PARTITION GEOCHEMISTRY OF SELECTED ELEMENTS OF SEDIMENTS FROM ZUARI ESTUARY, GOA, CENTRAL WEST COAST OF INDIA

Ph.D. THESIS

BY

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M.Sc.

PARTITION GEOCHEMISTRY OF SELECTED ELEMENTS OF SEDIMENTS FROM ZUARI ESTUARY, GOA, CENTRAL WEST COAST OF INDIA

THESIS

SUBMITTED TO THE GOA UNIVERSITY

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

IN MARINE SCIENCE

BY

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UNDER THE GUIDANCE OF

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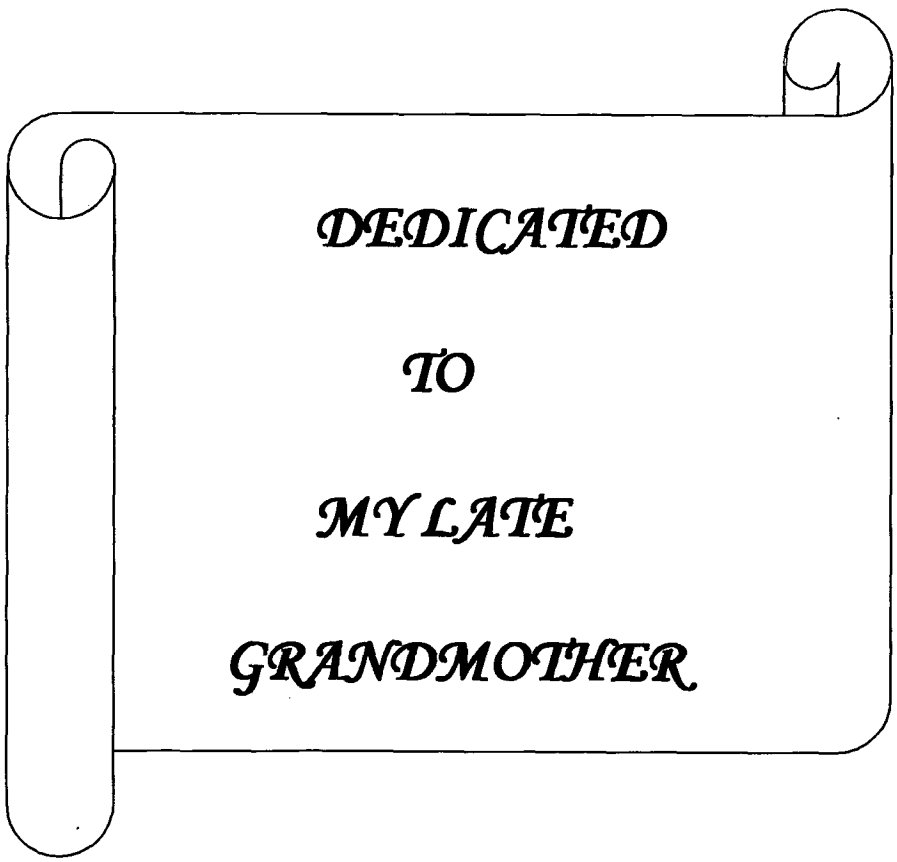
DEDICATED
TO
MY LATE
GRANDMOTHER

STATEMENT

As required under the University ordinance OB.9.9 (iv), I state that the present thesis entitled **"PARTITION GEOCHEMISTRY OF SELECTED ELEMENTS OF SEDIMENTS FROM ZUARI ESTUARY, GOA, CENTRAL WEST COAST OF INDIA"** is my original contribution and the same has not been submitted on any previous occasion. To the best of my knowledge, the present study is the first comprehensive work of its kind from the area mentioned.

The literature related to the problem investigated has been cited. Due acknowledgements have been made wherever facilities and suggestions have been availed of.

Place: Goa, India

Date: 10.12.2008

Deepti V. G. Dessai.

CERTIFICATE

This is to certify that the thesis entitled *"PARTITION GEOCHEMISTRY OF SELECTED ELEMENTS OF SEDIMENTS FROM ZUARI ESTUARY, GOA, CENTRAL WEST COAST OF INDIA"* submitted by *Ms. DEEPTI V. G. DESSAI* for the award of the Degree of Doctor of Philosophy in Marine Science is based on her original studies carried out by her under my supervision. The thesis or any part thereof has not been previously submitted for any other degree or diploma in any universities or institutions.

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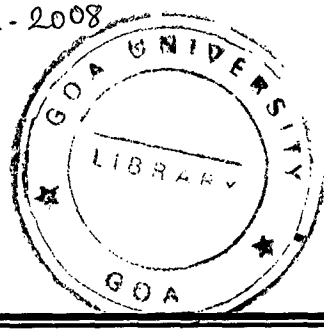

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PREFACE

Estuaries are unique environments of the coastal zone where freshwater meets and mixes with salty oceanic waters. They are highly productive supporting a wide range of habitats and species. The estuarine regimes are governed by several factors such as river inflow, tides, waves, wind and meteorological forces making the system dynamic, thus temperature, salinity, turbidity and other parameters fluctuate on tidal, daily, fortnightly and seasonal basis. Hence estuaries present a diverse and perhaps the most complex environment. Further estuaries are the important sites of ports and harbours, vital for shipping and transportation. In the recent years, due to increase in population and industrialization estuaries are under anthropogenic stress and have gained considerable scientific interest, especially because of their environmental significance with special reference to pollution.

Sediments play a key role in the geochemical processes in an estuarine environment. Estuaries receive sediments either in the form of suspended load or as bed load. Suspended load is a complex mixture of organic and inorganic substances. The behaviour of suspended matter is influenced by dynamic characteristics of estuarine waters. It acts as scavenger for trace metals because of its adsorbing characteristics and therefore plays a vital role in transport of metals within the estuary. Trace metal bound to suspended matter remain biologically available in the fluid medium, and may be incorporated in the food web. Flocculation process allows suspended matter to get settled down and deposit as bed load surface sediment. Sources of bed load sediments include input from terrestrial as well as marine environment. Estuary itself can be an important source of sediment through in situ processes. Bed load sediments are major sinks of

metals in the hydrological cycle and since the metals are partitioned with the surrounding waters, they reflect the quality of an aquatic environment. Metals are not necessarily fixed permanently to the sediment but may get recycled via biological and chemical agents, both within the sedimentary compartment and back into water column. Fine sedimentary deposits, or mud with high organic matter content are a most characteristic feature of estuaries which can, sometime through adsorption, play an important role in the mobilization of trace metals in the estuaries. It is well known that trace metals are micronutrients, which are essential for sediment ingesting organisms. Once deposited in the sediment, these metals can be accumulated by benthic-dwelling organisms, which live and feed on the sediment. But at higher doses even these nutritionally essential metals can cause adverse effects. Benthic organisms are food for several higher trophic levels and these transformations of contaminants can lead to several adverse effects.

In sediments, metals can be present in various forms, and generally exhibit different physical and chemical behaviour in terms of chemical interactions, mobility, biological availability and potential toxicity. Mobility of metals, as well as their bioavailability and their related toxicity to plants and animals depend upon the chemical form in which the metal is present under various environmental conditions. The availability of metals to the estuarine organisms depends on the nature of geochemical component which is considered to influence the bioavailability. The most important geochemical components which influence the bioavailability of the metals are organic matter, Fe-Mn oxides, and carbonates. Therefore studies of metal distribution in various geochemical phases in sediment is particularly important in estuaries as

speciation is likely to be influenced by the constantly changing environmental conditions including salinity, pH and sediment redox potential.

In view of the foregoing, Department of Marine Sciences, Goa University started a detailed program of study on estuaries of Goa. Being one of the major estuaries, Zuari Estuary was selected for present study. The principal objective of this thesis is to study the surface sediment characteristics and geochemistry of the estuarine sediments, both suspended and bed load and to establish the geochemical relationship with the sediment component to determine the abundance, distribution and source of metals and to evaluate the scale of pollution of Zuari Estuary.

The thesis comprises of five chapters. Chapter 1 deals with the introduction wherein, importance, definition, classification and evolution of the estuaries are briefed. The behaviour of sediments (suspended and bed load), their role in transport of metals in the estuary, metal speciation, role of finer sediments and organic matter in the distribution of contaminants are dealt in detail. A literature review on total metals in suspended and bed load sediments and speciation of metals in bed load sediments are presented in this chapter considering the contents of present work. This is followed by the description of the study area.

Chapter 2 presents details of materials and methods adopted. Collection, preservation and standard analytical methods followed to accomplish the objectives of the present study are presented in this chapter.

Chapter 3 describes the spatial variation of salinity, pH, total suspended matter (TSM) and its associated metals within Zuari Estuary. Variation of TSM was discussed with respect to salinity changes. TSM data was compared with earlier studies in order to perceive variation of TSM over the years. Data was subjected for R-mode factor and correlation analysis to understand the associations of metals and source. Abundance and distribution of metal content in TSM is described in relation to the processes occurring in the estuary. SEM photographs of selected samples are also presented in this chapter. TSM chemistry was normalized with Aluminium to understand the degree of anthropogenic influence. Also, in order to understand the seasonal variations of different parameters associated with TSM, data is plotted on isocon diagram.

Chapter 4 describes the sedimentological parameters viz. sand, silt, clay and organic carbon, their abundance and distribution along the estuary with seasons. Based on sand, silt and clay, prevailing hydrodynamic conditions in the estuary were discussed. Variations in clay minerals were discussed for the selected stations. This chapter also deals with the elemental chemistry of the surface sediments, their abundance and distribution. The environmental status of the estuarine sediments was discussed by using different pollution indices. Relation between organic carbon, sedimentological parameters and metals were established and variations were discussed. Data was subjected to correlation, R-mode factor and cluster analysis to understand their associations and source. Magnetic parameters viz. magnetic concentration, mineral and grain size were also discussed and relation between these and metals and grain size was obtained. To delineate the behaviour of metals with respect to land

and marine source, the Zuari Estuary was divided into two parts i.e. upper and lower estuary and the data from the two parts, including the data of TSM was subjected to correlation analysis separately and possible factors were identified.

Chapter 5 deals with speciation of metals of bed load sediments which involves five - stage sequential extraction. The variations of metals in different phases viz. exchangeable, carbonate, Fe-Mn oxide, organic bound and residual fractions are described with seasons along the Zuari Estuary. The results obtained were discussed with respect to source, mode of occurrence, biological availability and transport of trace metals. The inter-seasonal variations between the different parameters such as metals, sediment components along with near bottom water salinity and pH in five different phases / fractions were studied by using the isocon plots. The total metal concentrations in bioavailable fractions were compared with Sediment Quality Values (SQV) following Screening Quick Reference Table (SQUIRT) developed by NOAA to understand the risk of these metals to the benthic dwelling organisms. Finally, correlations were obtained between total metals and the metal species to understand their relations and source.

A summary of the thesis is presented at the end of the five chapters which briefs the generalized observations and conclusions derived from the interpretations and discussions. The references cited in the thesis are listed separately in alphabetical order.

Chapter I

INTRODUCTION

1.1 Introduction

The coastal zone is characterized by variety of landforms like the estuaries, lagoons, beaches, islands etc. Estuaries are one of the most important sub environments of the coastal zone which cover shallow marine waters, freshwater, salt marshes, swamps, sandy islands, mud and sand flats, oyster reefs, mangrove forests, tidal pools and sea grasses. Estuaries are rich in nutrients and are potential sources for flora and fauna and thus provide shelter to thousands of animal and plant species. Further, they are the important sites of ports and harbours, vital for shipping, transportation and industry. As the population grows, demands for the natural sources increases. Dredging, transportation, dumping, shoreline reconstruction to accommodate human housing, agricultural practices and industries affect the health of the estuaries by giving rise to pollution in many ways. Increase in population affects the natural balance of estuarine ecosystems threatening their integrity. Therefore, it is necessary to protect the estuaries to conserve the natural resources.

Estuaries are coastal bodies of water, occupying an existing river valley and their characters are typified by the discharge of rivers and therefore they are regarded as complementary extensions of rivers. In simple terms, an estuary is the region where a river meets an inlet of the sea. Estuarine regimes are governed by several factors such as river inflow, tides, waves, wind and meteorological forces making the system more complicated and dynamic thus temperature, salinity and turbidity fluctuate on daily, fortnightly and seasonal basis and reach more extremes in estuarine waters than they do at sea or in rivers. Thus estuaries present a diverse and perhaps the most complex environment, hence they pose a constraint on any attempts at giving a specific definition and organizing a systematic classification.

The term "estuary" is derived from Latin word, aestuarium meaning marsh or channel, which itself is derived from aestus, meaning tide or billowing movement, related to word aestas meaning summer. The definition of an estuary differs from

one researcher to the other based on their scientific approach. One of the widely used definitions of an estuary has been given by Pritchard (1967) and is as follows. "An estuary is a semi-enclosed coastal body of water, which has a free connection with the open sea, and within which sea water is measurably diluted with fresh water derived from land drainage." According to Fairbridge (1980) "An estuary is an inlet of the sea reaching into a river valley as far as the upper limit of tidal rise, usually being divisible into three sectors (Fig. 1.1): a) a marine or lower estuary, which has free connections with the open sea; b) a middle estuary subject to strong salt and freshwater mixing; and c) fluvial or an upper estuary, characterized by freshwater but subject to strong tidal action. The limits between these sectors are variable and subject to constant changes in the river discharge and tide.

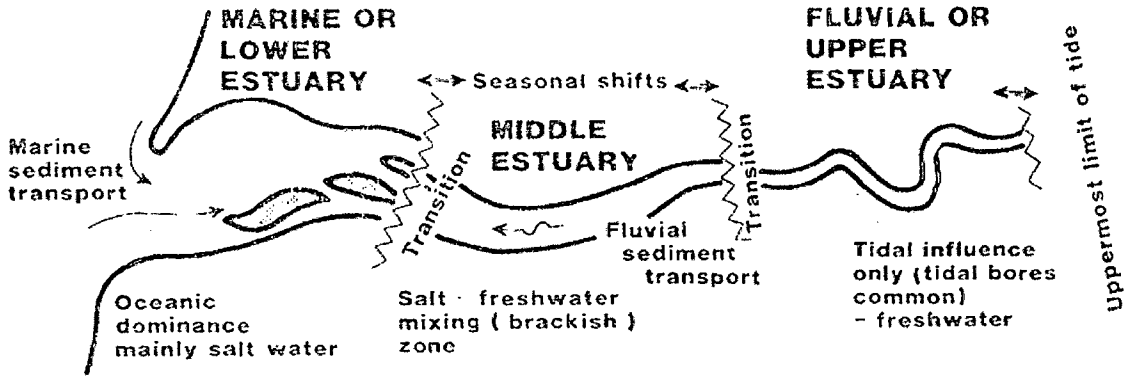


Fig. 1.1: Estuary showing three divisions – Lower, middle and upper estuary: The boundaries are the transition zones that shift according to season, weather and tides (After, Fairbridge, 1980).

