2.20	2.18	3.94
		2	1.93	3.12	3.61	4.20	7.57	10.70	10.90	3.96	2.18	1.84	2.07	3.00
		3	1.95	3.80	3.18	6.21	12.00	12.33	9.33	5.42	2.52	2.19	2.16	2.72
		4	2.17	4.45	6.35	8.76	14.00	24.30	30.30	8.47	2.76	2.60	2.39	6.97
		5	2.92	7.56	6.54	10.90	18.40	24.20	28.40	6.68	3.25	2.45	2.05	4.41
		6	4.20	7.73	16.40	30.70	32.40	29.80	43.20	9.69	2.85	2.42	2.43	4.81
		7	2.81	4.01	14.60	40.70	38.40	54.50	61.60	13.70	2.63	1.97	2.40	4.08
		8	2.23	46.70	51.40	80.50	104.00	101.00	125.00	4.62	3.22	2.54	1.76	2.90
		9	2.98	55.40	90.40	108.00	148.00	132.00	126.00	4.90	3.20	2.02	1.83	2.77
	Bottom water	1	3.00	3.27	3.92	5.04	10.90	72.40	23.00	4.15	2.37	2.03	3.91	3.62
		2	1.85	3.08	2.93	4.77	10.60	22.90	11.40	4.06	1.76	1.85	2.02	2.61
		3	1.87	3.62	3.12	6.34	11.80	8.39	9.60	4.96	2.33	2.13	2.26	2.66
		4	2.34	4.55	5.63	8.92	14.30	28.80	27.70	8.65	2.62	2.46	2.42	6.90
		5	3.40	6.82	6.71	12.60	19.70	24.80	31.70	7.25	3.18	2.11	2.02	4.54
		6	4.35	7.85	16.30	30.10	29.40	29.90	44.60	11.40	2.93	2.39	2.31	5.14
		7	2.92	4.03	15.10	42.60	35.80	50.60	69.60	13.80	2.77	2.12	2.45	5.84
		8	2.02	55.40	90.80	117.00	116.00	104.00	124.00	4.44	3.97	2.62	1.73	3.12
		9	1.97	88.90	49.20	127.00	152.00	132.00	128.00	4.99	3.21	2.06	1.73	2.88

Annexure - 1(Contd...).

Parameter	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
STRONTIUM ($\mu g l^{-1}$)	Surface water	1	25.5	35.1	30.9	48.8	74.6	610.0	336.0	39.8	20.8	21.0	22.0	40.0
		2	16.5	32.7	33.4	39.0	71.4	157.0	129.0	29.1	17.8	16.7	19.7	25.9
		3	15.8	36.3	25.9	62.9	111.0	200.4	96.4	37.2	19.4	18.6	18.4	20.2
		4	20.5	39.0	55.0	75.5	200.0	369.0	416.0	79.2	22.2	23.0	19.6	52.4
		5	24.5	40.3	55.9	106.0	171.0	386.0	390.0	60.1	26.5	21.6	19.2	35.4
		6	34.1	63.2	149.0	301.0	391.0	462.0	675.0	107.0	23.7	22.7	23.3	40.0
		7	27.1	45.4	224.0	730.0	680.0	866.0	1020.0	169.0	22.1	18.9	22.6	36.4
		8	24.0	917.0	986.0	1261.0	1940.0	1970.0	2360.0	49.0	32.2	28.5	19.6	39.5
		9	26.3	1470.0	1660.0	1610.0	3010.0	2720.0	2450.0	56.2	30.6	21.5	21.2	39.3
	Bottom water	1	25.3	31.1	37.6	48.0	126.0	1330.0	329.0	37.2	20.2	20.2	57.1	36.8
		2	16.5	30.2	25.1	43.3	99.2	373.0	135.0	29.9	14.2	17.5	18.3	21.7
		3	16.4	35.8	26.3	66.2	108.0	85.9	99.5	36.4	17.3	18.1	19.0	21.0
		4	22.2	39.0	48.8	76.8	205.0	396.0	401.0	76.1	21.8	22.0	20.8	52.1
		5	27.2	38.9	59.8	129.0	175.0	415.0	437.0	62.8	27.5	18.4	18.8	35.2
		6	35.4	64.3	146.0	308.0	389.0	486.0	693.0	120.0	26.2	21.4	22.0	42.0
		7	27.7	44.8	225.0	713.0	543.0	898.0	1160.0	165.0	24.5	20.0	22.4	65.2
		8	24.0	997.0	1820.0	877.0	2160.0	2070.0	2420.0	51.1	39.5	29.8	20.1	38.8
		9	25.9	1490.0	1601.0	2220.0	3150.0	2720.0	2500.0	59.6	30.9	23.4	20.1	37.7
BARIUM ($\mu g l^{-1}$)	Surface water	1	43.1	24.5	35.1	40.7	31.0	211.0	171.0	55.8	48.8	48.8	73.7	106.0
		2	25.2	24.2	31.1	34.7	31.3	75.9	99.9	39.5	39.1	39.1	37.9	48.5
		3	25.5	25.6	29.5	42.3	54.8	30.5	84.0	42.2	41.9	41.9	37.6	25.0
		4	19.6	27.2	40.3	53.6	106.0	182.0	211.0	51.8	30.7	30.7	24.7	19.1
		5	25.7	111.0	31.1	63.0	82.5	159.0	166.0	40.7	25.7	25.7	25.8	20.7
		6	24.8	33.3	93.9	177.0	174.0	129.0	172.0	56.6	22.9	22.9	23.8	19.7
		7	18.8	26.2	101.0	155.0	191.0	270.0	209.0	62.4	19.1	19.1	25.2	23.8
		8	14.9	70.5	84.9	115.0	128.0	189.0	123.0	25.9	23.8	23.8	18.4	20.3
		9	13.4	82.7	91.5	114.0	121.0	131.0	128.0	29.7	21.6	21.6	17.7	18.7
	Bottom water	1	48.0	19.4	33.3	29.0	50.9	222.0	154.0	51.2	41.6	41.6	53.9	42.2
		2	26.0	22.3	25.2	35.9	37.6	96.8	112.0	43.1	25.5	25.5	39.6	28.1
		3	25.0	24.8	20.7	43.4	73.0	92.7	92.4	32.1	32.1	32.1	36.0	21.6
		4	19.6	22.3	31.5	38.6	103.0	208.0	194.0	51.6	17.2	17.2	24.7	31.2
		5	28.7	27.2	32.4	69.9	74.0	151.0	168.0	42.1	32.1	32.1	24.8	17.7
		6	24.2	32.1	78.0	187.0	172.0	176.0	178.0	64.8	24.2	24.2	21.3	22.1
		7	17.9	23.8	103.0	143.0	159.0	237.0	143.0	58.9	23.7	23.7	23.1	29.9
		8	10.5	60.7	91.0	110.0	120.0	178.0	127.0	22.3	22.5	22.5	13.5	20.4
		9	12.1	85.8	94.1	112.0	118.0	128.0	129.0	25.8	21.0	21.0	17.5	21.4

Annexure - 1(Contd...).

Parameter	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
BORON ($\mu g l^{-1}$)	Surface water	1	14.0	22.1	26.7	28.7	48.9	277.0	182.0	21.0	13.6	14.6	22.1	18.7
		2	7.3	14.8	18.2	8.6	27.4	85.5	76.2	6.4	3.5	9.5	16.0	10.0
		3	8.5	18.1	14.8	20.5	41.4	13.6	48.6	12.7	4.3	9.7	25.4	5.8
		4	10.8	13.5	26.3	16.9	76.0	160.0	225.0	31.3	7.4	12.5	16.7	14.4
		5	7.8	29.0	25.9	46.1	77.6	202.0	220.0	19.4	8.9	10.0	10.3	9.1
		6	9.1	19.0	62.1	100.0	174.0	233.0	388.0	43.8	11.0	14.7	11.0	18.5
		7	16.2	26.8	115.0	347.0	324.0	390.0	572.0	74.4	4.8	9.1	12.9	12.5
		8	13.7	452.0	481.9	1280.0	988.0	1240.0	1600.0	27.0	13.7	19.5	14.4	20.4
		9	19.2	622.0	986.9	482.0	1470.0	1470.0	1390.0	32.7	12.7	13.8	18.2	18.2
	Bottom water	1	13.9	15.4	23.0	17.1	26.7	571.0	190.0	15.4	7.0	12.6	29.8	14.3
		2	8.1	14.6	14.3	7.0	36.0	192.0	75.6	8.3	3.4	9.1	26.2	8.6
		3	8.3	15.0	15.6	21.4	35.8	40.3	56.2	8.6	3.4	9.5	17.2	5.6
		4	9.7	20.5	24.2	41.3	75.4	189.0	230.0	29.9	5.0	9.6	18.2	15.9
		5	8.7	12.0	32.2	58.5	77.4	216.0	250.0	20.3	8.3	9.6	9.3	9.9
		6	16.7	25.4	61.9	102.0	168.0	231.0	363.0	50.7	8.7	13.0	34.8	16.2
		7	18.7	23.1	121.1	367.0	289.0	401.0	632.0	77.0	7.1	10.3	13.7	33.5
		8	13.5	715.0	993.6	890.0	1090.0	1160.0	1410.0	29.1	18.4	21.0	12.1	18.7
		9	14.4	656.0	990.0	1260.0	1490.0	1480.0	1380.0	35.4	11.7	15.4	20.2	17.1
SEDIMENT ORGANIC CARBON (mg/g)		1	42.52	36.02	24.35	38.78	35.79	36.60	32.68	35.83	40.30	33.53	37.55	28.67
		2	31.06	28.50	36.45	27.92	12.74	33.39	34.69	37.38	38.34	11.09	39.39	38.35
		3	37.54	47.88	30.43	30.21	37.70	40.32	36.15	32.64	42.95	41.20	35.90	26.00
		4	32.39	33.03	32.10	30.18	33.73	34.56	28.89	30.68	36.91	34.15	32.22	31.53
		5	14.58	31.76	9.88	32.03	30.37	29.67	27.30	32.64	30.82	36.81	26.31	23.20
		6	32.29	28.70	21.67	29.82	29.43	21.83	31.16	19.08	29.21	38.76	18.74	36.23
		7	31.58	35.44	33.43	34.78	35.65	26.57	39.56	32.24	21.48	10.33	26.59	29.74
		8	11.87	5.12	5.30	3.03	14.73	4.95	4.86	5.82	6.95	7.31	36.56	6.56
		9	6.03	5.50	6.99	16.19	12.78	6.09	5.06	1.04	3.94	22.38	5.83	3.95
SEDIMENT MOISTURE (percentage)		1	39.59	38.65	36.82	46.73	45.91	45.09	52.21	47.93	52.07	44.82	56.53	45.54
		2	43.99	43.07	39.08	42.40	45.44	48.47	48.08	48.61	51.06	26.94	54.27	54.43
		3	48.27	53.92	40.79	41.25	45.27	49.28	48.21	47.65	51.22	54.06	50.34	52.94
		4	40.33	43.07	44.57	45.14	45.33	45.51	49.91	47.32	50.52	46.30	50.08	48.64
		5	29.32	40.28	31.03	45.99	44.67	43.35	39.57	50.96	44.88	46.21	47.19	46.49
		6	40.97	38.35	37.64	40.23	40.02	39.80	42.46	41.34	39.65	43.98	38.77	49.23
		7	44.12	39.56	38.04	39.85	38.20	36.54	47.95	39.01	34.30	29.50	40.98	45.94
		8	32.25	29.85	23.67	20.05	21.47	22.89	21.23	24.61	23.04	34.18	63.86	30.07
		9	21.87	22.11	27.00	33.32	27.07	20.82	22.01	20.34	29.32	24.39	23.65	23.58

Annexure - 2. Station wise monthly data of dissoved trace metals in the surface and bottom waters (µg/l)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
CADMIUM	Surface water	1	3.35	3.41	4.45	3.00	3.25	2.85	2.75	1.60	1.75	1.80	1.85	2.25
		2	2.90	1.60	2.30	2.80	1.50	2.10	1.05	1.15	1.20	1.60	1.40	2.10
		3	4.11	3.25	3.90	2.00	1.80	1.50	1.50	1.32	1.65	1.90	1.45	2.45
		4	4.30	4.24	3.90	1.70	2.70	2.35	2.50	2.10	2.10	2.05	2.00	2.50
		5	3.00	4.60	3.35	1.80	2.25	3.25	2.35	1.19	1.45	1.85	2.05	2.75
		6	2.80	4.35	2.80	2.25	2.70	3.85	3.95	6.10	2.00	0.40	1.65	2.90
		7	2.45	4.00	2.90	2.55	3.05	4.50	1.20	1.46	2.75	0.45	1.35	2.05
		8	4.35	3.80	3.05	2.35	3.35	5.10	2.95	2.43	1.30	1.40	1.05	3.00
		9	4.30	4.40	3.15	2.50	4.05	4.95	2.60	3.97	1.80	1.60	1.00	3.10
	Bottom water	1	2.60	2.90	2.70	2.90	3.05	3.15	2.80	2.12	2.05	1.95	2.05	1.55
		2	2.45	1.65	1.85	1.55	1.70	2.10	2.15	0.96	1.40	1.75	1.60	1.95
		3	4.25	3.80	2.15	2.15	2.25	1.55	1.70	3.10	1.85	2.05	1.70	1.60
		4	3.90	4.36	4.30	2.65	2.95	2.30	3.45	0.90	2.40	2.15	1.80	1.90
		5	2.90	2.80	2.30	2.60	2.30	3.80	5.40	3.66	2.95	2.15	1.90	2.00
		6	3.30	4.51	3.35	2.80	2.85	4.45	5.75	4.13	0.23	0.60	1.85	2.40
		7	3.60	3.80	3.65	3.05	3.00	4.75	4.30	2.66	0.80	0.95	1.70	2.30
		8	4.25	4.20	3.35	3.20	3.35	5.10	4.85	3.08	1.35	1.60	2.05	2.65
		9	3.80	4.85	3.45	3.90	4.15	5.15	4.90	5.00	1.30	1.50	2.10	2.75
COBALT	Surface water	1	0.09	0.08	0.12	0.26	0.28	0.31	0.29	0.87	1.17	1.40	0.44	0.32
		2	0.09	0.10	0.10	0.25	0.22	0.29	0.31	0.57	2.64	2.24	0.78	0.92
		3	0.13	0.07	0.09	0.21	0.21	0.24	0.25	0.80	3.21	2.75	0.47	1.07
		4	0.14	0.09	0.13	0.18	0.09	0.15	0.19	0.91	3.21	2.81	0.53	0.90
		5	0.12	0.07	0.09	0.22	0.22	0.15	0.18	1.30	3.72	3.41	0.58	0.92
		6	0.13	0.10	0.07	0.32	0.75	0.24	0.21	1.93	0.86	4.36	0.76	0.62
		7	0.16	0.06	0.08	0.21	0.30	0.20	0.08	1.52	1.30	1.19	0.75	0.52
		8	0.13	0.14	0.15	0.25	0.63	0.15	0.07	2.41	2.31	1.51	0.65	0.36
		9	0.19	0.15	0.14	0.25	0.73	0.34	0.25	3.17	1.96	1.34	1.07	0.40
	Bottom water	1	0.11	0.06	0.13	0.18	0.23	0.19	0.23	0.85	1.81	1.71	0.53	0.44
		2	0.07	0.07	0.10	0.15	0.19	0.13	0.26	1.21	3.02	2.29	0.58	1.01
		3	0.13	0.07	0.08	0.15	0.15	0.07	0.24	1.15	3.97	3.01	0.59	0.97
		4	0.13	0.13	0.13	0.13	0.10	0.15	0.21	1.08	3.50	3.36	0.54	1.02
		5	0.12	0.11	0.10	0.18	0.19	0.06	0.16	2.18	3.76	3.36	0.65	0.84
		6	0.16	0.15	0.08	0.34	0.55	0.11	0.11	2.60	1.36	1.70	0.65	0.63
		7	0.20	0.15	0.11	0.26	0.77	0.25	0.10	1.95	1.42	1.29	0.68	0.57
		8	0.12	0.12	0.15	0.25	1.01	0.15	0.12	2.85	1.48	1.51	1.09	0.71
		9	0.17	0.06	0.17	0.24	1.12	0.18	0.13	2.62	1.25	1.45	1.23	0.74

Annexure - 2. (contd....)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
CHROMIUM	Surface water	1	0.12	0.50	5.00	0.56	0.62	5.85	5.85	0.92	1.77	2.11	0.57	2.16
		2	0.13	0.65	4.95	0.45	0.56	6.25	6.25	0.94	3.61	5.55	0.57	3.13
		3	0.57	0.15	5.20	0.51	2.47	6.30	6.30	1.30	4.93	4.24	0.98	3.18
		4	0.24	0.59	4.83	0.20	2.62	6.20	6.20	0.36	5.15	3.68	0.65	2.97
		5	0.66	0.29	5.35	5.10	2.68	6.20	6.20	1.07	5.35	4.35	0.73	2.94
		6	0.71	0.13	0.93	4.42	2.37	6.35	6.35	2.05	1.50	5.65	0.73	2.91
		7	0.73	0.22	1.05	4.74	0.64	6.45	6.45	1.07	1.53	1.34	0.83	3.03
		8	0.66	0.10	4.63	0.25	0.42	1.67	1.67	2.49	2.55	2.16	0.98	3.44
		9	0.72	0.17	5.00	0.62	2.45	1.80	1.80	2.85	2.90	2.63	1.66	3.66
	Bottom water	1	0.48	0.47	5.00	4.64	0.68	6.35	5.15	0.60	1.81	3.02	0.61	3.00
		2	0.36	0.18	5.05	0.08	0.65	6.00	0.69	1.54	4.17	3.66	1.28	3.11
		3	0.09	0.20	5.60	0.29	2.49	6.20	5.20	1.51	4.60	3.97	0.71	3.04
		4	0.29	0.80	4.91	5.20	2.71	6.25	5.30	0.79	5.35	4.17	0.74	3.03
		5	0.62	0.09	5.05	0.65	1.11	6.05	5.50	1.68	5.10	4.77	0.72	3.01
		6	0.71	0.66	0.63	0.65	2.11	6.60	5.40	2.12	2.12	6.25	0.77	2.84
		7	0.72	0.20	5.15	0.28	1.26	6.60	6.90	2.15	1.83	1.58	0.87	2.95
		8	0.65	0.12	4.74	4.71	2.52	6.90	5.40	2.35	2.78	2.61	1.41	3.74
		9	0.91	0.77	5.15	4.88	2.52	7.15	5.50	3.19	2.82	3.04	1.77	4.01
COPPER	Surface water	1	1.67	1.12	1.60	1.58	1.78	2.20	2.27	2.85	1.00	1.71	2.56	3.27
		2	0.94	0.90	1.54	0.92	0.95	0.99	1.57	4.80	1.61	4.19	8.85	4.58
		3	1.70	0.86	1.10	0.82	2.47	1.31	4.50	2.54	1.88	4.71	5.25	3.89
		4	1.14	0.97	1.69	1.92	2.72	1.02	1.06	2.59	2.30	4.22	2.15	3.00
		5	1.55	1.77	2.60	1.82	0.77	0.93	1.74	1.73	4.20	2.47	2.02	2.90
		6	1.43	0.52	1.39	2.25	3.55	0.80	0.81	2.38	3.43	3.33	0.30	3.11
		7	1.28	0.47	1.05	1.51	1.55	0.76	1.16	5.50	2.32	3.14	2.09	2.37
		8	1.07	0.71	1.73	1.04	2.24	1.13	1.80	2.63	2.35	2.13	1.65	2.27
		9	0.89	0.56	1.72	1.00	1.98	1.08	1.84	4.53	2.36	2.03	1.63	2.04
	Bottom water	1	2.10	1.24	1.66	1.85	2.01	1.17	2.49	2.33	1.30	2.07	3.36	3.51
		2	1.79	0.95	1.49	2.30	1.77	1.68	3.79	3.54	2.15	2.42	2.71	4.35
		3	1.01	1.09	2.52	1.19	0.77	1.18	1.97	2.40	1.98	2.72	1.90	3.17
		4	1.83	2.07	2.35	2.55	1.11	1.04	1.49	1.94	2.33	2.45	7.85	2.91
		5	2.29	1.03	1.04	1.91	1.60	1.10	1.40	2.58	2.83	3.25	2.90	3.61
		6	2.31	1.62	0.84	2.04	2.67	1.90	1.04	2.44	4.03	4.19	3.55	3.40
		7	1.81	0.61	1.34	1.48	1.81	1.11	3.29	2.91	3.51	4.12	3.45	2.87
		8	1.16	0.61	1.07	0.75	1.95	1.41	1.70	3.88	3.42	4.22	5.70	2.52
		9	0.94	1.28	2.82	1.08	1.95	1.51	1.49	4.94	3.30	3.62	5.10	2.24

Annexure - 2. (contd....)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
IRON	Surface water	1	52.00	29.80	42.50	115.00	33.00	128.00	109.00	127.00	44.50	59.60	35.60	34.30
		2	49.00	26.00	29.70	127.00	66.30	78.50	112.00	127.00	33.40	46.60	40.70	15.10
		3	65.00	37.00	34.70	129.00	29.20	149.80	111.00	129.00	71.50	32.70	100.00	35.90
		4	35.00	91.20	70.50	120.00	27.80	78.00	238.00	126.00	41.70	57.00	129.00	24.10
		5	47.00	106.00	32.60	37.60	31.00	72.70	123.00	113.00	36.80	39.70	40.40	34.30
		6	39.00	37.00	39.10	40.50	40.80	59.10	121.00	119.00	86.00	48.20	31.80	9.80
		7	43.00	49.20	72.70	118.00	139.60	283.60	213.00	111.00	32.30	57.70	40.20	41.30
		8	42.00	46.50	117.30	100.00	95.00	172.40	108.00	119.00	27.50	42.40	33.60	39.00
		9	38.00	35.40	34.30	105.00	97.00	99.60	394.00	109.00	30.90	48.70	50.30	40.20
	Bottom water	1	56.00	43.60	31.30	104.00	32.00	68.60	107.00	131.00	35.60	34.90	34.50	28.20
		2	51.00	48.00	39.00	106.00	38.60	64.80	191.00	140.00	110.90	30.20	43.00	47.50
		3	68.00	48.00	32.40	137.00	29.10	65.00	28.60	123.00	41.90	48.30	30.00	47.10
		4	35.00	50.80	32.30	29.00	59.90	59.60	104.00	108.00	27.40	54.80	32.50	44.10
		5	50.00	36.50	32.40	38.00	33.30	81.40	222.00	113.00	26.90	41.00	59.00	30.60
		6	40.00	49.00	42.20	73.70	25.00	64.30	109.00	136.00	38.30	35.10	41.90	39.80
		7	42.00	52.60	59.90	29.50	106.00	298.70	135.00	116.00	199.80	57.00	36.30	42.40
		8	47.00	57.60	23.80	29.20	94.00	96.70	199.00	108.00	45.70	71.60	34.40	40.50
		9	53.00	78.00	88.00	108.00	98.00	201.00	346.00	106.00	33.40	43.30	37.80	26.80
MANGANESE	Surface water	1	0.28	0.21	0.38	0.18	0.23	0.26	0.35	2.70	0.32	0.32	0.30	0.63
		2	0.19	0.20	0.45	0.16	0.19	0.24	0.28	0.51	0.56	0.46	0.32	0.34
		3	0.67	0.19	0.39	0.15	0.17	0.21	0.37	0.52	0.81	0.47	0.27	0.34
		4	0.22	0.23	0.47	0.16	0.05	0.26	0.47	1.61	0.46	0.48	0.27	0.33
		5	0.27	0.14	0.44	0.37	0.16	0.23	0.31	0.32	0.76	0.82	0.30	0.58
		6	0.25	0.22	0.37	0.24	1.38	0.19	0.33	0.41	0.26	0.95	4.45	0.84
		7	0.14	0.23	3.45	0.54	9.40	117.50	6.35	0.36	0.52	0.49	0.43	0.64
		8	0.21	0.35	0.34	1.08	0.50	0.74	1.10	0.54	0.31	0.31	0.30	0.49
		9	0.17	0.18	0.34	0.85	0.48	0.75	46.60	1.00	2.61	0.40	0.34	0.55
	Bottom water	1	0.18	0.23	0.36	0.26	0.28	0.32	0.21	0.65	0.90	0.37	0.20	0.30
		2	0.26	0.25	0.54	0.16	0.32	0.53	0.28	0.37	0.54	0.43	0.22	0.37
		3	0.16	0.29	0.79	0.17	0.17	0.38	0.28	0.41	0.58	0.48	0.22	0.38
		4	0.33	0.31	0.26	0.88	0.32	0.25	0.37	0.45	0.57	0.58	0.69	0.35
		5	0.13	0.45	0.31	0.15	1.12	0.26	0.68	0.49	5.25	0.69	0.24	0.25
		6	0.20	0.64	0.22	0.32	1.07	0.29	0.27	0.52	5.05	0.79	0.42	0.37
		7	0.20	0.27	8.80	2.39	5.05	67.00	8.95	0.52	7.00	0.65	0.22	0.27
		8	0.27	0.62	0.37	0.56	0.41	0.72	22.35	0.49	0.78	0.68	0.29	0.24
		9	0.20	1.23	0.44	0.81	0.41	0.55	49.20	0.78	64.00	0.74	0.33	0.25