Classification of estuaries is a difficult task. However attempts have been made to classify them on the basis of geomorphological set up of the estuary (Pritchard, 1967); on the basis of tidal range (Davies, 1964), which was further elaborated by Hayes (1975) and on circulation pattern or advection-diffusion criteria (Pritchard, 1967).

Based on geology / geomorphology, Pritchard (1967) gave the following classification a) Drowned river valleys estuaries or coastal plain estuaries: These

are formed as a result of sub aerial weathering and / or sea level rise. They usually are relatively shallow, V-shaped and show meandering characteristics. Their depth and width increases uniformly towards the mouth of the estuary. b) Rias: These are special type of drowned river valley estuaries which have dissected mouth. c) Fjords: Fjords are estuaries that have been formed by glacial erosion, generally occur at higher latitudes, are relatively long and deep, and possess a shallow sill at the fjord mouth and fjord intersections. d) Bar-built estuaries: These estuaries are formed by the same processes as in the drowned river valleys. The difference is that sedimentation has kept pace with inundation, with a characteristic bar forming at the mouth. e) Estuaries formed due to tectonic processes: These are formed due to faulting, folding, earthquake, volcanoes or other diastrophic movements.

Based on tides, estuaries are classified as follows. a) Microtidal estuaries: These are formed wherever the tidal range is less than 2 m and are dominated by freshwater discharge, which leads to "salt wedge" type estuary. These are highly stratified. b) Mesotidal estuaries: These are formed wherever the tidal range is between 2 to 4 m. These estuaries have meandering characteristics. In this type of estuaries, formation of two deltas takes place called as ebb tide delta and flood tide delta (Boothroyd, 1978) due to time velocity asymmetry. c) Macrotidal estuaries: These are formed wherever there are strong tidal currents (tidal range is more than 4 m). These are trumpet in shape. Long linear sand bars are formed parallel to tidal flow near the mouth of the estuary.

Based on flow pattern / circulation, Pritchard (1955) gave the following classification. a) Type A - Salt wedge estuary: These are highly stratified and are river dominated. These exist wherever there is small tidal range and they show sharp salinity changes. They hold large quantity of suspended load. b) Type B - Partially mixed estuary: This type of estuaries occur when the volume rate of flow of the estuary during a flood tide is about ten times the volume rate of inflow of freshwater from the river. Both advection and turbulent mixing occurs across the

freshwater-saltwater interface in this type of estuary. They show variation in salinity and there is large accumulation of suspended matter. c) Well mixed or fully mixed estuaries: These estuaries are shallow and wide with stronger tidal currents relative to the river flow in them. In well-mixed estuaries, salinity hardly varies with depth, although it may vary considerably across the width of the estuary. These estuaries have marine dominance and are influenced by the earth rotation.

The estuary is an ephemeral feature in long term geologic history and must be regarded as a dynamically evolving landform that will go through a life cycle from valley creation, followed by the drowning phase and ending with the progressive infillings. Every estuary is unique and is subjected to differing physical constraints and therefore, evolving at different rates. Almost all the estuaries have originated as a result of the recent rise in sea level which has initiated around 18,000 years ago when sea level was approximately 100 to 125 m below the present level. With warming up of the atmosphere, glaciers began to retreat, consequently raising the sea level. As a result, the sea advanced across the shelf and progressively drowned the river channels giving rise to present estuaries. Around 5000 to 3000 years ago estuaries reached their peak in development, in number, size and complexity (Schubel, 1984).

1.2 Estuarine Sediments

Estuaries are the favorable environments of deposition of sediments derived from both the catchment area (terrestrial) and the marine sources. So, the sedimentation in estuaries is within three distinguishable regimes viz. estuarine fluvial, estuarine brackish and estuarine marine. These sequences inter-finger with fluvial and marine sediments at the inner and outer limits of the estuary respectively (Dalrymple et al., 1992). Sediments are transported into the estuary from the sea as well as are washed in from the land surrounding the estuary either in the form of suspended matter or as bed load with considerable variations in size. Fine sedimentary deposits or mud are a characteristic feature

of estuaries. Sediment distribution in estuaries is mainly controlled by the influence of tidal and river currents and also on the particle size of the sediments. Erosion, transportation and deposition of sediments in different depositional environments may possess distinctive sediment size distributions (Priju and Narayana, 2007). However, other factors such as geo-morphology, bedrock geology and sediment input from the catchment area basically through runoff can modify the general pattern. The relations between these factors are complex and often inter-dependent. The dependence of the mobility of the sediment on the hydraulic conditions leads to a progressive sorting of the sediments with respect to composition and size. The most significant sorting is the coarse (gravel and sand), which are found in the more energetic areas and fine (silt and clay) sediments, which accumulate in low energy conditions or quiet waters. The rate of deposition or the settling velocity of sediments is related to particle diameter. Fine particles in estuaries are either single particles dispersed in suspension or they may coalesce and form composite particles which are referred as flocs, aggregates, or agglomerates (Nichols and Biggs, 1985). In many estuaries, the suspended matter develops "turbidity maxima". The position of the turbidity maxima is generally determined by the contribution of suspended sediment from the seaward end of the estuary. These suspended particles, which are derived from several sources act as scavenger for trace metals because of their adsorption characteristics and thus play a vital role in transportation of metals into the estuary. The adsorption of metals on to the suspended matter is mainly controlled by the grain size of the sediment. Seasonal differences in metal concentration in suspended matter due to the effect of grain size have been reported by Qiao et al. (2007). Further, suspended matter acts as food for many organisms present in the estuaries. Trace metals available and bound to suspended particles remain biologically available in the fluid medium, and then may be incorporated into the food web by filter or suspension feeders or even by direct ingestion of the nutrient. It is well known fact that trace metals are micronutrients, that are essential for biological life or others that are adsorbed on to the suspended matter or in suspension. But at higher doses even these

nutritionally essential metals can cause adverse effects. Therefore, estuaries are rightly described as chemical reaction vessels in which solutions with different chemistries are mixed in the presence of reactive particles (Goldberg, 1978).

Further, like suspended matter, bed load sediments also play a key role in the geochemical and biological processes of an estuarine ecosystem. Since they are major repositories of metal and, in addition to providing the environmental status; they are also used to estimate the level of pollution in a region (Burton Jr. and Scott, 1992; Caccaia et al., 2003; Simeonov et al., 2007). Once released into the environment, trace metals may interact with suspended matter and will be subsequently removed from the water column facilitating deposition. Metals are not necessarily fixed permanently by the sediment, but may be recycled via biological and chemical agents, both within the sedimentary compartment and also back into the water column (Salomons and Forstner, 1984). Once deposited in the sediment, these metals can be accumulated by benthic-dwelling organisms which live and feed on the sediment (Engel and Fowler, 1979; Bryan and Langston, 1992; Tessier et al., 1994; Zoumis et al., 2001). Benthic organisms are food for several higher trophic levels and these transformations of contaminants can lead to several adverse effects (Blomqvist et al., 1987; Ferns and Anderson, 1994; Thompson and Lowe, 2004; Anderson et al., 2007). Metals are natural constituents in nature, but anthropogenic activities can cause elevated levels of these metals in various parts of the system (Everrats, 1989; El. Hassan and Jiries, 2001; Homady et al., 2002). Once the metal concentration exceeds the certain level, they may lead to severe environmental problems.

It is also necessary to mention here that the sediments are composed of different geochemical phases such as clay, silt, sand, organic material, oxides of iron and manganese, carbonate and sulphide complexes that act as potential binding sites for metals entering an estuarine system (Shea, 1988; Jonathan et al., 2004). In the sediments, metals can be present in various forms and generally exhibit different physical and chemical behaviour in terms of chemical

interactions, mobility, biological availability and potential toxicity (Almas et al., 2006). Studies of metal distribution among various geochemical phases of sediment is particularly important in estuaries since speciation is likely to be influenced by the constantly changing environmental conditions including salinity, pH and sediment redox potential (Gambrell et al., 1980; Kersten and Forstner, 1986; Calmano et al., 1993; Paludan and Morris, 1999).

Dispersal of sediments in the estuary is controlled by the estuarine circulation pattern and also by the changes in the dynamic properties of river water in the estuarine environment, which results in the accumulation of fine-grained sediment with a high organic matter content. Sometimes finer sediments and organic matter through adsorption play an important role in the transport of trace metals to the sea floor (Krauskopf, 1956; Burton and Liss, 1976; Ip et al., 2007). Natural processes and human activities have resulted in elevated concentration of organic carbon in sediments. Sources of organic carbon include organic matter from land runoff, shoreline erosion and primary productivity all of which eventually settle to the bottom and are incorporated into the sediments. It has been also established that organic carbon gets selectively enriched in fine particles of estuarine sediments (Hunt, 1981). It is also well documented that metal concentrations increase in the regions that are dominated by fine particulate matter (Zhou et al., 2003; Hakanson et al., 2004). Sediment characteristics allow accumulation and integration of metal over time (Thompson et al., 1984; Tsai et al., 2003). So, it was obligatory to measure the abundance of different sediment parameters viz. sand, silt, clay and organic carbon and to understand their role in distribution of trace metals.

1.3 Objectives

Considering the importance of studying geochemistry of the estuarine sediments, both suspended and bed load, and to establish the geochemical relationship with the sediment component to trace the sources and further, to understand the present status and evaluate the pollution level of the sediments of Zuari Estuary,

Goa, central west coast of India, the present study was undertaken with the following objectives.

1. To study the seasonal variations in distribution of the suspended sediment and its geochemistry within the estuary.
2. To study the sedimentology, mineralogy (clay), geochemistry (selected elements) and magnetic susceptibility of bed load sediments.
3. To study the partition / speciation of selected elements in bed load sediments and to understand the anthropogenic impact.

1.4 Previous Studies

Vast literature is available on different aspects of the estuaries, all over the world. With rapid increase in population and industrialization during the last few decades, the estuaries have come under increasing stress due to anthropogenic activities that disturbs the pristine system. This made the researchers to work on estuaries on different aspects in order to understand environmental status and suggest remedies. Geochemical investigation in various Indian estuaries both along east coast and west coast have been undertaken to study the environmental conditions, by Venugopal et al. (1982), Nair et al. (1987), Biksham and Subramanian (1988), Ramanathan et al. (1988), Subramanian and Jha (1988), Subramanian et al. (1988), Zingde et al. (1988), Devavarma et al. (1991), Rao and Swamy, (1991), Modak et al. (1992), Nayak and Bukhari (1992), Nair and Balchand (1993), Nayak (1993), Bukhari (1994), Mohan, (1995), Bukhari and Nayak (1996), Nair and Ramachandran, (2002), Singh (2000), Singh et al. (2005), Balachandran et al. (2006), Alagarsamy, (2006) and Nayak et al. (2008).

Various parameters related to chemistry and biogeochemistry of estuaries was well studied by Burton and Liss (1976) and Olausson and Cato (1980). 'Metals in hydrocycle', a book by Salomons and Forstner (1984) is one of the contributions where different environments including estuaries are explained in detail. Currently, many periodicals and journals are available in which research articles

on different aspects of estuaries including geochemistry of estuarine sediments are well covered and published.

1.4.1 Total Suspended Matter (TSM)

Literature on the assessment of metals in total suspended matter and their distribution in the estuarine region is limited in India, but a large number of published literatures are available on different aspects on the suspended matter as a whole, all over the world. It is well established that estuaries are efficient traps of suspended matter and associated trace metals (Kennedy, 1984; Bewers and Yeats, 1989; Turner and Millward, 2002). Chemical composition of suspended matter in estuaries is affected by several processes such as mixing of riverine suspended matter and particles of marine origin (Nolting et al., 1990); resuspension of sediments (Turner et al., 1991); mobilization of Fe and Mn in reducing sediments (Feely et al., 1986); flocculation of colloidal material (Turner and Millward, 2002); sorption in low salinity and high turbidity zones (Gobeil et al., 1981); production of organic matter (Collier and Edmond, 1984) and industrial and urban waste water discharge (Nolting et al., 1999).

Both the major and minor elements of suspended matter in the Rhine and Meuse Rivers and Estuary were studied by Nolting et al. (1989), wherein they recorded decrease in trace metal concentration in suspended matter towards the sea, which they have related to mixing of river-borne and marine-derived suspended sediments. Manganese removal in the estuaries is a common feature of many estuaries. This phenomenon was observed by Byrd et al. (1990) in the Geum Estuary, Korea, which was attributed to scavenging of dissolved Mn by the suspended particles due to turbidity maxima. Also, Co and Zn were observed to be removed in the low salinity region due to precipitation with the iron or scavenging by particles in the turbidity maximum. Biksham et al. (1991) had studied the heavy metal distribution in suspended and bed load sediments from the Godavari River basin. They reported higher concentrations of metals in the suspended sediments than in the bed load sediments. In this study, all the metals

showed high correlation among themselves and the correlation was more pronounced in the suspended sediments than in the bed load sediments. Distribution of trace metals in suspended matter as a function of grain size has been studied by Regnier and Wollast (1993) in the Scheldt Estuary. Their attempt in normalizing the elements with Al has helped in evaluating the degree of pollution and also allowed characterization of origin. They also observed that the elements in the mixing zone did not behave conservatively and were affected by changing physico-chemical conditions such as salinity, pH and redox. Bukhari (1994) had studied the systematic distribution of total suspended sediments (TSM) in Mandovi Estuary, Goa. He observed general decreasing trend of TSM from mouth towards upstream of the estuary during pre-monsoon and post-monsoon seasons whereas, higher concentrations were reported towards the head region during monsoon season. He also reported high concentration of metals in the suspended sediments compared to bed load sediments. Herut and Kress (1997) reported particulate metal contamination in the Kishon River Estuary, Israel. They found reduction in the Mn concentration at the anoxic and low pH zone and precipitation of Mn oxides with increase in pH and dissolved oxygen concentration. Non-conservative behaviour of metals was reported in this estuary due to mixing between polluted river-borne particles and coastal origin. While studying the transport and transformation of trace metals in the Scheldt Estuary, Paucot and Wollast (1997) reported higher concentrations of Cd, Cr, Cu, Pb and Zn in the suspended matter. Higher concentration of metals was related to the river discharge during the study period by them, which suggested resuspension of fluid mud under high river discharge. Zwolsman and Van Eck (1999) had studied elemental concentration in the suspended matters from Scheldt Estuary. Their result emphasized that the composition of suspended matter were controlled by various processes such as resuspension, desorption, phytoplankton activity and the most importantly the physical mixing of fluvial and marine particulates which leads to a continuous decrease in the trace metal content with increasing salinity.