Annexure - 2. (contd....)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
MOLYBDENUM	Surface water	1	1.00	0.13	0.14	0.33	0.37	0.51	1.09	0.36	2.41	3.09	3.50	0.99
		2	2.00	0.12	0.40	0.06	0.26	0.48	0.96	0.34	2.17	6.55	6.05	1.15
		3	3.00	0.07	0.28	0.01	0.24	0.45	0.75	0.38	2.94	7.85	7.25	1.20
		4	4.00	0.01	0.18	0.17	0.28	0.05	1.18	0.56	0.83	8.65	4.70	1.15
		5	5.00	0.11	0.18	0.44	0.24	0.92	1.12	0.41	2.19	9.65	6.85	1.44
		6	6.00	0.18	0.24	0.04	0.20	1.58	1.00	0.42	4.37	0.84	9.15	1.54
		7	7.00	0.31	0.06	0.40	0.55	0.38	1.01	0.43	4.15	1.30	9.60	1.46
		8	8.00	0.48	0.28	0.20	0.32	4.07	1.07	0.77	3.39	2.79	9.10	1.32
		9	9.00	0.23	0.47	0.44	0.38	4.34	1.05	0.82	6.00	2.23	8.15	2.20
	Bottom water	1	0.25	0.46	0.24	0.30	0.48	1.05	0.32	0.83	3.82	5.55	1.06	0.30
		2	0.12	0.41	0.09	0.25	0.49	0.93	0.23	2.89	6.95	5.60	1.28	0.37
		3	0.10	0.26	0.02	0.23	0.47	0.94	0.27	4.26	8.70	7.55	1.19	0.38
		4	0.09	0.15	0.18	0.13	1.10	1.28	0.51	1.88	9.10	6.30	1.24	0.35
		5	0.14	0.26	0.18	0.20	1.00	1.19	0.49	4.02	8.55	7.45	1.19	0.62
		6	0.41	0.16	0.05	0.25	0.40	1.09	0.35	4.02	1.82	10.25	1.40	0.65
		7	0.38	0.48	0.61	0.14	1.21	0.69	1.88	4.38	1.38	9.90	1.14	0.60
		8	0.22	0.62	0.45	0.21	4.43	1.31	0.38	5.45	3.39	9.50	2.03	0.63
		9	0.09	0.80	0.58	0.33	4.43	0.98	0.77	6.80	3.83	8.50	3.01	0.67
NICKEL	Surface water	1	1.46	0.90	1.08	0.90	1.43	1.49	1.47	1.59	4.30	4.37	3.64	2.34
		2	1.19	1.68	1.18	0.68	1.18	1.12	1.12	2.57	8.35	10.30	4.17	7.75
		3	1.58	1.41	1.45	0.55	1.49	1.54	2.42	4.38	11.50	10.15	4.02	6.65
		4	1.88	1.77	1.51	1.06	1.67	1.47	1.92	0.75	14.75	10.25	4.75	7.65
		5	1.97	1.82	1.65	0.99	1.63	1.09	1.40	3.42	12.95	11.30	4.32	7.00
		6	1.95	0.99	1.06	0.36	2.66	1.51	1.63	3.20	3.54	17.15	8.90	8.10
		7	1.86	1.17	1.71	0.68	3.98	5.10	4.36	4.48	4.57	12.50	4.58	6.60
		8	2.14	1.11	1.32	0.42	10.35	1.63	3.53	2.44	3.72	7.05	8.10	4.98
		9	1.89	0.95	0.92	0.29	11.50	2.79	3.60	5.15	8.90	9.00	9.35	8.40
	Bottom water	1	1.33	1.16	0.72	0.47	1.22	1.49	1.51	9.05	4.67	7.90	4.77	9.10
		2	1.17	1.23	1.17	0.47	0.95	1.57	1.33	5.00	8.75	11.25	4.23	12.00
		3	2.09	1.17	1.15	0.75	0.68	1.47	1.75	4.30	11.25	12.25	4.16	6.55
		4	1.96	3.60	1.49	1.61	1.37	1.35	1.59	3.37	11.40	9.35	4.42	7.10
		5	6.72	1.18	1.15	1.12	1.55	1.32	1.65	2.44	11.80	12.70	3.67	6.90
		6	2.21	1.37	0.87	0.76	8.05	1.29	1.51	3.35	4.75	18.15	3.55	7.50
		7	2.06	1.17	2.04	0.86	5.45	4.66	4.93	4.40	3.90	13.40	3.62	6.05
		8	1.67	1.31	1.02	0.52	12.55	1.70	4.29	2.85	8.70	6.95	10.70	3.99
		9	1.50	1.15	1.77	0.62	12.55	2.46	3.82	6.45	7.00	8.00	11.60	7.85

Annexure - 2. (contd....)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
LEAD	Surface water	1	2.48	2.70	5.18	4.41	4.61	5.00	3.37	7.30	9.05	13.00	7.85	3.64
		2	3.21	2.82	6.48	4.66	4.99	5.55	3.20	9.45	25.95	21.95	7.85	4.35
		3	6.52	0.65	5.26	6.51	7.66	5.50	9.10	15.60	30.70	25.30	9.25	9.75
		4	6.17	5.24	14.80	10.54	10.20	4.66	16.45	11.25	29.70	22.50	9.65	11.80
		5	6.59	3.54	6.92	8.50	7.55	7.65	10.80	13.30	31.20	22.90	8.60	8.70
		6	7.94	3.29	2.90	4.86	8.80	6.45	4.25	32.60	6.65	32.20	9.25	10.50
		7	7.40	1.68	3.16	6.00	5.60	6.60	5.30	23.30	16.05	21.00	9.05	9.90
		8	7.16	2.31	4.71	5.38	16.80	11.85	6.70	27.30	20.40	13.90	10.75	10.65
		9	7.29	2.18	3.81	0.59	20.85	10.35	6.70	39.15	22.20	15.40	12.65	9.40
	Bottom water	1	2.27	3.99	3.78	5.62	4.68	5.55	3.93	9.15	11.90	12.75	8.75	4.50
		2	2.15	2.83	5.85	5.53	5.42	5.30	2.65	10.05	26.55	24.25	8.45	4.95
		3	1.94	2.32	12.20	6.20	7.90	5.85	2.44	17.65	26.50	25.65	8.15	9.75
		4	4.26	7.49	6.33	10.89	14.90	6.20	12.85	15.15	29.35	25.55	8.25	9.30
		5	5.67	1.49	2.54	8.63	2.86	6.40	5.40	24.25	34.50	27.85	8.95	12.95
		6	7.84	5.18	3.31	5.39	10.85	7.55	4.89	24.35	15.35	37.55	8.85	11.10
		7	6.76	2.58	3.27	5.24	11.45	8.30	7.60	28.55	16.30	19.45	8.50	9.35
		8	6.39	2.68	5.01	6.28	20.15	9.90	5.50	30.15	20.80	13.35	12.40	10.60
		9	7.04	1.94	5.97	6.45	20.15	12.45	6.45	40.95	20.00	15.05	14.20	9.90
ZINC	Surface water	1	18.95	9.60	6.55	6.00	4.50	2.94	8.05	75.00	8.90	8.30	5.55	12.85
		2	6.55	8.39	5.00	3.91	3.90	1.93	2.88	7.05	387.50	5.30	8.40	8.45
		3	11.47	7.65	9.80	6.00	3.40	2.82	12.85	7.45	36.20	4.87	12.30	5.20
		4	11.50	17.97	6.40	6.10	5.80	5.10	4.76	11.95	14.80	6.05	9.50	15.30
		5	12.49	8.65	8.70	6.95	2.77	1.73	3.18	3.77	24.40	3.82	5.50	13.10
		6	9.42	4.43	7.90	6.20	4.28	2.62	2.36	9.15	4.56	3.25	8.25	11.65
		7	17.00	5.25	8.45	6.40	9.00	12.95	6.50	12.75	3.92	5.18	6.50	10.40
		8	9.64	5.25	6.00	6.35	6.90	3.92	5.00	7.40	3.14	4.15	5.25	25.45
		9	5.05	3.92	4.86	8.95	7.75	5.85	5.50	10.40	4.21	7.79	11.90	17.05
	Bottom water	1	13.85	10.85	4.63	4.81	4.38	3.87	3.70	7.95	6.05	3.93	5.40	10.55
		2	10.05	7.25	4.62	4.05	3.50	2.94	2.81	15.70	5.10	3.83	5.90	7.95
		3	11.65	8.05	7.45	5.50	2.35	2.26	2.52	6.20	4.58	3.72	9.90	10.25
		4	12.50	75.37	5.70	12.20	4.79	4.55	5.50	9.45	97.00	8.20	9.75	24.25
		5	8.75	5.65	6.45	5.05	2.53	3.49	5.05	6.90	8.85	5.90	8.20	14.75
		6	16.09	12.98	4.60	6.10	3.39	3.57	2.54	6.95	6.20	6.00	15.85	19.10
		7	11.55	4.44	9.75	13.00	11.50	12.45	10.35	6.90	6.25	5.50	4.72	7.70
		8	8.53	5.70	5.30	6.15	14.50	7.25	9.30	23.05	4.83	6.25	7.40	21.75
		9	6.54	4.62	35.55	6.25	14.50	9.60	19.90	10.85	5.75	6.70	7.80	7.40