Contrasting geochemistry of suspended matter and deposited sediment was studied by Stecko and Bendell-Young (2000) with respect to metal concentration and organic matter. A distinct seasonality in geochemistry was observed for suspended matter relative to deposited sediments. A major implication of their study was the bioavailability of metals in the SPM which changes with the season. Niencheski and Baumgarten (2000) studied the trace metal distribution in the southern part of the Patos Lagoon Estuary. Their results indicated that the local inputs and industrial and harbour activities enriched suspended particles with the trace elements. Distribution of trace metals in the Hindon River system, India, was studied by Jain and Sharma (2001). Their study has revealed that the fine sediment fraction, organic matter and Fe / Mn played an important role in transport of metal ions. Turner and Millward (2002) had studied the role of suspended particles in the chemical and biological cycling of trace constituents in estuaries, with particular emphasis on the effects of and changes to particle reactivity and composition. While studying the heavy metal content in the bed and suspended sediments of Anyang River, Lee et al. (2003) found more than 99 % of the elements determined were associated with the river bed sediments. Also, they found high organic carbon in the estuary suggesting most of the metals in the estuary were complexed and settled down rather than transported as free ions or colloides. Wang and Liu (2003) had studied the distribution of heavy metals in Changjiang Estuary in eastern China. Their results showed that metal distribution in this estuary was mainly controlled by concentration of suspended matter and the salinity. Sadhuram et al. (2005) reported high values of total suspended matter in both surface and bottom water of Hooghly Estuary, India, showing the impact of fresh water on sediment transportation. Caetano et al. (2006) had studied the distribution of major as well as trace metals in suspended matter in the different flow and tidal conditions along the Guadiana Estuary. Their results indicated that the flood played an important role in transport of material to the estuary and adjacent coastal zone with lower metal content. Qiao et al. (2007) had studied the metals in suspended sediments from the Changjiang (Yangtze River) and Huanghe (Yellow River) to the sea. Their

results reflected that the parent material, weathering process and anthropogenic activities along their drainage basins contributed to the metals in suspended matter. They also reported the seasonal difference in the metal concentration and related the same to grain size. While studying input of particulate heavy metals from rivers and associated sedimentary deposits on the Gulf of Lion continental shelf, Radakovitch et al. (2008) noticed variations of particulate metal fluxes in the rivers, which were driven by water discharge and SPM concentration.

Several other researchers like Adamiec and Helios– Rybicka (2002), Guieu and Martin (2002), Lee et al. (2003), Cenci and Martin (2004), Nakatsuka et al. (2007), Schoellhamer et al. (2007) also carried out studies on suspended matter particularly on its geochemistry, in the recent years.

1.4.2 Bed Load Surface Sediments

Several studies were carried out on the geochemical behaviour and distribution of total concentration of metal contaminants in estuarine and marine sediments (Hamouda and Wilson, 1989; Gray, 1996; Kot et al., 1999; Shumilin et al., 2001 etc.). Geochemisry of surface sediments provide important clues regarding the source and the processes through which metals get accumulated. In the estuarine environment, the two processes that can potentially contribute to the surface sediment geochemistry include riverine input (Benoit et al., 1994) and sediment diagenesis (Canfield, 1989). Diagenetic reactions are important near the sediment-water interface in responding to redox changes and affecting metal concentration. Iron and manganese oxides (oxyhydroxides) are also considered as strong scavengers of metals, affecting trace metal mobilization because they precipitate under oxic conditions and dissolve in anoxic environment (Jingchun et al., 2006). According to Lin and Chen (1998), dissolved and particulate organic matter in the water column acts as scavenger for metals and once these elements are trapped they are precipitated and incorporated into the sediment. Metal concentration in sediments within the estuaries can be influenced by

factors such as salinity (Coakley et al., 1993), water discharge (Forstner and Whittmann, 1981), flow rates (Schoellhamer, 1995) and geomorphological setup. Most of the studies carried out on total metal concentration in sediments recognized the important role of organic carbon and grain size on the geochemical behaviour of these elements (Forstner and Wittmann, 1979; Horowitz, 1991; Lin and Chen, 1998; Bilali et al., 2002; Navas and Machin, 2002). Several authors (Loring, 1981; Palanquez and Diaz, 1994; Zhang et al., 2002) had observed that the high concentrations of many elements like Cu depend on finer sediments and the clay minerals present. They had also stated that the hydrodynamic conditions control the spatial distribution of grain size and metal concentrations. Luoma et al. (1995) observed that chlorine compounds help to keep the silver in solution in estuarine water, avoiding its precipitation; similar phenomenon can explain the low total concentration of Cu in sediment where the salinity of the upper lying water is high (Green-Ruiz, 1996). The processes involved in the distribution patterns of trace metals along the various parts of the estuaries have been found to be very complicated as a result of a great number of simultaneous and independent physical, chemical and biological factors (Salomons and Forstner, 1984; GESAMP/UNESCO, 1987; Bilinski et al., 1991). Spatial heterogeneity in the intertidal sediment geochemistry of estuaries has been reported by Luoma and Bryan (1981), Langston (1985), Luoma et al. (1990) and Morse et al. (1993). The metal concentrations reported by numerous researchers in the various Indian estuaries are presented in the table 1.1.

Biksham and Subramanian (1988) assessed the elemental composition of Godavari River sediments. They had stated that when compared to Indian mean value, Godavari sediments are enriched in heavy metals and are depleted in Al and K. Rodrigo (1989) had studied the heavy metal association in surface sediments in the Avon-Heathcote Estuary, New Zealand. He reported high concentration of metals in the coarser fraction of sediments as finer sediment particles tend to flocculate in saline conditions, thereby decreasing the effective adsorptive surface area of the sediments. He had made an observation that

estuaries with high coarse silt content may be more susceptible to heavy-metal toxification of surrounding waters, than those with high proportions of clay and very fine silts. Zwolsman et al. (1996) had studied the spatial distribution of trace metals in the sediments from the Scheldt Estuary, southwest Netherlands in order to identify trends in space and time. The concentrations of Cd, Mn, Ni and Pb in surface sediments of the lower Ulla River and its estuary (northwest Spain) were studied by Prego et al. (1999). They have used enrichment factor to evaluate the level of pollution.

Angelidis and Aloupi (2000) had studied the impact of river transported metals in coastal sediments of Evoikos, Gulf, Greece. They have used cluster analysis to clarify the pattern of metal distribution in the sediments and concluded that river mouth acts as a point source of metals for the marine sediments. Rubio et al. (2000) assessed the level of pollution in the surface sediments of Ria de Vigo (northwest Spain). Geoaccumulation indices and enrichment factors were used to study the contamination of sediments by the metals. Their investigations revealed that the Ria is slightly to moderately contaminated by some of the studied metals. Spencer (2002) had studied the spatial variability of metals in the inter-tidal sediments of the Medway Estuary, Kent, UK. He had investigated metal associations and their potential sources by using principle component analysis. Nair and Ramachandran (2002) had studied the textural and trace elemental distribution in the surface sediments of the Beypore Estuary. Their studies revealed that textural characteristics and organic carbon had substantial influence on the elemental distribution. Wilson (2003) evaluated the estuarine quality status at system level using the biological quality index and the pollution load index. Bareille, et al. (2003) carried out the study to understand the trace metal variability in sediments of Adour Estuary, southwestern France.

Table 1.1: Range and average concentrations of different metals in surface sediments from various Indian estuaries.

Location	Fe (%)	Mn (%)	Cr (µg/g)	Cu (µg/g)	Zn (µg/g)	Co (µg/g)	Reference
Zuari Estuary	2.97-16.81	462.50-5937.50	22.75-502.00	10.50-169.50	26.25-172.25	25.50-110.75	Present study
	8.23	**3035.06**	**186.6**	**58.67**	**87.51**	**48.4**	
Zuari Estuary	2.23-16.7	0.04-0.62	60.33-388.0	7.0-74.0	23.67-165.33	12.0-36.33	Singh, 2000
	7.09	**0.329**	**162.86**	**35.00**	**88.264**	**22.583**	
Mandovi Estuary	2.2-49.7	<DL-1.61		11.5-77.5	19.9-83.5	2.5-45.3	Alagarsamy, 2006
Mandovi Estuary	2.03-12.8	0.062-6.079	68.0-403	3.67-80.67	25.00 - 149.67	3.33-32.0	Singh, 2000
	7.909	**0.37**	**264.47**	**36.987**	**87.83**	**15.506**	
Mandovi Estuary	2.2-49.7	0.01-1.18		12.9-77.5	21.0-83.5	2.5-45.3	Alagarsamy, 1988
Mandovi Estuary	3.15-11.05	0.085-1.01	224-580	31-88	38.0-102	15-35	Bukhari, 1994
Godavari Estuary	2.67-8.03	0.04-0.17	88.0-243.0	61.0-157.0	66.0-323.0	22.0-89.0	Srinivas, 1998
	5.77	**0.1**	**137**	**107**	**207**	**50**	
Godavari Estuary	0.57-23.90	0.01-0.362	12-408	3-262	4-75		Biksham et al., 1991
	6.1439	**0.1056**	**142.565**	**75.304**	**53.434**		
Ganges Estuary	**-3.1**	**0.0553**		**26**	**71**	**36**	Subramanian et al., 1988
Gomati River	0.16-0.31	0.008-0.026	2.22-19.13	BDL-35	3.06-101.73		Singh et al., 2005
	0.266	**0.0148**	**8.146**	**5**	**41.66**		

Table 1.1 (continued).

Beypore Estuary	1.99-7.09	0.0205-0.0912	88-203	2-17	25-75	11-35	Nair and Ramachandran, 2002
	7.09	**0.038**	**133**	**5**	**44**	**21**	
Cochin Estuary	**4.47**			**32.42**	**592**		Balachandran et al., 2005
Vasamdhara Estuary	3.20-7.10	0.04-0.09	8.0-128.0	25.0-55.0	50.0-250.0	20.0-45.0	Devavarma et al., 1991 and 1993
	5.28	**0.05**	**106**	**37**	**152**	**32**	
Krishna Estuary	6.6	0.2	114	124	97	29	Rao and Swamy, 1991
Cauvery Estuary	1.35-7.6	0.02-0.14	20-220	10-50		10-200	Ramanathan et al., 1988
Vellar Estuary	3.93	0.4854	222	45	196	48	Mohan, 1995
Tuticorin coast	0.224-0.432	0.029-0.125					Ganesan and Kannan, 1995
	0.316	**0.078**					
Narmada	3.14	0.0514	55	46	50	36	Subramanian et al., 1985
Tapti	10.9	0.13	108	126	118	64	Subramanian et al., 1985
Indian River avg.	2.9	0.06	87	28	16	31	Subramanian et al., 1985
World River avg.	4.8	0.105	100	100	350	20	Martin and Maybeck, 1979
Surficial rock	3.59	0.07	97	32	129	13	Martin and Maybeck, 1979
Average shale value	4.67	0.06	83	45	95	19	Turekian and Wedepohl, 1961

*Bold values indicate average concentration.

Major and minor elements were studied in the recent sediments off Gulf of Mannar along the southeast coast of India by Jonathan et al. (2004). Their studies revealed that the enrichment of Cr, Pb, Cd, Cu, Co, Ni, and Zn along the Gulf of Mannar and indicated that the area has been contaminated by riverine sources and industries nearby. Factor analysis obtained by them showed higher loading in acid leachable and its association with $CaCO_3$. Issac et al. (2005) suggested that in the absence of a sequential extraction of metals in sediments, statistical procedures can be used for making inferences on the important pathways of elements. Alagarsamy (2006) had studied the systematic seasonal distribution of trace metals such as Fe, Mn, Co, Cu, Zn and Pb in the Mandovi Estuary, west coast of India. He has evaluated sediment enrichment of metals by using "Geoaccumulation Index". His results revealed that the surface sediments of Mandovi Estuary are moderately or strongly contaminated to some extent by Fe and Mn. Cu and Zn showed the influence of organic wastes from municipal sewage entering into the estuary, in the river mouth region. Balachandran et al. (2006) had studied the coastal and estuarine sediments of Cochin with reference to heavy metal concentrations to identify the different processes of deposition. They studied the element interactions using principal component analysis (PCA) which separated two clusters comprising of heavy metal possessing significant relation with texture, which belong to sediments in the shelf region and second set of heavy metals showing poor correlation with sediment texture, which are of estuarine region. Nasr et al. (2006) assessed the heavy metal pollution (Mn, Zn, Cu, Pb, Co, Cr and Ni) in bottom sediments of Aden Port, Yemen. They have used background values depending on the international standards and contamination factor to evaluate the level of sediment contaminations. Priju and Narayana (2006) had studied the spatial and temporal variability of trace metal concentration in a tropical lagoon, south west coast of India, in order to study the environmental implications. Based on the statistical analysis they have made an attempt to understand the natural processes and anthropogenic activities in the region. Ray et al. (2006) assessed trace metal content in sediments as well as in suspended matter in the Godavari mangrove ecosystem. They have observed

significant correlations between organic carbon and Co, Cr, Pb, Cu and Mn in sediments indicating organic matter as a metal carrier. They have also calculated pollution load index (PLI) to evaluate the level of pollution. Hyun et al. (2007) had studied the heavy metal distribution in the surface sediments of Masan Bay, Korea to trace the anthropogenic contributions. They have calculated enrichment factor, organic carbon and statistical analysis to evaluate anthropogenic influence. Rufo et al. (2007) had studied the surface geochemistry of sediments from Tinto River (Huelva, Spain) wherein they found abnormally high concentrations of heavy metals. They have reported less mobile elements in the mid region of the estuary and more mobile in the estuarine region where pH was major controlling factor.

Many researchers have explored the relationship between mineral magnetic measurements and chemical / physical properties of the sediments and soils (Oldfield et al., 1986; Oldfield and Yu, 1994; Clifton et al., 1997, 1999; Chan et al., 1998; Petrovsky et al., 1998; Xie et al., 1999, 2000; Booth, 2002; Booth et al., 2005; Zhang et al., 2007). With the development of environmental magnetism, magnetic measurements have been identified as a suitable tool for evaluating pollution studies. Many researchers have worked on monitoring environmental quality and discriminating pollution sources, either independently or in combination with geochemical analysis (e.g. Oldfield et al., 1978; Scoullos et al., 1979; Hunt et al., 1984; Heller et al., 1998; Hoffmann et al., 1999; Matzka and Maher, 1999; Shu et al., 2000; Muxworthy et al., 2001; Chan et al., 2001; Jordanova et al., 2003; Desenfant et al., 2004; Robertson et al., 2003; Plater and Appleby, 2004; Urbat et al., 2004; Booth et al., 2005; Shilton et al., 2005). Chan et al. (2001) had studied the magnetic properties and heavy metal contents of contaminated seabed sediments of Peny's Bay, Hong Kong. Their results revealed a difference in the magnetic properties between contaminated and uncontaminated sediments and also, they found relatively higher magnetic susceptibility and greater heavy metal content in < 63 μm fraction of sediment.

Mineral magnetic measurements serve as a proxy for geochemical radioactivity, organic matter content and particle size data (Bonnett et al., 1988; Oldfield et al., 1993; Hutchinson and Prandle, 1994; Lepland and Stevens, 1996; Clifton et al., 1997, 1999; Xie et al., 1999, 2000; Zhang et al., 2001).

Clay minerals are powerful source indicative tools in the interpretation of marine depositional processes. The clay mineral studies reflect weathering conditions imprinted on the rock particles that were found in the source terrains (Maldonado and Stanley, 1981; Stanley and Liyanage, 1986). Mineralogy of fine grained material has also been used to understand the nature of the sedimentary environment (Brown et al., 1977) and to understand the effects of diagenetic processes on mineralogy (Hower et al., 1976). Velde (1995) had related the clay mineral distribution to the climatic control as follows i) the presence of kaolinite suggests well drained source areas with intense hydrolyses under warm and humid climate. ii) chlorite is mainly available at higher latitudes as a result of physical erosion of magmatic and metamorphic rocks and the chemical alteration is limited. iii) illite also increases towards the higher latitudes and it reflects the decrease in intensity of hydrolysis and thus an enhancement of mechanical alteration. iv) smectite distribution is not straight forward due to their double source i.e. alteration and / or authigenesis. Several researchers carried out studies on the clay mineralogy viz. Edzwald and O'Melia (1975), Sawhney and Frink (1978), Nair et al. (1982), Knedler et al. (1983), Rao and Rao (1993), Bukhari and Nayak, (1996), Suraj et al., (1996), Brockamp and Zuther (2004), Bican-Brisan and Hosu (2006), etc.

1.4.3 Speciation of Metals

It is well documented that metals are bound to different components of the sediment (Salomons and Forstner, 1984; Usero et al., 1998; Fan et al., 2002), so that different phases have been defined (Tessier et al., 1979; Pempkowiak et al., 1999; Yu et al., 2001), e.g. exchangeable ions, adsorbed ions / carbonates, Fe and Mn oxides, sulphides / organics and metals bound to lithogenic minerals and

residual. Measurement of total concentration of metals may not reflect the potential availability for biota (Loring, 1981). Numerous extraction schemes for soils and sediments have been described in the literature (Chester and Hughes, 1967; Gibbs, 1977; Tessier et al., 1979; Sposito et al., 1982; Shuman, 1982; Welte et al., 1983; Kersten and Forstner, 1986; Archer and Hodgson, 1987; Martin et al., 1998; Clevenger, 1990; Ure et al., 1993; Howard and Vandenbrink, 1999; Stephens et al., 2001; Steve et al., 2001; Tuzen, 2003; Guevara-Riba et al., 2004; Yuan et al., 2004). Among these the procedure of Tessier et al. (1979) is one of the most thoroughly researched and widely used procedures to evaluate the possible chemical associations of metals in the sediments and soils.

Nair and Balchand (1993) had studied the trace metal speciation of Mn, Fe, Cr, Ni, Zn and Co in surface sediments from the tropical estuary of Cochin. Their studies revealed selective accumulation of Mn and Ni in the carbonate and organic / sulfide fraction. Large portion of Fe and Zn was observed in the residual fraction. The level of Cr and Zn indicated anthropogenic input into the estuary, while Co and Ni showed regional contamination exceeding natural levels. Their investigations also showed diagenetic processes in the estuarine sediment. Stamoulis et al. (1996) carried out studies on speciation of metals in surface sediments from Hudsen River Estuary. Their results indicated that most of the metals are associated largely within the fine fraction of the sediment. Also, they found that the dominance of metal concentration in the finer sediment was influenced by the importance of the coating chemical phase and the size of the organic particles in the estuary. Thomas and Bendell-Young (1999) had studied the significance of diagenetic verses riverine input in contributing to the sediment geochemical matrix of iron in the intertidal region of Fraser Estuary. Their result has shown heterogeneity in sediment matrix (Organic matter, reducible iron, easily reducible manganese and grain size) throughout the intertidal estuary. Pore water chemistry suggested that diagenesis was a major contributor of residual Fe (iron oxides) at the sediment-water interface, whereas the distribution

of easily reducible Mn (manganese oxides) appears to be influenced by both diagenetic processes and river input.

Mortimer and Rae (2000) had studied the metal speciation (Cu, Zn, Pb and Cd) and organic matter in oxic to suboxic salt marsh sediments from Severn Estuary, southwest Britain. Comparison of the oxic Rummey formation with the suboxic Wentlooge formations showed that the suboxic conditions control the iron cycling, and that in turn control the trace metal associations. Many metals are highly redox sensitive therefore better understanding of the effects of redox on metal speciation in estuarine sediments is necessary. Li et al. (2000) had studied the chemical partioning of heavy metals such as Zn, Cu, Ni and Co in sediments of the Pearl River Estuary. They found that the residual phase is the most important phase for these elements. Among non-residual fractions, Zn, Ni and Co were mainly associated with the Fe-Mn oxide fraction, while Cu was associated with the organic fraction. Zhang et al. (2003) used seven-step chemical fractionation procedure to assess the potential mobility of heavy metals from the muck sediments from the St. Lucie Estuary, U.S.A. Their study revealed that most of the metals in the muck sediments occurred predominantly in weakly mobile or nonbioavailable forms. Potential Bioavailability of heavy metals such as Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were studied by Green-Ruiz and Páez-Osuna (2004) in surface sediments from the Altata-Ensenada del Pabellon Lagoon, SE Gulf of California. They had observed that the highest metal bioavailable fractions are associated with agricultural discharges and river input. They found higher Pb content in bioavailable fraction and stated that it can produce adverse effects on the organisms. They had also observed that the organic carbon, fine sediments, Fe and Mn hydroxides and aluminosilicates influenced the behaviour of Cu, Fe, Ni and Zn in bioavailable fraction. Trace metal speciation in the Tees estuarine sediments was studied by Ibhadon et al. (2004). Their results indicated that the contamination of estuary was mainly from anthropogenic sources. They had observed that the Pb and Zn were associated with the reducible, residual and oxidizable fractions. They had also noticed that association pattern of Cd

was similar to that of Pb and Zn, but besides this it was also associated with the exchangeable and carbonate fraction while Cu was largely associated with the oxidizable and residual fractions. Yuan et al. (2004) had studied speciation of heavy metals in marine sediments from the East China Sea to evaluate the anthropogenic impact and also studied role of organic carbon in distribution of elements. They have reported significant amount of Fe, Co, Ni, Cu and Zn in the residual fraction and Mn and Cd in the non-residual fraction. Distribution and geochemical partitioning of heavy metals in sediments of the Bahia Blanca Estuary, Argentina, was studied by Marcovecchio and Ferrer (2005). Their results indicated that many bioavailable species occur within the system, including those of highly toxic elements such as cadmium. Singh et al. (2005) had studied the chemical fractionation in the Gomati River sediments and found that most of the metals are associated in the carbonate and exchangeable fractions indicating their bioavailability. Cuong and Obbard (2006) had studied metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. Farkas et al. (2006) had studied chemical speciation by using sequential extraction procedure and also evaluated geoaccumulation Index (I_{geo}) of the sediments to assess the heavy metal pollution in surface sediments of the River Po. Li et al. (2007) had studied the metal distribution in the coastal wetland of the Pear River Estuary, China, and found that the estuary was significantly polluted by Cd, Zn and Ni. Further they have also reported higher content of Cd and Zn in the exchangeable fraction indicating their ecological risk.

The fractionation / speciation studies were also carried out by several researchers e.g. Sekhar et al. (2003), Mathew et al. (2003), Takarina et al. (2004), Yuan et al. (2004), Jingchun et al. (2006) etc. to evaluate mobility, bioavailability, toxicity and also diagenesis, in the recent years.

Several studies have been carried out on the Zuari Estuary related to water, total suspended matter and sediment parameters. Sankaranarayanan and Reddy

(1973) reported high concentration of Cu during pre-monsoon in the Zuari waters. They had observed that the Cu concentration in the Zuari Estuary increases from the mouth towards upstream. Fondekar and Reddy (1974) had studied arsenic distribution in coastal and estuarine waters including Zuari around Goa and stated that the arsenic concentration in these waters seems to be of land origin. Zingde et al. (1976) while describing the distribution of As, Mn, Zn and Cu in flora and fauna of estuarine waters around Goa, had reported abnormally high concentration of dissolved Mn in waters, which they have attributed to mining operations in the catchment area. They have also observed gradual decrease of dissolved metals towards downstream. In the same paper with reference to Zuari Estuary, they have stated that the Zuari waters are rich in dissolved Fe and Mn, which they have interpreted as due to mining activity. Later, George (1993) had studied speciation of Cd, Pb and Cu in waters and reported low concentration of these elements during monsoon and higher concentration during pre-monsoon. Decrease in TSM content from mouth of the Zuari Estuary towards upstream during pre-monsoon and post-monsoon has been reported by Nayak and Bukhari (1992). Their study indicated that with the onset of monsoon TSM content increases remarkably in the estuary. Further, they have also observed that the Zuari Estuary maintains the zone of high TSM around the mouth of the Cumbharjua canal during pre-monsoon and post-monsoon, which disappears during monsoon. Based on foraminiferal studies, Panchang et al. (2005) concluded that there is reduction in pollution on the Zuari Estuary, which they have stated as due to reduced mining activity in the catchment area. Kumari et al. (2002) had undertaken study on Mandovi-Zuari estuarine system which was focused on primary productivity wherein they have also measured the suspended matter concentration. Their study reported three fold increase in TSM concentration in the estuarine system as compared to earlier studies reported by De Souza et al. (1981). Mesquita and Kaisary (2007) had studied the distribution of iron and manganese in water, suspended particulate matter and sediments from the Zuari Estuary. They have noted higher values in the middle estuary. They have related concentration of these metals to

mining activities. Nayak et al. (2008) have studied the abundance and distribution of total suspended matter (TSM) from Mandovi and Zuari estuaries in three different seasons over the last seventeen years. They have reported that in general, in Zuari Estuary, TSM concentration increase in both surface and bottom waters from year 1991 to 2004. Further they have reported lower values of TSM in the year 2007 in post-monsoon season when compared to 2004 data. Similar observations are also made for adjacent Mandovi Estuary which is connected to Zuari Estuary through Cumbharjua canal.

1.5 Study Area

The geomorphology, climate, geology, minerals and mining in and around the present study area within the state of Goa are described below.

1.5.1 Geomorphology of Goa

Goa encompasses an area of 3,702 km^2 and it lies between the latitudes $14^0$53'54" N and $15^0$40'00" N and longitudes $73^0$40'33" E and $74^0$20'13" E. It is flanked between the continuous range of rugged hills constituting the Western Ghats on the east and the Arabian Sea on the west. The region is marked by chain of high and prominent hills, deep gorges, steep valleys and ravines. Broadly there are three main physical divisions of Goa. a) Hill ranges of the Sahyadris in the east cover an area of about 600 Sq. km. b) Middle level plateaus in the center sub-ghats and c) The low-lying river basins and the coastal plains.

1.5.2 Climate

Goa, being in the tropical zone and near the Arabian Sea, has a warm and humid climate for most of the year. The average rainfall of Goa is about 3000 mm per year. The annual climate of Goa has been traditionally divided into three seasons: i) the monsoon season from June to September, the monsoon rains arrive by early June which last till late September. ii) winter season from December to February, these months are marked by cool nights of around 20^0 C

and warm days of around 29^0 C with moderate amounts of humidity and iii) summer season from March to May. The month of May, is the hottest with high humidity.

1.5.3 Geology

Goa is largely covered by the rocks of the Goa group belonging to the Dharwar Super group of Archaean proterozoic age, except for a narrow strip along the northern corner that is occupied by the Deccan traps of upper cretaceous to lower Eocene age. The Dharwarian rocks which extend in a general NW-SE trend are represented by metamorphosed basic and acidic volcanic rocks (Gokulam, 1972). The sediments at the base are overlaid by greywacke suite of rocks, followed by pyroclasts and tuffs with the associated chaemogenic precipitation of lime, manganese and iron and then by greywacke suit of rocks. The soil of Goa is mostly derived from laterites which are rich in ferric aluminium oxides and is reddish in colour. The alluvial and loamy soil is found along the riverbanks. It is rich in minerals and humus.