Annexure - 3. Station wise monthly data of particulate trace metals in the surface and bottom waters (µg/g)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
CADMIUM	Surface water	1	33.00	12.87	1.98	3.25	0.79	45.81	23.41	59.08	23.49	88.48	22.71	12.99
		2	10.01	14.32	6.82	1.55	33.31	81.65	34.30	130.49	50.78	129.22	26.70	24.86
		3	5.71	6.55	12.11	8.39	22.59	64.56	95.62	40.19	32.64	35.68	22.98	16.51
		4	7.88	49.78	13.75	1.24	6.47	20.08	33.17	81.06	48.82	86.18	32.57	28.01
		5	10.37	15.34	23.62	2.89	8.21	7.48	24.51	185.30	26.83	135.57	28.51	24.74
		6	16.56	13.41	21.59	4.69	13.56	42.40	46.72	31.85	22.16	136.02	59.33	40.28
		7	75.90	6.60	25.63	1.64	1.97	60.35	59.25	191.51	10.77	17.33	36.47	34.01
		8	38.30	7.01	16.46	6.68	2.58	30.93	13.44	66.37	24.80	38.01	34.64	27.52
		9	13.81	3.79	15.29	0.56	1.71	24.27	27.35	35.75	11.86	64.34	26.58	15.14
	Bottom water	1	6.59	10.50	11.58	2.89	0.53	32.81	25.91	62.49	15.20	66.78	17.18	11.46
		2	7.71	4.97	19.69	3.70	2.13	21.49	14.48	89.97	20.42	32.85	17.39	7.12
		3	6.59	15.59	11.89	6.67	2.68	9.35	2.49	21.41	8.94	2.40	10.66	7.91
		4	49.15	25.60	9.36	2.77	2.67	4.87	10.75	53.32	14.04	11.94	4.11	11.18
		5	20.22	12.89	7.52	3.32	5.21	2.64	8.70	12.70	3.02	11.00	7.57	8.17
		6	41.86	6.88	5.21	2.37	12.45	12.36	11.40	15.62	3.12	42.13	8.57	4.03
		7	19.24	5.46	13.16	2.08	1.01	3.31	2.69	40.76	12.03	165.91	8.98	15.61
		8	7.11	1.86	8.52	2.28	0.69	9.26	4.35	22.80	19.93	55.70	29.33	12.62
		9	18.49	2.23	7.20	7.82	17.71	22.23	19.23	62.75	8.72	47.85	8.08	13.55
COBALT	Surface water	1	346.84	79.79	90.48	120.70	30.61	654.77	473.44	277.23	237.11	199.86	98.80	51.04
		2	68.32	60.08	60.66	35.87	222.37	355.95	772.46	88.00	374.68	132.68	109.70	136.65
		3	89.63	84.10	81.16	372.71	165.02	167.98	832.89	27.29	151.01	174.48	123.70	68.78
		4	92.50	80.85	91.05	106.38	67.52	181.38	708.97	266.00	199.46	120.33	115.73	146.15
		5	80.78	73.31	88.28	66.31	55.32	217.27	359.39	76.56	109.71	370.53	107.51	123.71
		6	202.01	189.44	91.47	126.70	174.38	474.54	965.44	180.61	141.27	200.42	157.26	129.39
		7	277.73	99.87	244.70	98.28	48.64	442.71	1051.05	165.53	92.75	121.61	118.01	135.86
		8	116.90	80.47	56.07	97.14	5.84	167.28	238.66	185.98	126.48	131.25	104.80	91.71
		9	78.79	60.87	60.61	74.78	9.16	171.55	237.35	112.76	120.09	160.47	123.82	110.20
	Bottom water	1	42.96	47.50	64.82	193.32	27.70	768.11	343.75	41.61	49.60	146.05	92.80	64.62
		2	72.39	69.34	60.32	170.71	122.90	370.98	397.00	134.58	44.13	143.13	91.33	55.19
		3	115.54	117.50	111.44	54.73	70.30	138.64	109.62	218.67	102.64	18.58	104.84	92.62
		4	261.54	108.76	105.89	123.37	72.49	140.17	330.71	346.40	121.66	116.09	100.59	120.35
		5	228.30	99.08	73.76	65.21	61.73	150.53	237.57	79.43	103.29	115.98	90.14	81.38
		6	161.28	147.21	96.13	116.15	189.52	177.59	285.29	113.46	96.61	144.81	82.81	65.94
		7	67.71	75.06	198.61	90.89	43.42	163.17	177.96	32.20	96.75	18.47	99.50	135.00
		8	108.21	61.12	142.58	135.81	7.39	178.52	111.81	113.80	100.00	123.76	117.64	101.44
		9	114.37	98.87	131.33	174.65	75.74	146.35	175.59	116.44	100.35	128.42	84.50	94.34

Annexure - 3. (contd....)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
CHROMIUM	Surface water	1	389.23	104.08	98.44	205.04	9.72	294.86	302.02	543.02	119.79	654.92	266.48	150.77
		2	200.32	89.85	90.95	45.80	374.73	373.22	374.55	441.33	778.78	495.93	239.98	226.42
		3	141.28	85.71	121.49	295.21	233.65	280.29	496.26	128.37	339.38	455.21	225.42	142.98
		4	111.90	229.88	116.44	86.80	88.86	191.09	323.39	292.40	502.32	592.07	287.12	239.99
		5	114.23	161.81	157.87	55.93	76.73	172.41	244.95	530.58	233.82	925.00	229.40	398.52
		6	642.89	184.59	109.45	70.08	76.81	342.79	319.88	129.90	234.36	690.04	296.23	311.83
		7	431.85	202.42	108.23	126.84	15.32	564.44	430.59	546.45	215.79	285.16	247.12	375.56
		8	414.85	116.02	110.19	51.12	6.59	252.35	213.51	479.44	272.32	352.54	225.61	290.81
		9	190.08	57.19	80.00	66.93	13.75	248.75	261.05	315.86	246.25	537.02	288.25	288.74
	Bottom water	1	168.81	67.76	78.85	74.23	14.26	372.88	199.83	140.59	115.05	439.14	201.47	127.48
		2	199.04	78.77	115.24	73.92	51.62	205.06	213.57	252.69	75.66	359.49	192.04	95.10
		3	120.63	149.04	95.78	75.00	68.58	122.14	191.40	229.96	283.91	36.28	232.68	138.58
		4	534.40	166.42	130.30	122.61	108.42	167.80	182.41	289.15	215.54	211.77	208.24	375.02
		5	622.64	205.83	108.64	89.99	87.08	143.56	182.24	149.80	226.60	237.16	199.61	296.99
		6	211.79	164.04	94.87	91.66	95.49	153.68	179.31	92.98	266.15	360.87	148.43	138.24
		7	239.91	176.51	104.63	147.12	15.98	173.45	215.28	119.50	200.03	728.51	201.62	556.82
		8	111.24	93.70	104.53	97.47	9.98	225.37	184.43	247.76	210.27	353.06	418.91	386.44
		9	129.38	80.00	90.00	140.73	183.46	191.31	172.50	336.82	240.48	302.94	148.60	426.32
COPPER	Surface water	1	1398.81	300.85	80.26	106.56	8.21	237.54	234.41	350.03	67.33	388.06	120.25	135.66
		2	157.28	142.86	62.19	37.53	208.86	316.22	516.40	262.19	533.93	301.05	219.99	180.61
		3	168.02	153.15	115.04	210.17	160.61	371.90	580.25	178.61	331.48	263.63	130.91	112.47
		4	136.11	120.34	69.18	73.73	54.36	113.98	315.23	775.67	320.09	510.77	115.57	223.32
		5	156.92	300.82	132.70	115.59	50.65	230.32	154.48	942.33	169.39	523.17	179.14	276.80
		6	179.93	164.10	142.69	204.49	79.00	198.74	272.65	180.22	135.54	570.97	161.61	220.00
		7	960.17	131.95	121.88	50.87	10.76	455.31	210.45	500.38	189.83	124.10	116.32	210.01
		8	1559.88	123.65	122.81	39.02	7.62	324.26	96.62	281.52	272.55	250.81	185.02	235.00
		9	414.24	83.92	70.20	70.01	7.84	93.84	159.98	119.24	185.30	195.06	336.59	338.58
	Bottom water	1	144.01	236.13	63.22	81.36	11.47	148.75	276.47	299.76	173.30	171.55	125.02	81.01
		2	208.52	62.15	872.81	48.82	34.01	141.74	424.44	835.69	100.61	240.97	128.53	93.76
		3	238.51	108.44	147.92	82.60	44.75	100.83	98.20	204.94	99.26	22.03	121.92	92.76
		4	847.01	228.64	74.42	80.84	46.65	64.98	155.92	330.36	174.32	122.75	66.46	106.96
		5	802.04	175.57	64.50	45.68	38.48	127.24	92.69	78.68	110.95	165.88	84.06	191.68
		6	1014.87	147.08	61.49	54.46	79.60	115.83	85.74	94.02	74.11	174.41	66.95	66.19
		7	687.23	58.46	255.23	34.78	12.88	50.79	53.30	71.36	193.11	444.83	114.31	569.52
		8	111.85	64.96	74.07	49.83	7.90	162.15	58.94	112.48	148.29	1138.87	785.42	674.35
		9	211.21	70.17	66.90	78.64	88.95	98.27	78.29	155.79	129.63	430.13	100.62	270.37

Annexure - 3. (contd....)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
IRON	Surface water	1	106.65	53.86	83.61	82.91	3.34	191.47	166.58	77.42	295.47	232.04	108.34	95.39
		2	146.13	43.39	55.91	25.15	198.22	216.94	198.19	58.98	432.79	141.94	210.87	174.64
		3	129.41	44.34	68.94	284.23	135.01	138.46	349.62	6.93	193.96	240.22	178.49	130.39
		4	146.68	100.08	77.40	62.23	52.56	118.31	138.64	110.35	218.64	153.14	155.46	151.67
		5	23.75	66.00	61.44	33.09	40.63	115.46	125.88	38.06	119.23	419.02	165.83	221.42
		6	74.08	76.86	32.39	55.45	29.81	153.30	187.82	49.16	160.19	270.83	203.93	165.91
		7	366.28	107.87	46.39	68.01	7.37	238.30	207.99	36.29	133.07	127.61	170.15	196.27
		8	151.59	72.89	33.71	45.99	2.50	90.66	90.45	186.05	129.15	168.93	135.09	114.16
		9	42.64	34.06	44.52	44.60	5.43	116.45	100.32	108.83	118.38	166.99	142.48	109.15
	Bottom water	1	113.60	39.24	67.63	158.66	32.79	408.49	126.25	11.06	67.08	181.95	141.59	112.50
		2	144.16	47.64	58.20	149.36	163.40	242.99	138.05	61.68	21.53	194.62	127.36	103.50
		3	143.51	79.25	103.72	138.30	68.06	125.91	96.18	158.93	118.58	23.41	143.89	124.92
		4	198.39	97.31	89.22	90.96	68.78	112.94	110.15	171.87	143.58	147.77	139.84	149.43
		5	187.19	98.16	62.33	55.55	58.75	110.03	106.77	69.58	123.42	139.06	130.40	123.61
		6	98.76	95.95	67.24	68.00	56.54	110.79	113.44	49.13	127.08	184.04	116.91	9.15
		7	92.17	90.03	73.24	68.59	11.41	116.33	113.66	8.54	132.90	53.78	151.68	147.30
		8	137.80	59.93	55.30	81.44	4.15	104.61	85.82	112.74	115.54	142.64	120.31	107.39
		9	172.43	72.41	69.99	72.41	56.55	99.83	84.10	99.25	117.58	127.84	94.61	103.45
MANGANESE	Surface water	1	12.95	4.67	18.80	10.98	0.95	187.47	65.46	5.44	0.21	6.57	3.96	3.82
		2	8.34	4.50	7.15	3.77	66.04	121.36	97.44	5.31	6.66	5.86	6.89	7.27
		3	5.60	4.05	13.50	24.81	47.19	39.38	152.31	3.27	6.43	9.04	6.71	8.59
		4	7.17	18.92	8.75	8.74	18.87	96.81	88.52	30.78	7.50	6.99	5.86	40.19
		5	3.40	6.71	13.12	8.98	29.77	98.83	48.90	5.69	2.93	18.21	5.32	40.49
		6	23.24	24.24	21.34	24.30	92.68	271.88	164.16	24.49	4.54	10.84	14.21	23.47
		7	21.25	16.25	86.05	8.89	6.37	272.64	163.65	17.84	1.70	2.86	5.80	24.00
		8	7.33	28.11	33.91	36.22	4.33	120.90	42.54	7.87	3.92	2.66	3.54	2.84
		9	25.83	25.69	101.16	13.70	2.67	45.02	40.68	5.54	3.02	5.11	3.84	2.81
	Bottom water	1	4.20	2.78	7.33	26.70	6.51	152.23	39.82	0.81	1.48	5.08	2.91	2.48
		2	6.91	2.22	13.35	19.84	28.56	99.82	45.99	11.97	1.90	7.01	3.04	2.39
		3	5.33	7.07	21.96	10.59	15.95	60.28	5.31	11.90	1.57	0.55	3.24	4.50
		4	16.30	12.19	7.12	4.92	11.25	41.83	36.01	29.65	3.58	4.27	2.51	20.12
		5	16.65	11.39	11.78	5.50	14.93	59.04	24.72	6.04	2.57	4.04	2.71	8.25
		6	8.74	14.00	15.23	16.18	80.01	76.37	37.91	13.48	2.16	5.89	4.79	4.23
		7	5.40	5.23	48.88	3.75	6.39	12.29	10.08	3.39	1.87	0.81	3.13	12.54
		8	5.02	10.81	86.59	45.60	4.40	74.15	7.01	4.13	3.53	4.64	33.04	2.34
		9	8.15	10.62	22.54	28.00	26.31	32.09	19.66	6.83	3.12	3.68	2.43	2.07