1.5.4 Minerals and Mining

Iron ore, manganese, bauxite, high magnesia limestone and clay are the chief minerals found in Goa. Mining belt along the Zuari Estuary is presented in the figure 1.2. The annual production of iron ore is around 15 million tones (Nayak, 2002). In 1996 – 97 the total mineral ore produced in Goa was 137.37 lakh tonnes, of which iron ore consists 136.43 lakh tones. The ore is mainly exported to Japan, European

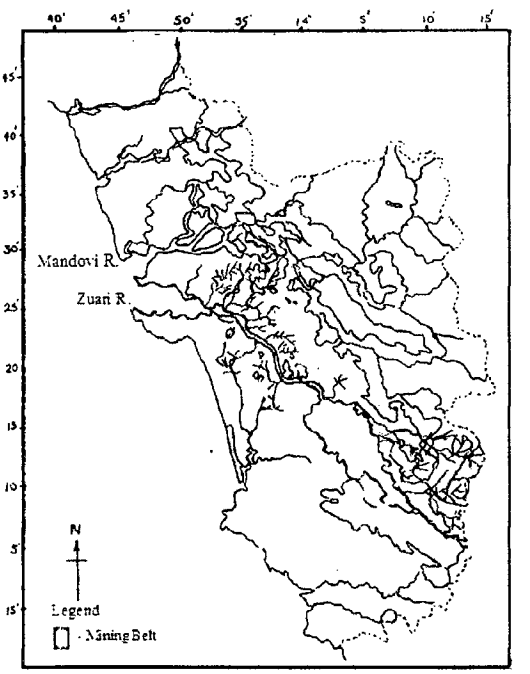


Fig. 1.2: Mining belt along the Zuari Estuary.

countries, China and South Korea through the Mormugao Harbour. The iron ore deposits of Goa are essentially of hematite and are associated with the ferrogenous quartzite and phylites. From north to south the iron concentration reduces and in the South Goa, the ore is mainly ferruginous manganese. Mining in Goa is both manual and mechanical employing open cast method, which involves the systematic removal of overburden by performing bench and slope method along hilltops and slopes, as iron ore deposit lie under a thick mantle of laterite. During the production of ore large quantity of waste is generated which leads to severe environmental pollution.

1.5.5 Rivers in Goa

Goa is blessed with seven main rivers namely Tiracol, Chapora, Mandovi, Zuari, Sal, Talpona and Galgibagh that flow through the Sahyadri range. Among these Mandovi and Zuari are the major rivers. Rivers Mandovi and Zuari together with the Cumbharjua Canal form an important estuarine system along the west coast of India. These are confined between latitude $15^0$09' and $15^0$33' N and longitude $73^0$45' and $74^0$14'E and their basin covers 69 % of the total geographical area of the state.

The present study is restricted to Zuari Estuary. River Zuari within the state of Goa is one of the dynamic tropical estuaries along the west coast of India. It originates from Dighi Ghats of Sahyadri hills, which meets the Arabian Sea near Marmugao-Donapaula point. River Zuari is about 67 km in length with a basin area of 973 sq km of which the catchment is 550 sq km. It has wide mouth, approximately 5.5 km, maintains almost the same width up to 12 km upstream, which narrows down to less than 0.5 km further upstream within the estuarine limits. It is a tide dominated coastal plain estuary (Murty et al., 1976), as it is located on the alluvial coastal plain between the Sahyadris and the Arabian Sea. As mentioned earlier, the region experiences well defined three seasons. The monsoon season (June-September) followed by cooler post-monsoon (October-January) and then the pre-monsoon (February-May). Zuari receives copious

rainfall during monsoon season leading to high runoff into the estuary. During early monsoon the channel of the estuary is completely flushed with the freshwater. Such episodes are expected to turn the estuarine water fresh from head to mouth (Shetye et al., 2007). During monsoon estuary becomes stratified and a salt wedge is formed which extends up to about 12 km upstream from the mouth. The quantity of freshwater flow to the estuary during pre-monsoon and post-monsoon is negligible i.e. about 0.03 km^3/yr (Wagle et al., 1988) and therefore flow within the estuary during these seasons is largely regulated by tides of semidiurnal nature having a maximum range of 2.3 m. During pre-monsoon, estuary remains well mixed and during post-monsoon partially mixed. Zuari Estuary has smaller tributary system. It receives major supply of water and sediments from its tributary known as Kushawati. The drainage area of Kushawati consists of alluvial land, subdued plateau and prominent hills especially in upstream. In the downstream, the tributary develops alluvial flats and marshes on either side.

The catchment area of Zuari Estuary is known for considerable anthropogenic activity in the form of mining, sewage outfall, agricultural practices, coastal construction and indiscriminate dumping and also tourism. There are 10 large open cast mines along with many small-scale mines of manganese ore with associated lesser amount of iron ore within the catchment area of Zuari River. Southern part of mining belt, through which the Zuari Estuary flows, holds the highest grade of manganese and ferromanganese deposits in the state. Thus the mines in southern part of mining belt are best suited to satisfy manganese demands. In addition, many mining associated activities such as transporting ore to platforms, ore loading, and effluents from beneficiation plants and barge-building activities within the river do takes place. Marmugao port, one of the best natural harbour is situated on the southern bank of the Zuari Estuary near its mouth. More than 10 million tons of iron ore are being exported annually through Marmugao port. It is also important to mention here that Mandovi Estuary, which is connected to Zuari Estuary through Cumbharjua Canal, also passes through

extensive mining activity. Zuari Estuary receives large input of mining material from Mandovi through the connecting canal, as water flows from Mandovi to Zuari during monsoon as well as during ebb tide. Further, during monsoon barges move through Cumbharjua Canal and Zuari from Mandovi to Marmugao port.

Chapter II

MATERIALS AND METHODS

2.1 Introduction

In order to produce a good set of data, it is necessary to have a thorough knowledge on sample selection, collection, preservation and subsequent analysis. The criteria of selection of samples depend on the objectives of the study. It is necessary to acquire thorough information about the study area before selection and collection of sample. Care should be taken while sampling to avoid contamination, as it may lead to incorrect results. Subsequent to sample collection, is preservation. If not preserved appropriately, there is probability of alteration of chemical components in the sediment or water sample which may lead to erroneous results. Further, standard methods to carry out the analysis of the samples should be employed. Thorough knowledge on the analytical methods by screening the published literature is very important before commencement of the experiment. The experiment should be repeated to attain accuracy. Minimizing errors should be a primary goal.

Considering the importance of every step involved in the generation of quality data, they were strictly maintained in the present study. The methods adopted in collection and analyses are detailed in this chapter and are also outlined in the figure 2.1.

2.2 Field Methods

Field surveys and sample collection were carried out during August, December and April months representing monsoon, post-monsoon and pre-monsoon seasons in the Zuari Estuary on board fishing trawler during the year 2004-05.

2.2.1 Collection of Water Samples

A total of 18 stations were selected within the estuarine limits of Zuari River for the collection of samples (Fig. 2.2). Near surface and near bottom water samples were collected at every selected station during all the three seasons using a Niskin plastic water sampler fastened on to a rope and was triggered by a messenger. Collected water samples were stored in precleaned plastic bottles.

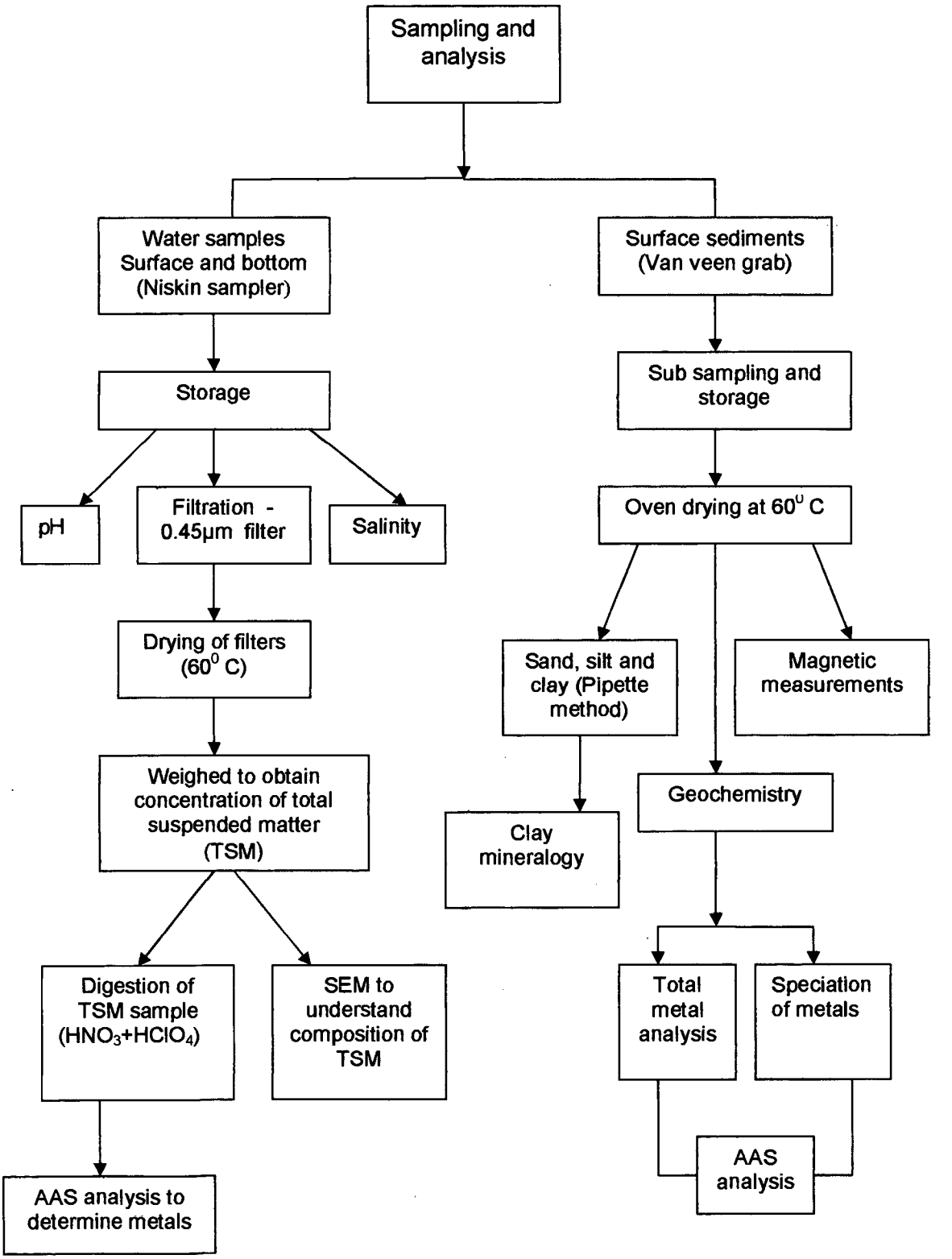


Fig. 2.1: Flowchart of methods followed.

2.2.2 Collection of Sediment Samples

Sediment samples were collected by using a stainless steel Van Veen grab sampler from all the selected 18 stations during all the three seasons. Sub sampling was done by taking upper 5 cm of the sediment from the grab with the help of plastic spatula. Care was taken to avoid any contamination. Sediment samples were then transferred to prelabeled polyethylene bags and were kept in ice boxes containing ice during transport to laboratory. Upon transferring to laboratory, sediment samples were maintained in the deep freezer for further analyses.

2.2.3 Locations of Stations

Station locations were obtained by using the instrument, Global positioning system (GPS).

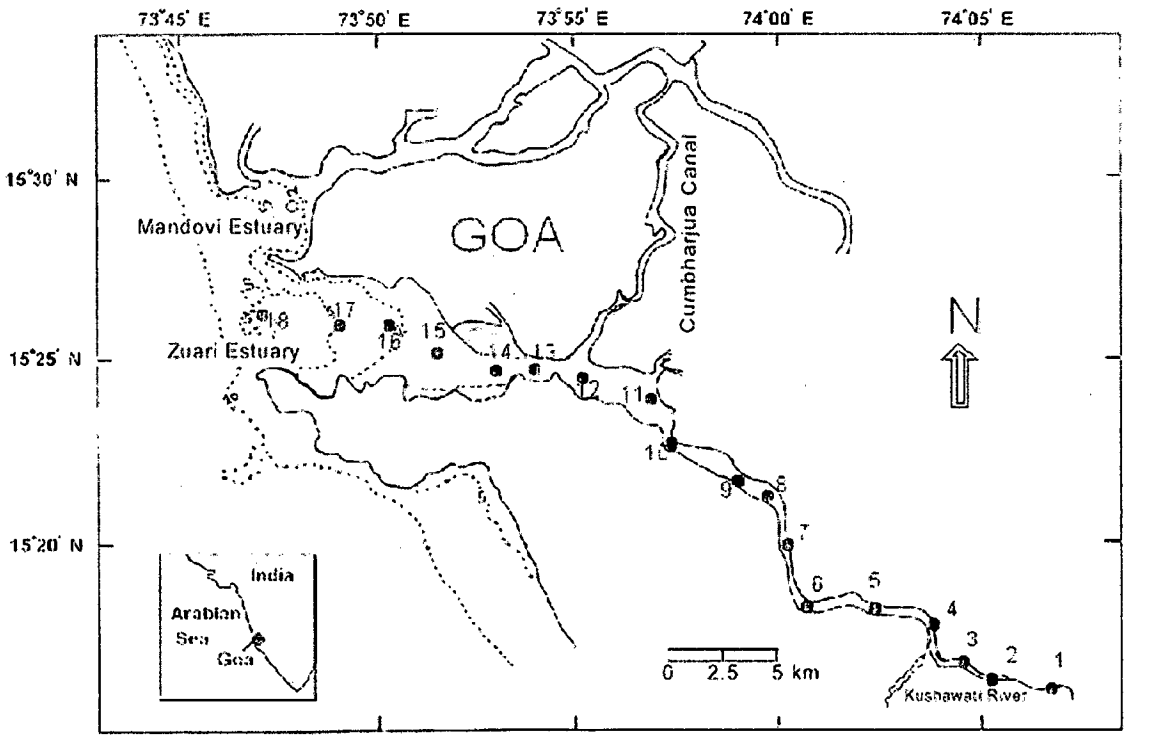


Fig. 2.2: Map showing the station locations of samples along the Zuari Estuary.

2.3 Laboratory Procedures

2.3.1 Water Samples

Analyses of the parameters mentioned below were carried out within 10 hours after collection of water samples.

a. pH

pH of the both surface and bottom water samples was measured by using a pH meter (Thermo orion 420 A^+ model). Before the analysis, pH meter was calibrated with standard buffers of pH 4.0, 7.0 and 9.2.

b. Salinity

Salinity was measured by Mohr Knudsen chlorinity titration method (Grasshoff, 1983), which involves the following procedure. 10 ml of sample was taken into the conical flask, 25 ml of chloride free distilled water and 6 drops of potassium chromate (K_2CrO_4) indicator were added to it. The contents of the conical flasks were mixed well and then titrated against standardized silver nitrate solution until colour changed to pink. Standardization of the silver nitrate solution was done by using the standard seawater.