Annexure - 3. (contd....)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
MOLYBDENUM	Surface water	1	12.45	50.85	40.84	64.18	13.59	19.69	155.30	713.51	254.65	639.33	331.18	160.18
		2	135.58	49.45	33.50	31.62	202.16	174.62	207.79	126.33	604.43	459.79	230.00	259.44
		3	92.28	53.38	41.18	357.71	125.63	192.57	193.82	206.63	185.60	186.72	269.21	142.39
		4	104.81	98.22	100.62	81.39	139.14	118.05	191.01	60.29	286.68	188.62	306.80	388.42
		5	3.02	109.25	78.73	47.82	24.36	218.37	144.40	830.77	180.75	341.67	244.53	352.22
		6	92.10	89.95	26.46	62.77	32.57	42.12	86.09	34.44	147.05	58.90	315.17	285.86
		7	319.07	169.36	129.99	103.46	18.16	156.76	59.71	110.68	166.69	178.77	225.33	312.60
		8	198.20	95.07	75.12	61.81	3.33	161.79	184.02	267.31	232.64	229.98	263.41	328.29
		9	136.68	59.11	46.00	32.81	9.30	164.77	145.28	202.99	203.95	167.15	298.74	333.18
	Bottom water	1	109.96	35.71	52.94	37.83	6.32	6.76	145.96	56.49	73.60	390.21	283.40	149.34
		2	137.91	69.34	16.20	43.24	8.17	110.38	174.49	125.06	78.46	185.34	277.46	92.35
		3	170.42	102.07	49.03	46.00	48.64	95.17	149.09	266.78	189.41	31.65	232.24	172.97
		4	304.91	101.40	114.85	111.79	86.46	118.29	123.53	83.18	171.67	139.98	160.21	296.17
		5	196.86	188.95	52.08	56.00	61.02	89.83	130.95	78.98	142.68	175.24	158.00	228.61
		6	239.36	105.10	43.66	69.47	49.98	81.98	93.53	48.55	141.13	131.32	128.85	42.67
		7	179.99	164.66	49.09	94.14	11.12	100.29	99.33	2.43	152.69	150.62	170.83	398.71
		8	113.93	88.65	59.63	105.41	6.30	182.60	124.39	183.63	181.12	382.90	602.38	674.52
		9	116.83	92.00	63.06	71.49	77.25	161.73	125.58	190.93	179.81	199.30	126.81	184.50
NICKEL	Surface water	1	188.54	97.13	153.49	65.70	9.89	588.79	292.90	627.04	131.24	534.27	183.81	254.51
		2	90.06	65.24	106.20	54.02	321.46	450.36	404.09	629.94	398.72	618.37	189.07	434.09
		3	60.12	61.40	121.48	193.98	241.36	378.57	743.55	221.57	254.15	263.98	111.31	226.88
		4	114.26	235.73	107.54	86.28	94.69	245.54	378.80	568.35	344.90	664.02	191.94	432.49
		5	104.37	160.50	167.66	115.56	97.58	186.70	259.53	844.16	227.01	763.21	196.04	371.59
		6	350.03	270.21	366.73	155.82	333.41	673.08	609.15	277.12	189.62	860.38	250.07	374.59
		7	513.63	168.37	194.72	65.80	8.96	751.72	278.31	801.94	76.17	133.09	171.18	415.86
		8	319.21	193.98	269.27	123.97	17.39	731.81	95.86	347.85	180.77	326.88	175.27	410.99
		9	251.50	144.59	212.20	124.76	16.08	232.54	201.23	199.45	98.70	444.28	183.67	363.24
	Bottom water	1	55.31	63.86	68.87	17.71	21.76	368.29	214.31	365.24	87.36	314.14	75.01	130.97
		2	85.29	38.92	133.88	1.54	50.31	128.33	228.24	365.15	98.83	179.12	88.35	124.08
		3	81.35	77.75	108.07	27.98	31.91	81.74	45.52	239.60	64.55	19.24	85.12	137.31
		4	784.62	135.59	84.02	55.91	51.90	78.14	145.85	349.44	143.42	95.63	40.32	206.15
		5	468.08	186.23	121.18	68.55	46.81	137.52	106.43	99.88	54.66	95.65	92.77	177.68
		6	318.08	192.14	140.45	97.82	280.53	177.64	126.68	153.73	30.27	237.21	70.54	70.99
		7	110.96	83.36	89.34	40.09	12.28	15.09	14.13	165.68	88.25	847.11	64.78	414.92
		8	59.59	65.90	218.93	76.37	19.51	372.42	26.15	147.99	125.39	339.14	564.56	246.47
		9	126.97	89.02	102.28	39.93	170.13	217.80	93.88	240.86	99.37	224.34	83.32	184.09

Annexure - 3. (contd....)

Metal	Stations		Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
LEAD	Surface water	1	703.95	142.36	101.81	126.13	8.82	525.70	501.84	840.92	204.00	1996.07	343.48	820.67
		2	261.97	188.41	89.79	57.74	479.93	645.00	801.77	385.21	831.80	1671.54	345.89	1612.93
		3	171.46	118.02	125.90	349.03	290.57	733.04	977.25	668.81	371.10	627.86	514.17	965.97
		4	300.21	722.40	142.60	156.14	89.65	249.55	524.59	706.24	895.00	1333.33	783.88	2116.04
		5	221.94	364.44	151.09	96.67	136.72	224.03	340.27	2379.74	437.23	1880.08	454.25	2556.89
		6	210.95	262.56	241.53	171.43	96.14	463.77	655.42	168.30	244.89	1955.30	778.77	1558.78
		7	220.98	178.83	190.99	103.79	29.25	1702.08	878.27	1084.17	310.00	301.43	602.55	1549.38
		8	340.47	163.94	112.49	151.89	34.36	515.89	169.85	1037.98	520.79	590.85	434.38	949.46
		9	138.14	99.80	98.75	115.94	19.59	414.58	436.97	521.72	276.27	1159.11	628.69	914.23
	Bottom water	1	140.57	187.53	51.71	117.03	16.61	461.59	477.31	889.79	130.97	1178.70	394.86	434.94
		2	329.98	111.90	61.61	114.17	39.21	491.34	320.12	748.35	99.47	595.16	357.07	373.48
		3	238.79	236.99	76.35	79.55	60.76	188.00	114.67	346.43	150.48	25.36	237.93	467.09
		4	1497.65	356.93	193.25	162.31	100.74	113.97	196.83	640.81	342.80	278.89	138.50	944.22
		5	1419.03	319.04	28.79	85.47	108.37	149.75	202.71	152.75	215.22	201.39	179.66	354.63
		6	703.46	313.56	93.50	124.43	123.98	211.14	171.94	244.62	115.21	749.84	218.94	149.14
		7	352.69	82.24	32.88	72.54	36.86	140.14	121.76	305.26	179.31	2130.79	258.58	752.05
		8	140.55	89.60	152.59	138.77	20.56	408.51	102.54	408.58	319.04	845.75	1444.42	344.88
		9	91.81	89.46	106.45	110.58	392.09	520.64	324.15	1009.39	233.65	419.21	135.54	312.30
ZINC	Surface water	1	2601.58	653.15	784.85	732.33	54.00	1215.85	1806.94	2493.02	397.12	1667.42	459.15	340.23
		2	1170.74	482.58	454.41	183.80	2604.13	1708.89	1822.47	1953.50	1791.53	1634.34	372.18	554.12
		3	636.14	319.60	659.20	1737.59	1154.06	1359.22	2963.84	636.19	939.51	941.41	603.47	536.93
		4	909.04	1284.89	358.30	747.35	387.01	513.11	911.91	3688.60	1439.64	1787.20	749.07	791.25
		5	751.59	1418.26	609.02	459.56	901.95	551.04	599.84	2600.48	647.69	1995.33	634.13	643.49
		6	4602.59	1597.60	946.20	1192.94	1250.40	1307.05	1421.12	708.40	537.67	2334.75	998.72	874.77
		7	4451.17	825.96	471.27	329.09	109.67	2220.83	1012.50	2234.83	657.30	539.77	605.88	641.30
		8	3263.66	1055.04	779.72	447.32	122.15	1158.67	295.73	1287.10	780.48	1680.18	682.36	693.78
		9	2261.98	613.29	729.25	551.63	169.60	637.98	626.83	611.23	619.01	1290.79	784.72	701.56
	Bottom water	1	875.84	751.41	574.83	705.11	85.85	1831.21	978.98	1031.10	331.04	1030.84	1039.03	646.75
		2	641.15	260.80	664.53	314.17	264.49	994.01	929.80	1194.61	385.63	1003.14	541.14	260.73
		3	614.00	668.55	800.07	473.06	600.98	677.06	197.39	1073.22	261.71	75.25	441.80	393.80
		4	3619.02	988.14	448.46	287.04	262.11	364.04	381.54	1267.25	647.10	416.53	251.43	304.08
		5	3840.09	1214.34	495.26	282.31	369.55	562.00	334.18	468.22	386.71	386.90	263.73	261.77
		6	2090.64	1346.26	617.41	713.23	1288.13	618.78	405.65	532.34	274.27	1061.72	326.83	223.25
		7	2190.57	369.76	324.70	207.83	98.73	140.09	122.40	483.01	465.97	2155.58	451.47	412.99
		8	845.78	386.75	755.59	350.04	272.69	981.38	125.75	564.98	747.44	2964.68	2704.04	1537.27
		9	1075.34	388.05	497.90	329.56	1317.69	692.38	349.15	954.24	616.35	996.97	356.91	395.70

Annexure-4. Monthly data of total trace metal concentrations in sediments (µg/g)

Metal	Stations	Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
CADMIUM	1	1.05	0.75	1.03	1.99	0.63	0.74	2.41	3.15	2.11	3.14	3.59	0.75
	2	1.40	0.96	1.12	2.17	1.06	0.89	2.94	3.56	2.64	2.18	3.37	0.90
	3	1.10	1.38	0.90	1.62	1.06	1.15	3.34	3.35	2.87	3.23	3.33	0.58
	4	1.15	1.58	1.18	2.31	1.11	0.52	2.93	3.45	3.21	3.69	4.13	1.14
	5	1.36	1.49	1.18	2.40	0.99	1.48	3.69	4.59	3.00	3.81	3.80	0.89
	6	1.88	1.45	1.27	1.84	1.29	1.30	3.31	3.66	3.29	5.23	4.03	1.01
	7	1.68	1.32	1.76	1.38	1.00	1.07	3.46	3.73	3.07	1.57	3.87	0.79
	8	0.56	0.53	0.59	0.98	0.63	0.69	2.60	3.60	2.42	2.95	3.70	0.49
	9	0.58	0.50	1.06	1.62	0.73	0.47	1.72	3.60	2.74	1.72	2.90	0.47
COBALT	1	42.64	50.85	33.74	52.68	56.53	68.30	56.03	61.58	69.85	49.31	57.79	63.54
	2	53.03	59.86	34.83	66.87	35.05	74.43	66.24	67.69	58.46	30.24	78.65	64.79
	3	53.51	58.11	42.17	113.56	86.98	77.52	64.30	59.17	60.70	70.84	69.56	51.73
	4	74.06	78.54	80.59	92.58	84.04	118.60	84.89	90.78	92.87	73.69	98.44	87.18
	5	103.13	52.73	101.10	93.37	91.45	120.18	93.36	92.16	83.98	65.87	96.08	102.15
	6	75.28	90.86	106.48	73.66	108.93	171.51	96.04	87.92	83.34	69.07	116.53	68.26
	7	59.44	56.03	44.57	32.18	73.21	119.74	69.26	69.86	49.81	20.42	87.31	52.90
	8	13.36	12.75	12.89	12.81	10.67	11.76	14.94	15.27	11.91	20.55	60.28	13.93
	9	8.92	8.79	15.23	17.00	18.87	19.49	15.85	5.41	34.46	12.47	16.68	8.86
CHROMIUM	1	200.28	165.90	148.87	148.30	158.04	184.01	154.35	191.13	193.07	146.00	178.00	182.17
	2	235.59	212.62	168.52	167.52	79.87	201.89	218.70	228.86	165.24	82.22	247.82	206.89
	3	249.22	202.05	201.15	211.26	174.67	217.00	211.88	194.91	192.33	206.75	223.99	161.77
	4	265.18	245.62	245.94	210.20	195.87	218.91	230.16	221.42	205.83	161.55	231.11	221.69
	5	283.73	180.51	214.06	195.56	184.26	216.79	222.96	214.55	174.90	142.90	209.95	206.07
	6	245.75	223.99	262.34	148.27	203.87	237.16	217.51	198.87	178.99	161.36	217.84	176.60
	7	195.16	155.69	155.96	65.92	141.78	183.96	186.27	183.37	97.17	37.47	183.06	134.36
	8	48.41	31.22	27.43	37.94	13.55	26.15	30.29	34.04	23.66	42.29	157.96	24.99
	9	30.89	27.06	36.63	30.03	28.66	29.56	33.68	13.00	73.44	22.51	34.04	16.81
COPPER	1	44.47	36.38	35.00	38.58	44.43	45.87	42.74	52.07	60.78	36.62	45.90	48.22
	2	60.42	51.02	38.92	48.14	20.86	56.87	65.73	65.40	42.44	21.12	69.55	66.44
	3	68.44	64.24	53.87	42.78	32.12	66.94	66.31	61.44	63.32	63.18	66.60	48.12
	4	47.82	46.83	44.41	22.15	42.35	41.99	45.58	49.77	54.22	36.68	42.17	45.24
	5	19.42	22.87	13.74	33.70	29.15	34.06	35.91	35.31	32.60	26.94	30.77	28.41
	6	29.75	20.41	22.94	22.83	20.80	19.12	34.49	21.53	27.56	20.92	17.34	23.85
	7	30.34	20.48	16.61	14.66	17.18	20.55	35.79	32.31	14.83	6.83	19.01	17.89
	8	9.50	7.69	7.43	9.88	4.14	5.33	8.26	7.57	6.88	12.85	31.90	6.82
	9	6.43	3.97	9.81	8.57	7.92	5.27	7.94	3.09	12.42	5.28	7.64	4.29

Annexure 4 (contd...).

Metal	Stations	Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
IRON (%)	1	6.40	5.80	5.64	6.02	6.54	6.45	6.30	6.69	7.71	5.76	6.74	6.88
	2	7.94	7.28	5.47	6.98	3.72	7.01	8.09	8.41	6.46	3.25	8.41	8.22
	3	8.53	7.45	6.76	7.18	7.17	7.17	7.73	6.70	7.09	7.26	7.51	6.16
	4	10.92	9.42	10.14	10.29	9.28	9.25	9.19	8.82	9.08	9.78	9.58	10.24
	5	18.26	5.71	14.22	13.23	10.28	10.83	10.82	9.08	9.40	8.76	10.31	11.34
	6	11.31	11.18	14.10	10.25	11.47	13.98	10.38	9.07	8.54	10.14	12.83	7.92
	7	8.55	6.25	6.83	2.73	7.02	9.97	7.54	7.07	6.02	2.66	9.25	6.34
	8	1.86	1.78	1.21	1.20	0.91	0.93	1.28	1.28	1.16	2.46	5.61	1.35
	9	1.34	0.90	1.41	1.61	1.60	1.12	1.44	0.50	3.52	1.50	1.51	0.86
MANGANESE (mg/g)	1	0.38	0.37	0.37	0.38	0.36	0.39	0.41	0.33	0.49	0.34	0.47	0.46
	2	0.49	0.54	0.35	0.50	0.44	0.42	0.48	0.50	0.46	0.29	0.55	0.48
	3	0.52	0.45	0.47	1.16	0.92	0.42	0.46	0.39	0.47	0.42	0.36	0.32
	4	0.97	0.86	0.98	0.85	0.80	0.82	0.80	0.79	0.73	0.79	0.89	0.80
	5	1.05	0.70	1.12	0.78	0.76	0.70	0.66	0.73	0.61	0.56	0.84	0.70
	6	0.94	1.04	1.19	0.84	1.04	1.38	0.65	0.77	0.55	0.81	1.06	0.60
	7	0.73	0.61	0.72	0.34	0.70	0.78	0.50	0.55	0.46	0.26	0.71	0.58
	8	0.21	0.15	0.15	0.16	0.15	0.13	0.14	0.13	0.11	0.21	0.73	0.15
	9	0.22	0.13	0.37	0.15	0.14	0.24	0.14	0.07	0.35	0.17	0.18	0.12
MOLYBDENUM	1	140.31	118.57	110.41	87.63	129.45	129.45	95.15	111.01	123.11	149.48	106.85	149.48
	2	194.72	156.32	130.10	105.65	154.15	154.15	136.90	127.94	96.57	172.80	149.70	172.80
	3	194.51	165.54	166.99	55.95	163.23	163.23	137.13	120.55	121.02	131.14	138.38	131.14
	4	148.33	137.92	149.92	97.46	123.77	123.77	107.56	112.43	126.78	132.15	109.97	132.15
	5	67.91	97.76	53.84	78.42	102.69	102.69	86.62	81.52	74.98	94.99	78.99	94.99
	6	101.64	82.45	77.98	54.62	68.57	68.57	79.69	58.41	59.69	89.24	50.20	89.24
	7	102.43	80.72	64.81	29.93	69.23	69.23	84.81	72.45	32.72	64.03	56.10	64.03
	8	30.08	19.20	24.79	18.39	10.97	10.97	15.94	16.67	21.56	17.29	77.72	17.29
	9	19.52	13.54	22.64	15.92	14.99	14.99	17.07	6.39	28.27	11.86	17.42	11.86

Annexure 4 (contd...).

Metal	Stations	Oct-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Sep-96	Oct-96	Nov-96
NICKEL	1	69.13	58.54	58.00	58.62	65.63	79.31	62.94	70.45	76.63	63.88	70.56	73.25
	2	83.01	67.54	60.39	73.46	32.42	71.35	86.93	91.55	63.55	30.04	90.16	79.23
	3	75.52	79.43	72.44	57.11	56.41	79.76	80.45	70.41	77.30	77.29	81.97	59.37
	4	74.48	78.29	73.37	72.20	70.33	66.15	75.80	78.95	80.10	69.08	75.95	72.07
	5	48.37	55.84	38.18	65.78	63.30	52.21	67.37	60.88	62.24	62.68	62.26	56.57
	6	62.72	53.88	54.63	53.14	60.76	47.71	65.67	48.19	50.47	65.86	50.82	58.91
	7	54.64	45.33	44.87	29.15	48.81	46.55	61.78	46.97	35.17	23.90	48.43	41.54
	8	16.99	12.46	15.42	16.97	9.33	8.95	17.00	15.98	13.76	29.05	57.55	12.88
	9	12.87	12.12	15.95	15.43	12.80	11.68	16.86	8.89	27.31	16.70	17.53	12.22
LEAD	1	61.61	60.21	102.58	53.54	57.53	56.82	67.37	75.82	68.78	56.74	77.54	62.95
	2	72.49	73.11	49.22	63.02	34.50	64.56	78.51	81.68	70.56	34.89	103.85	75.35
	3	76.98	77.72	58.00	51.16	52.92	67.33	81.49	78.87	74.59	78.68	93.71	55.54
	4	64.39	76.50	74.14	55.52	61.70	59.88	80.08	85.22	82.56	50.13	89.85	65.05
	5	62.59	51.91	51.31	72.33	56.90	58.59	80.56	84.41	63.85	36.10	85.82	54.22
	6	55.45	57.58	58.73	62.38	55.80	51.02	76.58	73.17	62.97	39.29	66.47	44.45
	7	53.15	49.74	41.35	43.45	44.71	45.75	68.46	71.73	49.53	11.41	67.10	37.27
	8	16.86	13.49	12.36	36.01	18.08	14.55	38.40	44.67	27.51	15.29	73.91	15.88
	9	11.13	15.54	11.60	27.14	21.56	15.45	34.44	33.91	39.40	5.08	39.21	12.26
ZINC	1	151.62	134.62	141.54	86.50	98.28	126.54	142.96	176.81	192.99	168.84	228.38	107.26
	2	159.58	123.78	151.39	95.97	52.38	136.08	179.62	184.97	188.33	155.67	276.55	112.41
	3	165.13	145.96	157.80	111.87	110.88	137.59	177.70	169.24	198.14	203.68	267.01	88.64
	4	171.59	156.93	193.29	120.06	115.79	141.21	224.12	193.89	196.77	180.05	272.01	120.76
	5	166.00	133.23	183.62	109.92	108.02	128.53	188.07	182.16	180.11	162.61	220.13	116.47
	6	174.23	154.79	196.15	116.56	106.43	141.02	193.44	175.57	204.52	162.66	183.15	95.84
	7	141.70	132.25	156.42	79.29	87.23	128.49	172.81	169.65	153.24	109.51	250.09	82.22
	8	56.33	59.17	89.38	61.12	22.51	56.39	99.38	98.20	81.13	125.83	242.45	27.54
	9	47.06	49.87	83.06	36.78	24.32	54.61	92.63	78.63	132.03	125.28	187.05	21.06

Annexure-5. Monthly data on distribution of different chemical fractions of trace metals in sediments

Metal fraction	Stations	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96	Metal fraction	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96
Cd_1	1	0.21	0.26	0.15	0.01	0.01	0.01	0.04	0.24	0.24	0.02	Co_1	3.68	1.48	0.97	0.88	1.53	0.17	4.07	2.58	2.68	1.95
	2	0.23	0.24	0.21	0.01	0.00	0.02	0.02	0.27	0.30	0.04		2.72	1.88	2.37	0.88	1.52	2.94	2.62	4.38	3.94	3.27
	3	0.23	0.35	0.20	0.02	0.02	0.01	0.03	0.29	0.25	0.01		3.74	3.35	2.30	1.06	2.17	3.71	4.50	3.72	5.00	1.34
	4	0.19	0.31	0.14	0.01	0.01	0.01	0.01	0.21	0.17	0.02		2.39	3.57	2.37	1.33	0.79	2.34	1.49	3.25	2.98	1.89
	5	0.14	0.30	0.14	0.01	0.01	0.02	0.02	0.21	0.19	0.01		1.45	1.39	2.26	1.11	1.25	0.97	0.80	1.89	2.03	1.08
	6	0.17	0.24	0.20	0.01	0.01	0.03	0.02	0.23	0.20	0.02		2.77	1.41	1.55	0.35	0.06	0.87	0.87	1.97	2.29	0.56
	7	0.19	0.28	0.16	0.01	0.00	0.02	0.02	0.17	0.21	0.02		1.51	1.34	1.39	0.43	0.26	0.91	0.81	1.34	1.60	0.32
	8	0.14	0.16	0.11	0.00	0.00	0.01	0.02	0.11	0.26	0.01		1.17	1.31	0.63	0.36	0.15	0.29	0.39	0.73	1.81	0.32
	9	0.08	0.16	0.13	0.01	0.01	0.01	0.01	0.17	0.11	0.01		0.71	0.78	0.86	0.21	0.39	0.05	0.04	1.12	0.57	0.22
Cd_2	1	0.31	0.42	0.45	0.45	0.58	0.45	0.55	0.62	0.76	0.66	Co_2	11.49	12.43	16.61	17.78	20.82	15.48	16.07	19.45	23.97	23.28
	2	0.40	0.42	0.46	0.41	0.58	0.52	0.26	0.56	0.87	0.70		20.06	14.43	10.20	16.71	19.46	18.33	10.93	17.15	22.19	24.59
	3	0.43	0.60	0.49	0.45	0.60	0.52	0.20	0.57	0.69	0.55		17.32	17.40	15.49	19.51	24.81	20.32	8.71	17.03	20.84	18.04
	4	0.30	0.54	0.38	0.33	0.25	0.26	0.18	0.50	0.56	0.61		13.14	18.19	13.51	14.30	10.27	11.76	7.83	15.43	19.25	23.53
	5	0.30	0.43	0.36	0.45	0.28	0.46	0.25	0.56	0.68	0.52		9.57	7.46	8.62	11.82	12.38	15.01	9.95	22.08	20.04	18.86
	6	0.33	0.36	0.48	0.43	0.16	0.47	0.13	0.52	0.67	0.51		9.94	8.73	12.32	12.01	7.61	13.86	5.24	13.38	15.01	12.45
	7	0.45	0.42	0.27	0.28	0.53	0.41	0.11	0.32	0.90	0.46		12.32	9.70	4.21	9.66	15.98	9.80	4.92	6.33	14.78	8.95
	8	0.27	0.26	0.22	0.15	0.06	0.18	0.09	0.18	1.19	0.20		6.26	4.49	4.61	3.83	2.59	3.97	2.86	3.10	23.39	5.34
	9	0.16	0.19	0.25	0.26	0.15	0.09	0.05	0.28	0.40	0.18		3.75	3.19	6.32	7.19	4.55	3.54	1.45	9.15	6.06	3.76
Cd_3	1	0.53	0.07	0.43	1.52	0.14	1.95	2.56	1.25	2.60	0.08	Co_3	27.46	36.93	16.16	34.01	45.96	40.39	41.44	47.82	31.14	38.31
	2	0.77	0.29	0.45	1.75	0.31	2.39	3.28	1.80	2.20	0.16		30.25	43.56	22.27	49.28	53.45	44.97	54.15	36.93	52.52	36.93
	3	0.44	0.42	0.21	1.15	0.53	2.82	3.12	2.01	2.38	0.03		32.45	37.36	24.38	92.99	50.55	40.27	45.96	39.94	43.72	32.35
	4	0.66	0.73	0.66	1.97	0.27	2.67	3.26	2.50	3.40	0.51		58.53	56.78	64.71	76.95	107.54	70.79	81.45	74.19	76.22	61.76
	5	0.91	0.76	0.68	1.94	1.19	3.21	4.33	2.23	2.93	0.36		92.11	43.88	90.22	80.44	106.56	77.38	81.42	60.02	74.01	82.21
	6	1.38	0.85	0.58	1.40	1.13	2.81	3.52	2.55	3.16	0.48		62.57	80.72	92.61	61.29	163.83	81.32	81.82	67.99	99.23	55.25
	7	1.04	0.62	1.32	1.09	0.53	3.03	3.61	2.58	2.76	0.31		45.62	44.99	38.98	22.08	103.50	58.55	64.13	42.14	70.93	43.63
	8	0.15	0.10	0.26	0.83	0.63	2.41	3.49	2.13	2.25	0.28		5.93	6.95	7.66	8.62	9.02	10.68	12.02	8.09	35.08	8.27
	9	0.33	0.15	0.68	1.35	0.31	1.62	3.53	2.29	2.40	0.28		4.47	4.82	8.04	9.60	14.56	12.26	3.92	24.18	10.04	4.87