Salinity was then calculated using the formula

Salinity = 1.80655 * chlorinity (Cl) psu.

c. Total Suspended Matter (TSM)

A known volume of water sample (1 litre) was vacuum filtered through pre-weighed millipore membrane filters having a pore size of 0.45 µm. The filter papers were then oven dried at 60^0 C and reweighed on the four-decimal balance. Total suspended matter (TSM) concentration was then calculated using the sample volume and sample weight. TSM was expressed as mg/l.

d. Scanning Electron Microscopy (SEM) Analysis of TSM Samples

Sample preparation for SEM analysis was done by taking a portion of the dried filter paper containing suspended matter which was mounted onto a stub coated with platinum in a sputter coater. SEM photographs were obtained by using model JEOL 6360. SEM uses a beam of electrons to scan the surface of a sample to build a three-dimensional image of the specimen. In order to take better resolution image, the SEM was operated at an accelerating voltage of range 6 Kv. Low magnification (1000-2000X) was used for a quick overview of the sample. When a particle was seen, magnification was increased to fill the area of the viewer (3000-11000X) and a photograph was taken. Five images for each selected samples were digitally captured and among these best ones were chosen for analysis.

e. Digestion of TSM and Metal Analysis

Digestion of filter papers containing suspended matter was carried out for the entire surface as well as for bottom water samples following the procedure given by Satyanarayana et al. (1985). Filter paper containing suspended matter and blank filters were treated with the mixture of concentrated perchloric acid and nitric acid (each 1 ml) and evaporated almost to dryness by heating at 100^0 C. The residue after cooling was dissolved and diluted to 50 ml with 1N nitric acid. Diluted samples were then analyzed for seven different elements viz. Fe, Mn Cr, Cu, Zn, Co and Al using atomic absorption spectrophotometer (GBC – 932 AA model) equipped with deuterium background corrections. Blank corrections were applied for all the metals.

2.3.2 Sediment Samples

Surface sediment samples collected were first oven dried at 60^0 C. Care was taken to avoid any contamination. A part of the sample was used to determine the sediment components i.e. sand: silt: clay ratio, clay mineralogy and magnetic susceptibility. Another part of the sample was finely ground (passed through 200

μm sieve) for the determination of organic carbon, total metal digestion and for metal speciation.

a. Sediment Size Analysis (Sand: Silt: Clay)

Pipette analysis was carried out to determine the sand: silt: clay ratio (Folk, 1968) which is based on Stoke's settling velocity principle. 15 g of oven dried (60^0 C) sediment sample was taken and transferred into 1000 ml beaker. Distilled water was added to this beaker and stirred. Sediment was then allowed to settle. Next day water from the beaker was decanted by using decanting pipe. This step was repeated at least 4 to 5 times to remove the salinity. After decanting, 10 ml of 10 % sodium hexametaphosphate was added. The role of sodium hexametaphosphate is to dissociate clay particles. On the next day 5 ml of 30 % of hydrogen peroxide was added to oxidize organic mater. Contents of the beaker were then poured over 63-micron (230 mesh) sieve and filtrate was collected in 1000 ml cylinder. The contents from the beaker were washed till solution becomes clear and then volume was made up to 1000 ml. The solution from the cylinder was used for pipette analysis. Before withdrawal, the contents are homogenized by stirring for about 2 minutes using a stirrer. This was then allowed to settle for certain time according to the room temperature. Stirring time was noted down and pipetting time was kept by referring table 2.1.

Table 2.1 Time schedule to be used for pipette analysis.

Size Ø	Depth to which pipette is to Inserted (cm)	Time after which water is to be pipetted out Hours: Minutes: Seconds				
		28^0C	29^0C	30^0C	31^0C	32^0C
4	20	0:00:48	0:00:46	0:00:46	0:00:44	0:00:44
5	10	0:01:36	0:01:34	0:01:32	0:01:29	0:01:28
6	10	0:06:25	0:06:15	0:06:06	0:06:57	0:05:52
7	10	0:25:40	0:25:02	0:24:25	0:24:49	0:23:27
8	10	1:42:45	1:40:13	0:37:42	1:37:15	1:33:51
9	10	6:30:00	6:40:40	6:32:50	6:32:10	6:11:30
10	10	27:06:00	26:30:00	-	-	-

25 ml of solution was pipetted out at 8 ϕ by inserting pipette up to 10 cm depth from the cylinder. Pipetted solution was then transferred into preweighed 100 ml beaker and dried at 60^0 C over night. After drying, beaker containing clay was weighed. The sand, which remained on the sieve, was transferred on preweighed beaker. This was then dried and kept in dessicator to remove any moisture and then weighed.

Percentage of sand, silt and clay were calculated as follows

% Sand = (Wt. of sand / Total Wt.) * 100

% Clay = (Wt. of clay / Total Wt.) * 100

% Silt = 100 - (% of sand + % of clay)

b. Clay Mineral Analysis

The procedure followed is same as that followed for pipette analysis. The sample was pipetted out at 10 cm depth to 500 ml beaker at 9 ϕ from the cylinder. To this 5 ml of acetic acid and 10 ml of hydrogen peroxide was added to remove carbonates and organic matter and stirred well. The contents from the beaker were then kept overnight for settling. The top clear liquid was decanted and distilled water was added. This step was repeated several times to free clay from excess reagents. Slide preparation for clay mineral analysis was done by pipetting 1 ml of the clay and spreading uniformly over a pre-numbered slide. The prepared slides were exposed to ethylene glycol vapours at 100^0 C for 1 h. The slides were then scanned from 3^0 to 15^0 2θ at 1.2^0 2θ/min on X-ray diffractometer (1840 Model) using nickel-filtered Cu Kα radiation. Also samples were scanned again in the range of 24 to 26^0 2θ at 0.5^0 2θ/min to distinguish kaolinite and illite peaks. The percentages of different clay minerals were computed by weighting the integrated peak areas of basal reflections in the glycolated X-ray diffractograms by semi-quantitative method given by Biscaye (1965).

c. Magnetic Susceptibility Measurements

Sample preparation: A known weight of sediment sample was packed in a 10 cc plastic sample container, which was wrapped with 'cling' film to reduce the

possibility of cross contamination and generally to keep the sediment fixed and also to reduce all movements within the sample container to a minimum while handling the sample. The containers containing the packing material were pre-measured for mass and susceptibility and the values were corrected.

A Bartington MS2 system was used for magnetic susceptibility measurements. Both the high (4.7 kHz) and low (0.47 kHz) frequency measurements were performed using a dual frequency Bartington MS2 susceptibility meter. Magnetic susceptibility (χ) measurements of very weak samples were carried out employing the more sensitive Agico's Kappabridge KLY-4S instrument. Frequency dependent susceptibility (χ_{fd} %) was calculated using the formula (χ_{LF}-χ_{HF}) / χ_{HF} * 100 where χ_{LF} is magnetic susceptibility at low frequency and χ_{HF} is susceptibility at high frequency.

Anhysteretic remnence magnetization (ARM) was imparted in a steady 0.05 Mt field superimposed over decreasing alternating field (A.F.) from 100 mT to 0 mT using a Molspin A.F. demagnetizer. ARM created within the sample was then measured using Molspin spinner magnetometer.

Isothermal remnant magnetization (IRM) was acquired by first exposing the samples to series of successively larger fields along one direction and then in the opposite direction (backfields, -20mT, -30mT, -40mT, -100mT, -200mT and -300mT) using a Pulse magnetizer (Magnetic measurements Ltd.). After each forward and reverse field (DC demagnetization), samples were measured using the Molspin spinner magnetometer. The IRM achieved at 2T is referred as the saturation isothermal remnant magnetization (SIRM).

Using the above magnetic parameters various other parameters were evaluated in terms of magnetic concentration, mineralogy and grain size as summarized by Thomson and Oldfield (1986) and Oldfield (1999). The descriptions of different magnetic parameters are presented in the table 2.2.

Three samples from pre-monsoon collections were selected for a thermal demagnetization experiment to identify the type of mineral based on the curie temperature. Curie temperature is the temperature at which certain magnetic materials undergo a sharp change in their magnetic properties or the temperature above which a ferromagnetic material loses its permanent magnetism, for e.g. curie temperatures of minerals such as hematite and magnetite are 675^0 C and 575 – 585^0 C respectively. First, IRM was imparted to the selected samples up to 2T (saturation IRM). After applying the field, thermal demagnetization of the samples was carried out by subjecting the samples to stepwise increased temperatures from 100 to 725^0 C, considering the curie temperature of magnetic minerals. MMTD60 thermal demagnetizer was used for heating of the samples. The magnetization was measured after each step, using the Molspin spinner magnetometer. Also temperature-dependence of magnetic susceptibility was measured for selected samples using a Bartington temperature susceptibility to clarify the magnetic mineral phase system.

Table 2.2: The different magnetic parameters, definitions and their applications.

Magnetic parameters	Definitions / formulas	Significance
1. Magnetic susceptibility, χ (10^{-7} m^3/kg)	It is a measure of the ease with which a material is magnetized. $\chi = M / H$. Where M is the volume magnetization induced in a material of susceptibility and H is the applied field.	Gives the concentration of magnetic minerals

2. Frequency dependent susceptibility, χ_{fd} (%)	Variation in χ between low (0.47 kHz) and high frequency (4.7 kHz).	It is representative of grain size. Higher the value finer is the grain size. χ_{fd} % of ~10 % or 5-10 % indicates a large fine viscous (magnetite) component of super paramagnetic range.
3. Isothermal remnant magnetization, IRM (10^{-5} Am^2/kg^{-1})	Acquired at different DC forward and backward fields at a given temperature, particularly at room temperature.	
4. Anhysteretic remnant magnetization, ARM (10^{-5} Am^2/kg^{-1})	It is achieved by subjecting a sample to a strong alternating field which is decreased to zero in the presence of small steady field.	ARM gives an estimation of the concentration and presence of fine grain minerals.
5. Susceptibility of ARM, χ_{ARM} (m^3/kg^{-1})	It is a form of normalized ARM for the strength of a steady field.	It reflects concentration and grain size.
6. Saturation isothermal remnant magnetization, SIRM (10^{-5} Am^2/kg^{-1})	It is measured as the highest volume of magnetic remnence that can be produced in a sample by applying a very high field	It is a characteristic of mineral type and concentration.
7. S-ratio (%)	It is define as IRM $_{(-0.3T)}$/SIRM	S-ratio provides a measure of the relative proportions of higher coercive magnetic minerals (haematite) to lower coercive minerals (magnetite).
8. Soft IRM, IRM_S, (10^{-5} Am^2/kg^{-1})	Remnant magnetization after magnetization either in a relatively low forward field	It is a measure of low coercivity minerals.

	or reverse fields 'back IRM_S'.	
9. Hard IRM, HIRM (10^{-5} Am^2/kg^{-1})	Difference between SIRM and IRM_S in a reverse field of 300 mT $HIRM = SIRM-IRM_{-300mT}$	It is a measure of high coercivity minerals.
10. ARM/ χ (10^2Am^{-1})	It is the ratio of Anhysteretic remnant magnetization to magnetic susceptibility.	High values indicate significant stable single domain (magnetite) grains.

d. Organic Carbon in Sediments

Organic carbon was determined for all the sediment samples by using the Walkey-Black method (1947), adopted and modified from Jackson (1958). It was mainly determined to assess the role played by the organic component of the sediment in the transport, deposition and retention of trace metals. The Walkey-Black method utilizes exothermic heating and oxidation with potassium dichromate and sulphuric acid (H_2SO_4), which involves the following steps.

Before performing the experiment all the glassware's were washed with chromic acid, which was prepared by adding potassium dichromate to the concentrated H_2SO_4. An aliquot of the sample (0.5 g) was treated with a known excess of the standard dichromate solution (10 ml) and 20 ml of concentrated H_2SO_4 with silver sulphate (Ag_2SO_4). This was then mixed by gently rotating the flask for about 1 minute. The mixture was then allowed to stand for 30 minutes. After 30 minutes the same solution was then treated with 200 ml milliQ water, 10 ml of 85 % phosphoric acid (H_3PO_4) and 0.2 g sodium fluoride (NaF). This solution was then back titrated with standard ferrous ammonium sulphate solution using diphenylamine as an indicator to a one-drop end point (brilliant green). Silver sulfate was used to prevent the oxidation of chloride ions. Standardization blank without sample was run following the same above procedure. Dextrose was taken as a reference standard for the determination of organic carbon.

Percentage of organic carbon was calculated as follows

% Organic carbon = 10 (1-T/S) * F

Where,

S = Standardization blank titration, ml of ferrous solution

T = Sample titration, ml of ferrous solution

F = Factor which is derived as follows:

F = (1.0 N) * 12/4000 * 100/Sample weight

= 0.6 when sample weight is exactly 0.5 g

Where,

12/4000 = m. eq. wt. carbon

e. Digestion of Sediment for Total Metal Analysis

0.2 g of finely ground sediment sample was transferred into a clean acid washed Teflon beaker. To this, a mixture of 10 ml of HF, HNO_3 and $HClO_4$ (7:3:1) was added slowly to avoid excessive frothing and was completely dried on the hot plate at 150^0 C. After drying, again 5 ml of the above mixture was added and dried on the hot plate for 1 hr and then 2 ml of concentrated HCl was added and dried completely. Final residue was then dissolved in the 10 ml of 1:1 HNO_3. After ensuring complete digestion (clear solution) of the sediment sample, the contents from the Teflon beakers were transferred into the acid washed polypropylene volumetric flaks and the solution was made up to 50 ml with millique water. Same procedure was followed for two reference standards namely i) MAG-1 (Marine mud) and ii) GR-1 (Green River sediment) to ensure accuracy of the analytical method. The diluted solution was used for total metal analysis for six different metals viz. Fe, Mn, Cr, Cu, Zn and Co, using Atomic Absorption Spectrophotometer.

f. Chemical Partition / Speciation of Elements

A modified sequential extraction procedure (Tessier et al., 1979) was adopted in the present study. Although the sequential extraction procedure is time

consuming, the results obtained furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals.

A total of 27 sediment samples were chosen (8 from monsoon, 9 from post-monsoon and 10 from pre-monsoon) to evaluate Chemical partition / speciation of sediments. The procedure involves following five steps, which are referred here as fractions/phases.

i. Exchangeable metal fraction (F1): The metals in this fraction are easily released by the ion-exchange processes. Changes in ionic composition of water are likely to affect the sorption-desorption processes. Metals at the weathering site get adsorbed forming an electrical double layer. This, with increase in ionic strength gets desorbed due to ion-exchange reaction. Magnesium chloride is an effective reagent for desorbing specially adsorbed trace metals.

The previously dried, finely-ground sediment sample (1 g) was extracted at room temperature with 8 ml of magnesium chloride solution (1 M $MgCl_2$, pH 7) in 50 ml plastic centrifuging tube with frequent agitation for 1 h. After centrifuging at 8000 rpm for 10 minutes the supernatant was collected for metal analysis. The residue was washed with deionised water.

ii. Carbonate metal fraction (F2): The metals in this fraction are sensitive to pH changes and are thought to have been present as co-precipitated with carbonate minerals. This includes both biogenically and chemically precipitated carbonates. Buffered acetic acid and sodium acetate was applied to leach the metals in this fraction.

The residue from fraction F1 was leached at room temperature with 8 ml of 1 M sodium acetate (NaOAc) adjusted to pH 5 with acetic acid (HOAc) and then periodically agitated for 5 h at room temperature on orbital shaker. Solution was

then centrifuged and the supernatant was collected for metal analysis. The residue was washed with deionised water.

iii. Fe - Mn oxide metal fraction (F3): It is well established that iron and manganese oxides exists as nodules, concretions, cement between particles, or simply as coating on particles; these oxides are excellent scavengers of trace metals and are thermodynamically unstable under anoxic conditions. By controlling Eh and pH of reagents, dissolution of some or all the metal-oxide phases can be released. The most successful method used for leaching iron and manganese oxides involves the combined action of the reagents reducing these metals to their ferrous and manganous form respectively, and capable of keeping relatively large amounts of these ions liberated in solution. Hydroxylamine hydrochloride – acetic acid was used in the extraction.

The residue from fraction F2 was extracted with 20 ml of 0.04 M Hydroxylamine hydrochloride ($NH_2OH.HCl$) in 25 % (v / v) HOAc. The later experiments were performed at 96 $\pm$ 3^{0}C with occasional agitation for 5 h. Solution was then centrifuged at 8000 rpm and the supernatant was collected for metal analysis. The residue was washed with deionised water.

iv. Organic matter bound metal fraction (F4): In sediments, metals may be associated with organic matters, such as living organisms, organic coatings on inorganic particles and biotic detritus. The complexation and peptization properties of natural organic matter are well recognized. Under oxidizing conditions, the organic materials may be destroyed and the trace metals associated with them may be released into the environmental water system. Metals in this fraction are more stable than the above three fractions and difficult to take part in the geochemical cycle. It cannot be said that metals in this fraction are not harmful. The metals in this fraction act as a sink and reservoir for pollution. Hydrogen peroxide in acid medium is generally used to oxidize organic

matter in soil and sediment. Ammonium acetate is used to prevent adsorption of extracted metals on the oxidized sediment.

To the residue from fraction F3, 3 ml of 0.02 M HNO_3 and 5 ml of 30 % H_2O_2 which was adjusted to pH 2 with HNO_3 were added. This mixture was heated to 85 ± 2^0 C for 2 h with occasional agitation. A second 3 ml aliquot of 30 % H_2O_2 (pH 2 with HNO_3) was added and the sample was then heated again to 85 ± 2^0 C for 3 h with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20 % (v/v) HNO_3 was added and the sample was diluted to 20 ml and agitated continuously for 30 minutes. After agitation, solution was centrifuged and then decanted and was collected for metal analysis.

v. Residual metal fraction (F5): This fraction mainly contains primary and secondary minerals, which may hold trace metals in their crystal structure. Metals in this fraction are inert and may not take part in the biochemical or chemical reactions under normal conditions in the environment.

The residue from fraction F4 was washed with deionised water and was transferred into the acid washed teflon beaker and then digested completely following the same procedure used for the total metal digestion.

The centrifuging machine used for the sequential extraction procedure was Remi Cooling Compu fuge (model CPR 30) and orbital shaker used for agitation of samples was Orbital shaking incubator (model RC2100).

Mineral analysis were performed for selected bulk sediments as well as for final residue after sequential extraction (i.e. residual fraction) in order to check the variability of the mineral content before and after extraction and also to ensure minerals (especially Fe related minerals) released in the extraction steps. For this finely ground sediment samples were taken and were scanned on X-ray diffractometer in the range of 6 to 60 ^{0}C 2θ at 0.02 2θ/0.5 sec.

g. Atomic Absorption Spectrophotometer (AAS) Analysis

The digested total suspended matter samples, sediment samples for total metal analysis and sequentially extracted samples were analyzed for various metals viz. Fe, Mn Cr, Cu, Zn, Co and Al on Atomic Absorption Spectrophotometer (AAS) (GBC 932 AA model) with air acetylene oxide fuel mixture and nitrous-oxide. The instrument is equipped with deuterium background corrections. Blank corrections were applied wherever it was necessary. Atomic absorption spectrophotometry is one of the versatile techniques for the determination of trace metals. It is fast, accurate and free from interference. It is mainly based on the measurement of the light absorbed by the un-excited atoms of the wavelength of one of its resonance radiation. It basically consists of four parts: i) a source of the resonance radiation (Hollow cathode lamp) ii) a means for atomizing and vaporizing the sample (Burner and flame) iii) a monochromator and iv) a detector. The precision for different parameters were evaluated from replicate analysis of standard solutions of known concentration and also of samples and it was ± 3 - 5 %. The accuracy of the analytical method was assessed by the analysis of standard reference materials MAG-1 (Marine mud from the United States Geological Survey) and GR-1 (Green River sediment). The recoveries of all the total metals were good which lie between 89 to 95 % except for Cr, for which it is 80 %. Also the recovery of each metal species from sequential extraction procedure was good which was calculated using the following formula.

$$\text{Recovery} = \frac{\text{Fraction 1+ Fraction 2+ Fraction 3 + Fraction 4+ Fraction 5}}{\text{Total metal concentration obtained after total acid digestion}} \times 100$$

The average recoveries and ± SD found for each metal were 91 ± 15, 82 ± 21, 85 ± 14, 79 ± 15, 78 ± 24, 83 ± 22 % for Fe, Mn, Cu, Zn, Cr, and Co respectively.

2.4 Data Processing

The softwares MS Excel and Grapher were used for computations and plotting different parameters. The data was subjected to different statistical analysis for studying large and cumbersome data. Correlation was obtained between the different parameters by using the Computer software known as STATISTICA (StatSoft, 1999). All the values were normalized from the same software. Varimax R-mode factor analyses and cluster analyses were computed by means of principal components extraction method (PCA) by using the same software.

Geoaccumulation Index (I_{geo}) (Muller, 1979), Contamination factor (Pekey et al., 2004), Pollution load index (PLI) (Tomlinson et al., 1980) and Degree of contamination (Hakanson and Jasson, 1983) were computed to evaluate the pollution level in the surface sediments of Zuari Estuary.

Further, to understand the potential bioavailability or the risk of the studied metals to the biota, the average data on total metal concentrations obtained after total acid digestion as well as average total metal concentrations from sequentially extracted fractions (sum of the bioavailable fractions viz. exchangeable, carbonate, Fe - Mn oxide and organic bound) were compared with the Sediment Quality Values (SQV) following screening quick reference table (SQUIRT). The implication of the SQV was to achieve information on toxicity of metals to biota. SQUIRT was developed by NOAA for screening purposes. Based on SQUIRT, the guideline values are categorized by Buchman (1999) into five classes which elucidate the toxicity level of the metals.

Chapter III

SUSPENDED SEDIMENTS

3.1 Introduction

The suspended matter generally comprises of inorganic and organic particles which are suspended in the water column, either permanently or temporarily and are in a state of exchange with the bed load sediment reservoir (Turner and Millward, 2002). The episodic resuspension, deposition and generation of particles, coupled with their high reactivities, ensure that they play a key role in the availability, transport, recycling and fate of chemical elements in the aquatic environment (Baskaran and Santschi, 1993; Leppard et al., 1998; Uher et al., 2001). The role of suspended matter in estuaries is particularly significant because of regular and sporadic variations in particle concentration and character. The role of suspended particles in biogeochemical processes in estuaries is given in figure 3.1.

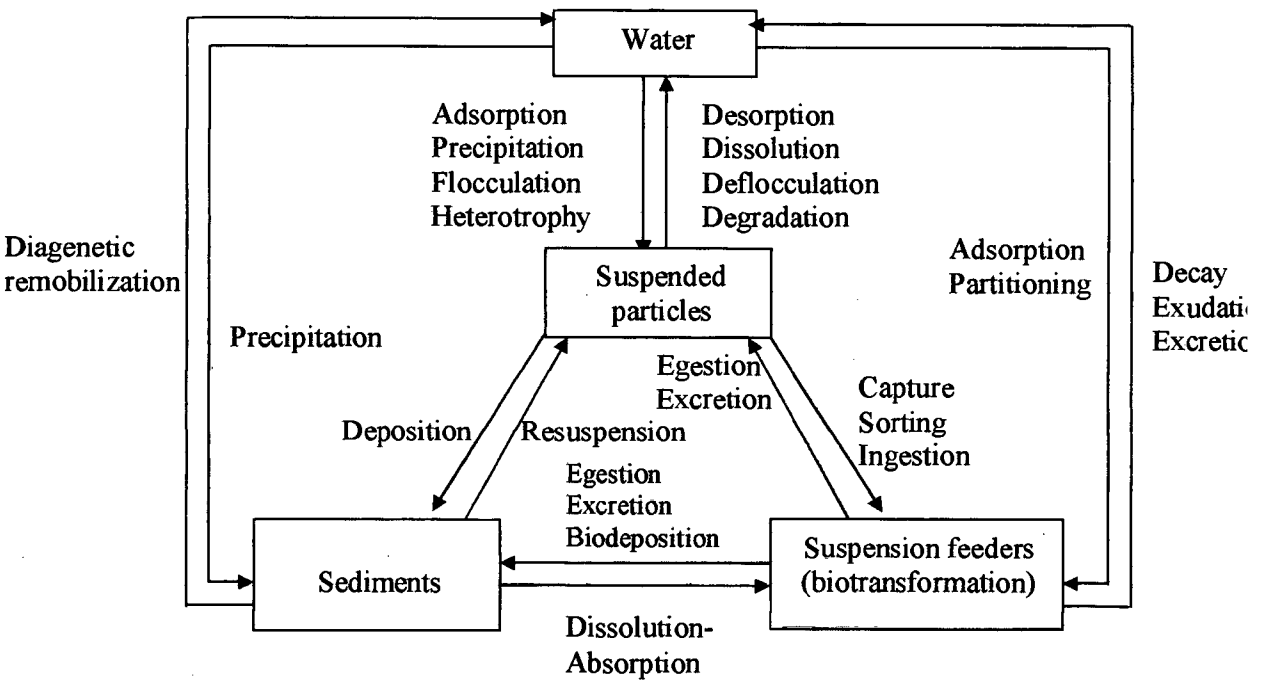


Fig. 3.1: Diagram representing the role of suspended sediments in estuarine biogeochemical processes, after Turner and Millward (2002).

The suspended particles within the estuaries are derived from continental weathering, coastal erosion, offshore waters, the atmosphere, in situ chemical and biological processes and industrial activities. Their composition can be broadly categorized into four components. The lithogenous component is an

inorganic material derived mainly from the weathering of crustal material and is mainly composed of quartz and other primary silicate minerals such as feldspars, and secondary silicate minerals (clay). The hydrogenous component is generated in situ by chemical processes, and exists either as coatings on lithogenous material, or as discrete phases. Hydrogenous phases include iron and manganese oxides, carbonates, sulphides and humic aggregates. The biogenic component is generated in situ or supplied externally by biological processes and includes microorganisms (bacteria, fungi, protozoans), plankton, decaying remains of organisms, faecal matter and marine and terrestrial plant debris, or from a bio-chemical standpoint, proteins, carbohydrates, lipids and pigments. An anthropogenic component includes sewage solids, plastics, tar, solvents, surfactants, mine tailings, coal dust and fly ash, and many occur as discrete particles or as non-aqueous phase liquids adhered to or entrapped within the particle matrix (Luthy et al., 1997).

3.2. Physico-chemical Parameters

3.2.1. Results

a. Salinity

Salinity is defined as the amount (in grams) of dissolved solid material in a kilogram of seawater after all the bromine has been replaced by an equivalent quantity of chlorine, all the carbonate is converted to oxide and all the organic matter is destroyed. In simple terms it is a measure of the quantity of dissolved salts in water. It is one of the important physico-chemical factors used to define the limits and characteristics of an estuary. It provides valuable information on the sea intrusion and distribution in the estuary which varies with the tide and the river flow. At the high tide, the salinity of an estuary will rise due to intrusion of seawater into the estuary which mixes with the fresh water coming downstream.

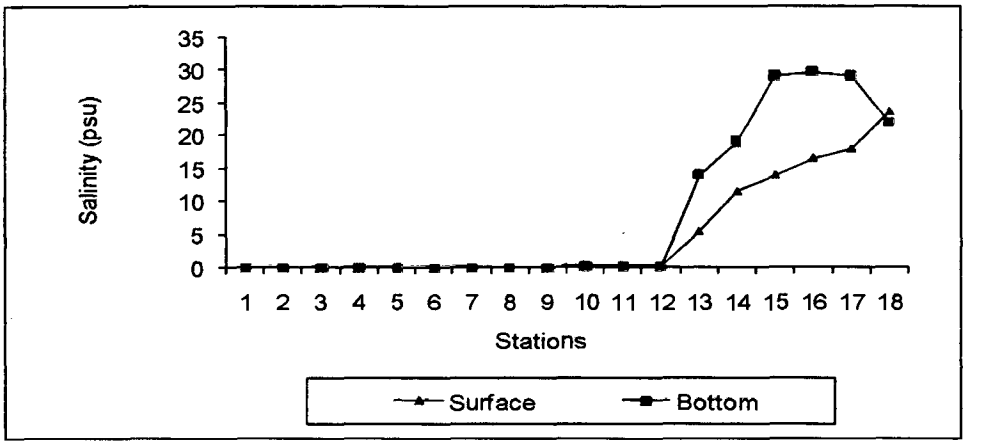


Fig. 3.2a: Variation of salinity in surface and bottom waters of Zuari Estuary during monsoon.