Annexure-5 (contd...).

Metal fraction	Stations	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96	Metal fraction	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96
Cr_1	1	4.94	5.84	4.19	1.10	1.30	0.20	0.82	5.00	6.23	2.31	Cu_1	0.20	0.13	0.06	0.01	0.02	0.03	0.20	0.22	0.16	0.10
	2	4.48	4.37	4.37	0.54	1.52	1.22	1.03	5.36	5.82	0.97		0.40	0.13	0.14	0.11	0.02	0.08	0.18	0.24	0.27	0.15
	3	5.65	7.75	4.63	0.65	1.10	1.28	1.54	6.91	4.72	1.04		0.31	0.21	0.11	0.05	0.01	0.31	0.40	0.46	0.34	0.02
	4	4.42	5.94	3.00	0.75	0.81	0.44	0.51	5.26	4.26	0.83		0.09	0.16	0.16	0.08	0.00	0.09	0.05	0.37	0.13	0.03
	5	3.32	5.14	3.82	0.96	0.45	0.72	0.69	4.29	4.58	1.85		0.06	0.15	0.15	0.03	0.02	0.05	0.06	0.13	0.11	0.02
	6	4.17	4.03	5.43	0.41	1.53	1.65	0.94	5.74	4.70	1.86		0.07	0.13	0.10	0.03	0.02	0.04	0.05	0.18	0.15	0.01
	7	3.92	6.44	3.42	0.32	0.42	0.83	0.41	3.26	4.15	2.00		0.11	0.14	0.08	0.04	0.03	0.04	0.02	0.12	0.12	0.01
	8	3.58	2.94	2.42	0.22	0.33	0.20	0.24	2.86	5.33	0.92		0.04	0.09	0.05	0.02	0.01	0.02	0.02	0.08	0.16	0.01
	9	2.12	3.57	3.37	0.23	0.40	0.34	0.89	4.31	2.14	0.24		0.04	0.08	0.07	0.02	0.01	0.01	0.02	0.09	0.06	0.01
Cr_2	1	20.38	21.20	23.71	24.47	32.73	22.07	24.33	27.74	36.63	32.40	Cu_2	1.23	1.16	1.46	0.48	1.01	0.94	1.37	1.55	1.70	2.34
	2	25.77	22.17	19.21	20.61	27.17	27.44	18.50	24.92	32.62	36.15		4.09	1.88	1.19	1.00	2.26	2.24	1.70	3.63	3.77	4.43
	3	25.95	25.86	27.57	25.39	32.76	29.06	15.69	23.44	35.57	28.98		3.76	1.97	2.37	3.15	1.40	2.56	1.61	4.03	3.00	1.64
	4	11.35	17.59	12.47	15.52	25.82	13.90	12.75	20.10	19.53	25.23		1.08	1.36	0.96	0.92	1.54	1.09	3.57	3.80	1.08	1.38
	5	12.00	13.19	8.50	14.74	19.18	21.15	17.23	28.56	26.38	26.22		0.61	0.30	0.79	0.43	0.86	0.71	0.47	0.47	0.82	0.70
	6	12.78	12.80	14.54	15.68	16.65	17.18	7.14	19.36	18.14	20.98		0.42	0.42	0.59	0.44	0.27	0.50	0.19	0.46	0.53	0.20
	7	16.07	15.94	7.06	12.59	10.63	16.63	7.36	8.63	23.88	16.05		0.68	0.27	0.18	0.34	0.47	0.22	0.13	0.36	0.40	0.14
	8	7.84	5.60	5.16	3.66	3.03	4.57	3.47	3.53	30.40	6.28		0.42	0.26	0.33	0.08	0.15	0.24	0.23	0.32	0.84	0.39
	9	3.40	3.20	6.47	9.49	4.92	4.35	1.03	7.93	8.07	4.42		0.39	0.24	0.34	0.17	0.22	0.33	0.18	0.80	0.32	0.42
Cr_3	1	174.96	138.86	120.97	122.73	149.98	132.08	165.98	160.34	135.14	147.47	Cu_3	43.04	35.09	33.49	38.09	44.85	41.77	50.50	59.01	44.05	45.79
	2	205.34	186.08	144.94	146.38	173.20	190.04	209.33	134.96	209.38	169.78		55.92	49.00	37.59	47.03	54.59	63.41	63.52	38.58	65.50	61.85
	3	217.62	168.43	168.94	185.22	183.14	181.54	177.69	161.97	183.70	131.75		64.38	62.07	51.38	39.58	65.53	63.45	59.43	58.83	63.26	46.46
	4	249.41	222.09	230.47	193.93	192.28	215.82	208.16	180.46	207.32	195.63		46.66	45.30	43.29	21.15	40.44	44.40	46.14	50.05	40.97	43.82
	5	268.41	162.17	201.74	179.86	197.16	201.10	196.62	142.06	178.99	178.00		18.75	22.41	12.79	33.24	33.18	35.14	34.77	32.00	29.84	27.69
	6	228.80	207.16	242.37	132.17	218.97	198.68	190.80	153.88	195.00	153.76		29.26	19.86	22.25	22.36	18.83	33.95	21.29	26.92	16.66	23.63
	7	175.17	133.31	145.48	53.01	172.91	168.81	175.60	85.28	155.03	116.31		29.55	20.06	16.35	14.29	20.05	35.54	32.16	14.35	18.49	17.74
	8	36.99	22.68	19.85	34.06	22.79	25.52	30.33	17.28	122.23	17.80		9.05	7.35	7.05	9.78	5.18	8.00	7.32	6.48	30.89	6.42
	9	25.37	20.29	26.79	20.31	24.24	28.99	11.08	61.20	23.84	12.15		6.00	3.65	9.39	8.37	5.05	7.60	2.90	11.53	7.26	3.87

Annexure-5 (contd....).

Metal fraction	Stations	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96	Metal fraction	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96
Fe_1	1	79.39	82.15	8.38	1596.74	1149.98	382.69	43.67	830.00	1756.99	288.67	Mn_1	152.73	164.71	98.99	176.03	185.76	119.39	106.20	193.29	241.56	221.97
	2	118.56	212.32	78.71	90.65	1452.08	1422.04	1037.01	729.27	998.06	710.10		179.51	281.75	196.31	225.39	117.93	241.76	170.19	234.55	257.27	273.83
	3	750.04	992.36	567.31	1088.38	844.06	1076.12	709.16	118.21	1016.74	1329.13		276.22	147.94	219.19	248.12	215.66	245.22	186.91	164.62	201.50	119.72
	4	315.04	672.83	294.41	1206.16	607.70	713.77	390.09	341.66	288.36	960.24		431.33	421.22	358.34	243.49	206.15	260.89	135.72	245.84	369.09	305.60
	5	183.86	63.54	7.52	718.33	8.73	107.18	463.55	540.39	285.41	673.60		157.16	276.53	200.88	297.20	394.20	256.03	105.47	165.93	307.73	195.75
	6	151.50	41.57	30.24	199.25	0.82	2.09	2.65	253.46	2.58	32.93		295.01	307.87	288.26	295.61	40.29	283.56	62.62	103.81	248.90	139.75
	7	190.20	30.33	5.73	54.01	0.47	536.30	2.13	67.06	390.18	64.83		195.98	88.17	87.51	141.87	183.28	178.33	40.93	51.23	97.17	115.09
	8	106.44	11.24	3.14	17.71	213.05	1.13	1.59	4.14	288.64	27.66		111.90	84.32	36.14	46.23	27.72	33.06	29.53	23.54	276.33	53.46
	9	1.12	8.24	1.23	2.18	383.52	1.14	1.36	0.15	2.30	1.13		44.56	50.06	53.92	55.49	66.04	6.32	2.62	34.30	42.13	64.22
Fe_2 (mg/g)	1	19.51	21.58	28.38	30.37	26.49	12.88	13.39	32.71	16.29	15.26	Mn_2	51.24	94.66	139.79	102.46	114.31	178.18	64.55	118.19	172.51	132.42
	2	26.22	26.49	14.30	22.01	17.34	15.93	10.51	30.43	14.47	18.70		144.79	140.75	57.77	198.69	111.68	109.98	78.79	110.69	187.18	128.41
	3	25.75	28.21	24.10	19.34	22.78	14.01	8.80	25.06	13.64	14.18		108.31	122.12	120.37	228.03	151.52	146.62	61.41	126.46	78.85	110.95
	4	13.67	23.18	14.50	20.53	12.72	15.13	5.51	32.32	9.66	14.36		299.51	172.21	247.67	192.17	75.49	142.66	173.36	188.88	264.95	234.09
	5	13.98	13.40	19.17	29.21	13.57	10.25	11.51	40.02	12.83	14.86		136.32	176.23	277.29	205.95	109.11	130.62	130.24	146.07	305.65	160.33
	6	13.79	13.48	14.38	14.76	10.59	10.05	4.39	24.44	8.08	9.71		128.80	170.29	217.53	214.38	143.81	99.26	94.82	75.30	220.36	163.19
	7	18.51	19.89	6.13	14.56	12.54	15.03	6.48	10.94	10.87	8.11		172.12	101.88	79.00	158.33	112.35	52.11	48.16	36.09	90.75	81.12
	8	9.11	8.94	5.71	5.06	2.67	2.94	2.09	3.82	13.61	3.14		66.05	50.93	57.64	78.56	45.26	36.74	23.84	33.45	360.59	64.18
	9	4.46	4.57	7.88	11.24	3.26	3.71	1.19	12.01	3.39	2.38		102.18	76.69	289.38	69.85	115.04	36.07	22.77	108.39	83.99	38.93
Fe_3 (mg/g)	1	44.45	36.35	28.05	28.24	36.82	49.76	53.43	43.54	49.36	53.30	Mn_3	174.37	113.27	131.46	103.44	94.39	109.71	157.04	177.99	57.59	100.64
	2	53.06	46.14	40.32	47.74	51.29	63.58	72.54	33.46	68.60	62.80		163.58	118.88	100.58	77.51	190.44	126.03	246.35	114.82	108.98	75.83
	3	58.79	45.31	42.89	51.38	48.10	62.21	57.54	45.70	60.44	46.05		134.02	184.63	127.09	685.09	49.51	66.98	137.50	183.61	79.34	84.93
	4	95.23	70.31	86.63	81.16	79.14	76.01	82.26	58.17	85.84	87.12		240.42	261.60	373.05	418.48	541.46	393.94	476.07	295.67	256.33	259.03
	5	168.47	43.69	122.99	102.40	94.71	97.81	78.80	53.45	89.96	97.88		752.89	252.00	641.64	279.21	201.53	269.55	490.42	295.82	225.35	345.40
	6	99.14	98.28	126.64	87.55	129.16	93.73	86.30	60.76	120.18	69.48		514.95	561.57	683.09	326.37	1196.70	263.76	610.91	366.82	587.61	298.34
	7	66.75	42.60	62.17	12.72	87.20	59.86	64.17	49.21	81.27	55.21		363.99	423.98	556.25	38.64	480.64	268.33	456.26	373.74	525.49	386.34
	8	9.39	8.87	6.36	6.95	6.42	9.86	10.74	7.79	42.24	10.34		35.15	15.10	51.33	38.11	60.45	70.54	72.65	50.67	89.15	27.70
	9	8.96	4.43	6.23	4.84	7.58	10.69	3.85	23.17	11.69	6.22		68.90	2.30	29.48	20.74	59.07	93.35	43.37	211.39	55.95	14.75

Annexure-5 (contd....).

Metal fraction	Stations	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96	Metal fraction	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96
Mo_1	1	2.28	2.71	1.93	2.52	2.37	1.91	2.93	2.71	2.77	2.67	Ni_1	10.52	5.07	3.05	7.37	3.30	0.89	5.37	3.54	2.70	4.66
	2	2.63	2.50	2.61	3.28	3.57	2.99	2.89	2.90	3.38	2.18		9.55	4.87	8.55	8.43	3.35	3.57	4.14	6.81	5.62	6.51
	3	2.57	3.53	2.51	3.18	1.96	1.61	1.83	3.09	2.59	2.72		9.64	9.47	6.68	10.38	3.93	5.35	5.31	7.13	6.74	3.16
	4	1.99	3.20	1.72	2.13	2.45	2.26	1.67	2.53	1.82	2.34		7.63	7.35	4.18	8.01	2.55	3.17	1.77	4.75	3.00	3.73
	5	1.82	2.99	1.95	2.44	2.41	1.65	1.93	2.33	2.13	2.61		5.18	2.68	4.22	9.04	3.12	1.98	2.11	2.25	3.24	2.94
	6	1.99	2.35	2.46	3.01	2.19	2.59	1.57	2.62	2.10	2.26		6.92	2.88	5.72	8.01	2.08	2.72	1.74	4.19	3.55	3.42
	7	2.26	2.96	2.05	2.42	3.02	2.27	1.10	1.89	2.22	3.22		5.39	2.84	4.24	6.57	3.20	2.35	1.83	3.13	3.52	4.17
	8	1.69	1.17	1.36	1.85	1.21	1.35	1.51	1.31	3.09	2.03		5.85	2.76	2.12	5.06	1.24	1.88	1.96	2.51	3.47	3.22
	9	1.01	0.91	1.64	2.93	1.08	1.38	1.78	1.97	1.22	1.94		2.70	2.31	2.23	2.17	0.89	1.12	0.99	2.95	1.20	2.56
Mo_2	1	8.25	7.49	7.65	8.34	11.01	9.11	9.37	9.48	11.35	9.66	Ni_2	14.74	21.33	19.13	17.11	19.68	16.08	14.37	23.35	26.02	24.61
	2	9.55	8.18	9.24	8.93	11.62	12.04	8.05	10.01	14.43	11.42		20.20	19.74	19.24	20.34	19.79	17.73	19.40	21.23	28.82	22.99
	3	11.16	10.53	9.81	9.37	11.79	11.56	6.42	9.99	11.62	9.35		19.54	25.16	19.45	18.54	22.58	15.07	10.07	23.28	22.57	20.17
	4	7.20	8.61	6.92	6.83	8.57	9.19	4.23	9.10	8.61	8.01		14.85	25.54	14.54	15.27	15.89	18.03	16.83	19.19	19.69	22.19
	5	6.16	9.09	5.43	8.53	7.03	10.17	6.19	8.33	8.79	8.17		13.45	18.82	15.36	18.08	14.77	16.61	11.22	21.13	18.98	17.99
	6	7.92	7.13	7.78	8.17	5.16	9.32	3.75	8.05	8.31	8.35		14.61	15.14	19.78	16.91	10.69	17.00	7.60	21.39	19.30	16.26
	7	8.51	7.30	5.66	6.84	10.45	7.11	3.45	5.38	9.34	8.05		19.03	18.18	10.45	13.13	15.50	11.33	7.88	12.99	19.74	14.71
	8	5.53	3.69	3.45	3.38	2.42	3.55	2.87	2.72	13.94	3.22		10.89	9.57	9.00	10.00	6.03	6.91	6.18	8.10	29.83	7.89
	9	2.84	2.59	3.90	5.92	3.35	3.52	2.07	4.44	4.46	3.16		8.17	9.20	11.72	11.33	6.99	8.03	6.43	14.65	10.90	8.41
Mo_3	1	129.78	108.37	100.82	76.78	116.08	84.14	98.71	110.93	92.73	137.15	Ni_3	43.87	32.14	35.82	34.14	56.33	45.96	50.71	49.75	41.84	43.99
	2	182.55	145.65	118.25	93.44	138.96	121.87	117.00	83.66	131.89	159.20		53.25	42.93	32.60	44.69	48.21	65.63	68.01	35.51	55.72	49.73
	3	180.79	151.48	154.67	43.41	149.48	123.96	112.30	107.94	124.17	119.08		46.35	44.80	46.31	28.19	53.25	60.03	55.03	46.89	52.66	36.05
	4	139.15	126.11	141.28	88.50	112.75	96.11	106.54	115.15	99.55	121.80		52.01	45.39	54.66	48.92	47.70	54.60	60.36	56.17	53.26	46.15
	5	59.93	85.68	46.46	67.44	93.25	74.79	73.40	64.32	68.07	84.21		29.74	34.34	18.60	38.66	34.32	48.78	47.55	38.86	40.03	35.63
	6	91.73	72.98	67.74	43.44	61.22	67.78	53.10	49.01	39.78	78.63		41.19	35.86	29.13	28.21	34.94	45.95	38.85	24.89	27.97	39.23
	7	91.66	70.46	57.10	20.66	55.76	75.43	67.90	25.45	44.53	52.76		30.22	24.30	30.18	9.45	27.85	48.10	37.26	19.05	25.17	22.65
	8	22.85	14.35	19.97	13.16	7.34	11.04	12.30	17.53	60.69	12.04		0.25	0.13	4.30	1.91	1.68	8.21	7.83	3.15	24.25	1.77
	9	15.67	10.04	17.10	7.08	10.57	12.16	2.54	21.85	11.74	6.76		1.99	0.61	2.00	1.94	3.81	7.71	1.47	9.70	5.43	1.25

Annexure-5 (contd....).

Metal fraction	Stations	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96	Metal fraction	Oct-95	Dec-95	Jan-96	Feb-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96
Pb_1	1	6.96	7.29	4.21	0.51	0.47	0.34	0.89	6.88	7.37	0.69	Zn_1	7.11	0.66	0.38	0.73	0.97	0.24	7.48	1.66	1.04	1.59
	2	5.61	6.91	6.34	0.20	0.73	0.55	0.69	8.03	8.74	0.71		2.74	0.56	2.21	0.95	1.17	2.34	3.20	3.24	2.60	4.26
	3	5.74	10.27	6.09	0.27	0.28	1.10	0.83	8.22	6.65	0.71		3.80	1.54	1.04	0.79	0.60	6.09	8.08	3.50	7.39	0.70
	4	4.28	9.25	3.96	0.26	0.49	0.76	0.46	6.48	5.00	0.95		2.58	0.87	0.91	0.69	0.36	1.13	0.70	1.30	0.79	0.89
	5	3.60	8.06	3.93	0.03	0.23	0.50	0.55	5.91	5.37	0.46		3.60	0.45	0.51	0.72	0.59	0.93	0.72	0.39	0.65	0.48
	6	4.09	6.36	5.85	0.32	0.07	0.50	0.40	6.44	5.25	0.45		1.89	0.53	0.30	0.37	0.10	0.56	0.79	0.53	0.75	0.34
	7	4.61	8.42	4.25	0.26	0.35	0.32	0.38	4.69	5.92	0.74		0.50	0.46	0.29	0.27	0.17	1.59	0.66	0.60	0.58	0.96
	8	3.57	4.81	3.19	0.19	0.38	0.07	0.44	3.36	7.35	0.32		0.38	0.48	0.13	0.25	0.17	0.34	0.36	0.21	0.47	0.28
	9	1.99	4.61	3.65	0.20	0.28	0.32	0.29	4.70	2.78	0.18		0.30	0.25	0.18	0.38	0.26	0.07	0.10	0.23	0.09	0.15
Pb_2	1	19.70	15.53	16.41	12.82	17.42	11.86	15.73	19.53	23.45	20.22	Zn_2	12.36	14.91	14.62	18.52	26.28	17.16	20.67	22.89	30.60	27.93
	2	16.86	15.55	15.44	13.89	19.18	17.15	8.60	20.53	31.02	25.56		23.17	14.87	20.53	21.87	27.93	23.60	17.23	23.77	34.32	30.96
	3	17.57	21.07	19.14	12.26	12.56	18.13	7.86	22.05	28.52	19.91		23.62	23.19	18.47	19.23	23.53	27.74	14.30	22.59	30.50	26.54
	4	11.58	17.38	12.33	12.10	15.77	9.29	5.20	17.16	17.86	20.13		12.78	17.66	15.95	13.35	21.59	13.54	15.83	22.93	21.14	25.39
	5	8.63	13.33	10.17	13.38	8.63	12.83	6.94	16.58	19.68	16.50		12.38	8.10	10.33	16.07	12.91	20.31	11.90	17.48	23.36	21.47
	6	11.33	10.88	14.26	11.61	5.06	12.60	3.55	14.92	18.44	15.02		13.51	9.78	16.68	17.00	10.44	19.99	7.67	16.88	18.78	14.87
	7	13.44	11.19	5.52	7.57	14.89	10.49	4.70	9.51	20.96	11.41		15.27	11.36	7.72	10.60	18.36	14.01	6.27	8.96	20.12	15.01
	8	8.26	6.02	6.20	4.30	2.28	4.87	2.68	5.23	30.02	6.39		8.52	5.39	4.67	4.06	2.67	5.11	3.96	4.12	27.79	6.66
	9	4.59	5.03	7.13	7.96	4.36	3.05	1.90	8.63	10.03	5.69		4.27	3.54	4.31	12.13	4.87	3.88	1.88	9.31	6.63	4.75
Pb_3	1	34.95	37.38	81.95	40.21	38.94	55.16	59.19	42.37	46.72	42.03	Zn_3	132.15	119.05	126.54	67.25	99.29	125.56	148.67	168.44	196.74	77.75
	2	50.03	50.65	27.44	48.92	44.65	60.80	72.39	42.00	64.08	49.09		133.68	108.36	128.66	73.15	106.98	153.68	164.53	161.33	239.62	77.19
	3	53.67	46.38	32.76	38.63	54.50	62.25	70.18	44.31	58.54	34.92		137.71	121.22	138.30	91.85	113.46	143.87	146.85	172.05	229.13	61.40
	4	48.54	49.87	57.85	43.16	43.62	70.03	79.56	58.93	66.99	43.97		156.23	138.39	176.44	106.02	119.26	209.45	177.36	172.53	250.07	94.48
	5	50.36	30.53	37.21	58.92	49.74	67.24	76.92	41.36	60.77	37.26		150.02	124.68	172.78	93.13	115.03	166.83	169.54	162.23	196.12	94.52
	6	40.03	40.34	38.63	50.44	45.89	63.48	69.22	41.61	42.78	28.99		158.82	144.49	179.18	99.19	130.48	172.89	167.11	187.11	163.62	80.63
	7	35.11	30.13	31.59	35.61	30.51	57.64	66.65	35.33	40.21	25.12		125.93	120.42	148.41	68.42	109.97	157.21	162.72	143.69	229.39	66.25
	8	5.03	2.66	2.98	31.53	11.89	33.45	41.55	18.92	36.54	9.17		47.43	53.31	84.58	56.82	53.56	93.94	93.89	76.80	214.20	20.60
	9	4.56	5.89	0.82	18.98	10.81	31.07	31.71	26.07	26.39	6.39		42.49	46.08	78.57	24.28	49.47	88.68	76.65	122.49	180.33	16.16