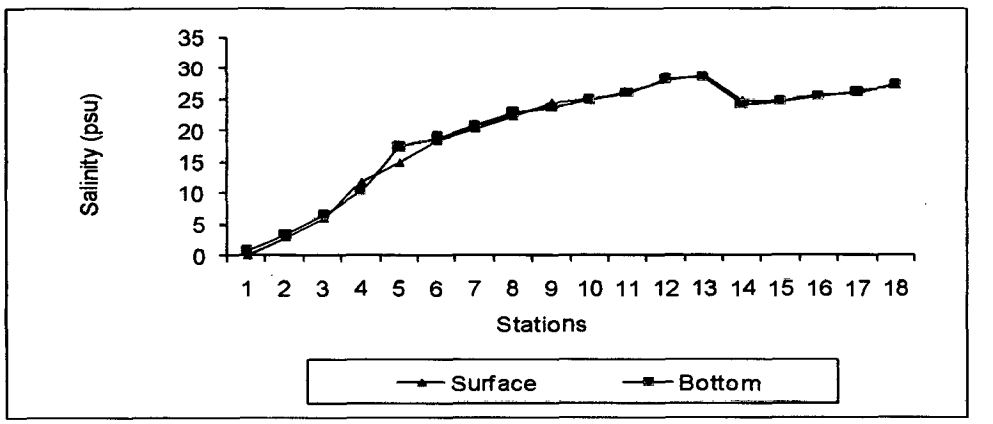


Fig. 3.2b: Variation of salinity in surface and bottom waters of Zuari Estuary during post-monsoon.

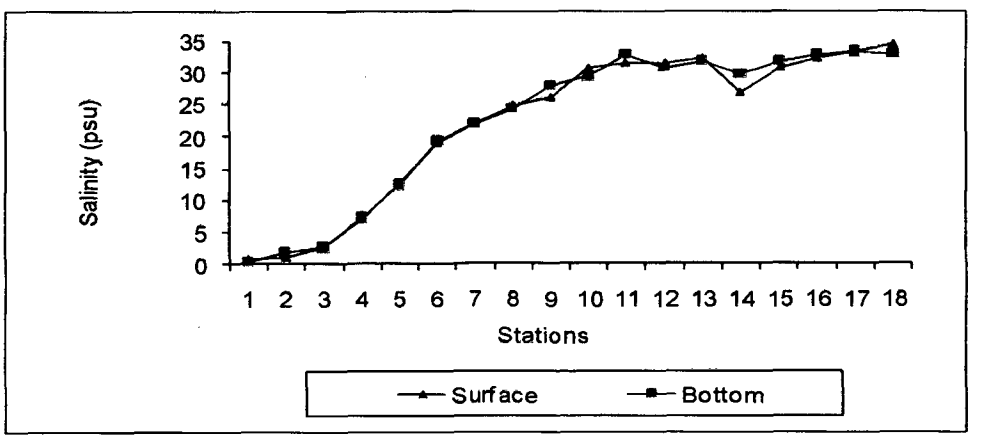


Fig. 3.2c: Variation of salinity in surface and bottom waters of Zuari Estuary during pre-monsoon.

Salinity in Zuari Estuary, during monsoon season varies from 0 to 23.7 psu (Avg. 5.0) in surface waters and from 0 to 29.6 psu (8.0) in bottom waters. Salinity of both surface and bottom waters remain almost zero from head of the estuary (station 1) up to the station 12, shows a sudden increase at station 13, and then shows a general increasing trend towards the mouth (Fig. 3.2a). Large variation in salinity between surface and bottom waters is observed during this season. In case of post-monsoon season, salinity varies from 0.0 to 28.6 psu (Avg.19.8) and 0.8 to 28.6 psu (20.1) in surface and bottom waters respectively. Salinity shows a general increasing trend from head up to mouth in both surface and bottom waters but a slight decrease is observed at station 14 (Fig. 3.2b). During pre-monsoon, salinity varies from 0.8 to 34.3 psu (Avg. 22.2) and 0.4 to 33.3 psu (Avg. 22.4) in surface and bottom waters respectively. An increasing trend of salinity is observed from head to the mouth of the estuary. A slight decrease in salinity is observed at station 14 in both surface and bottom waters and at station 12 only in case of bottom waters (Fig. 3.2c).

On an average, salinity value is observed to be relatively higher during pre-monsoon season followed by post-monsoon and monsoon season. During monsoon, salinity was almost zero at most of the stations for both surface and bottom waters except for some stations towards the mouth region. This is due to heavy monsoon precipitation, runoff and discharge. Also, large distinction can be seen between surface and bottom water values in consequence of overlying freshwater. Salinity variations between surface and bottom waters during post-monsoon and pre-monsoon are lesser hence could be considered as a mixed estuary during these seasons. The quantity of freshwater discharge during pre-monsoon and post-monsoon period is negligible (0.03 km^3/yr - Wagle et al., 1988) and their flow is largely regulated by the semidiurnal tides. This result, estuary to remain mixed due to the major influence of tides in these seasons. It is also observed by Nayak (1993) that Zuari Estuary behaves as a salt - wedge during monsoon, partially mixed during post-monsoon and fully mixed during pre-monsoon season.

b. pH

pH is characteristic of a degree to which the water is acidic (pH < 7) or basic (alkaline) (pH > 7). It is defined as a measure of hydrogen ion (H^+) activity in a solution and is expressed as a negative logarithm. The pH in seawater is controlled by CO_2^- - HCO_3^-, - CO_3^{2-} system. Other electrolytes such as borate, phosphate, silicate also affect the pH.

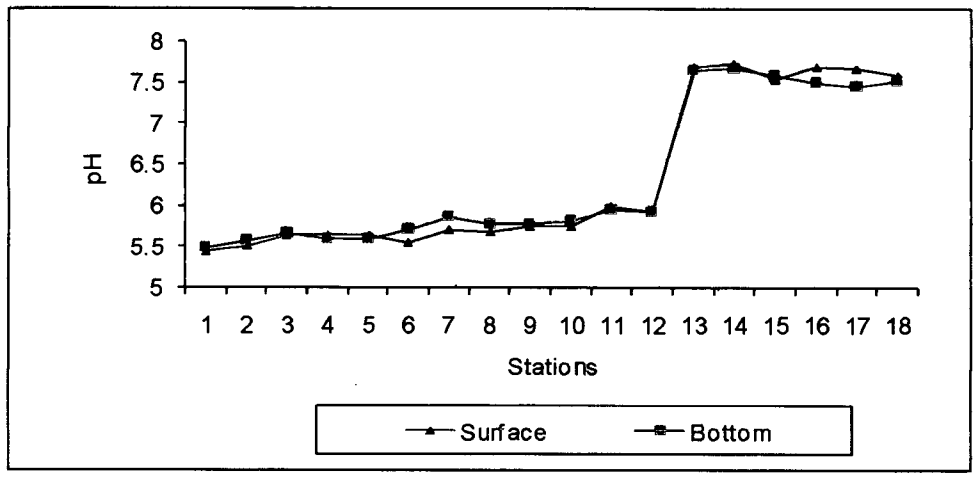


Fig. 3.3a: Variation of pH in surface and bottom waters of Zuari Estuary during monsoon.

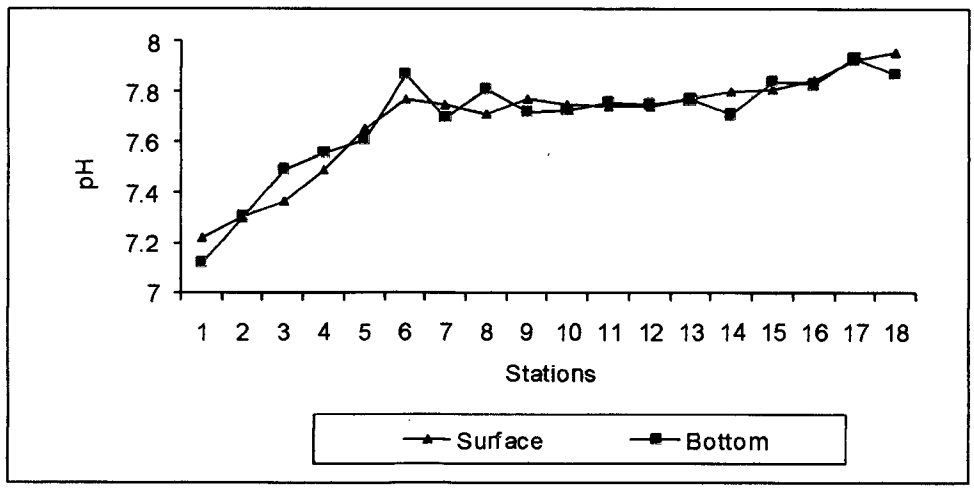


Fig. 3.3b: Variation of pH in surface and bottom waters of Zuari Estuary during post-monsoon.

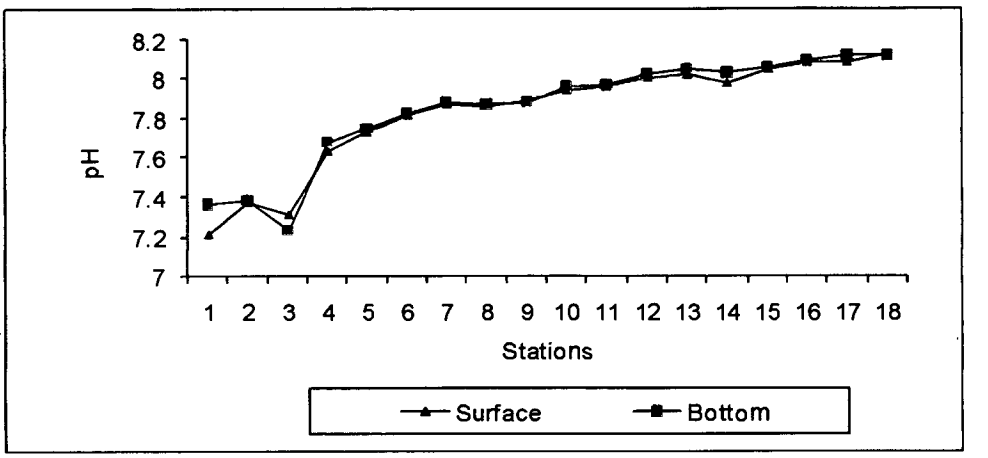


Fig. 3.3c: Variation of pH in surface and bottom waters of Zuari Estuary during pre-monsoon.

Within the Zuari Estuary, surface water pH ranges from 5.4 to 7.7 (Avg. 6.3) and bottom water from 5.5 to 7.7 (Avg. 6.3) during monsoon. In general pH shows an increasing trend from the head to the mouth of the estuary. A sudden increase in pH is seen at station 13 in both surface and bottom waters. In case of post-monsoon, it ranges from 7.2 to 8.0 (Avg. 7.7) and 7.1 to 7.9 (Avg. 7.7) in surface and bottom waters respectively. Surface and bottom water pH shows a general increasing trend from head to the mouth of the estuary with minor fluctuations in between. pH value varies from 7.2 to 8.1 (Avg. 7.8) in surface waters and from 7.2 to 8.1 (Avg. 7.9) in bottom waters during pre-monsoon season. In general, both surface and bottom water pH shows an increasing trend from head to the mouth of the estuary with a slightly lower value at station 3 (Fig. 3.3 a to c).

On an average, pH is observed to be relatively higher during pre-monsoon season followed by post-monsoon and monsoon season. Variation of pH observed in the Zuari Estuary in all the three seasons can be due to several factors such as influence of tidal surge, freshwater discharge, pollution, photosynthesis and interaction of water with suspended matter.

c. Total Suspended Matter (TSM)

The concentration of surface TSM in Zuari Estuary ranges from 6.4 to 32.4 mg/l (Avg. 20.0) and of bottom TSM from 7.6 to 117.4 mg/l (Avg. 59.2) during monsoon season (Fig. 3.4a).

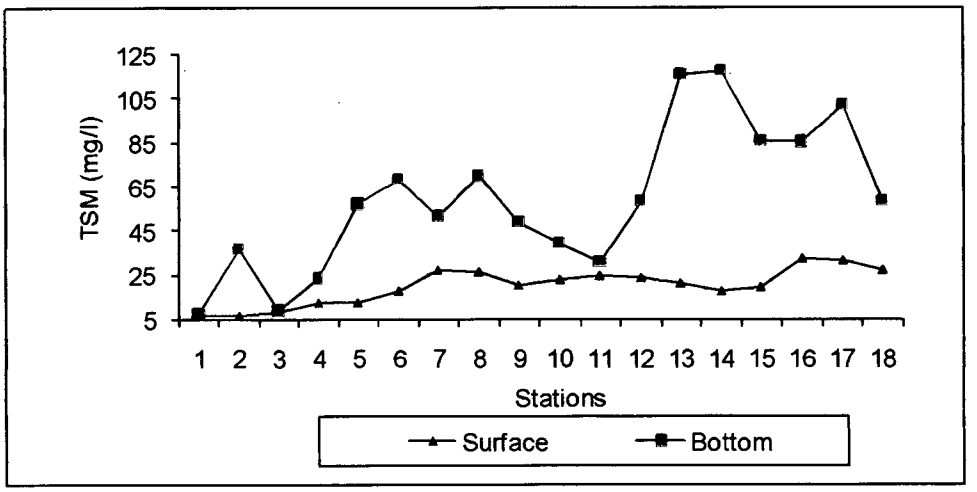


Fig. 3.4a: Distribution of total suspended matter (TSM) in surface and bottom waters of Zuari Estuary during monsoon.

Surface TSM shows an increasing trend from the head up to station 7 and then shows a slightly decreasing trend till station 9, followed by an increasing trend up to station 11. Further downstream, the value decreases up to station 14 and then shows an increasing trend up to station 16 and from here the value decreases towards the mouth. Higher values are seen at stations 7, 16 and 17 in surface waters. In case of bottom waters, relatively higher values are noted at stations 13 and 14 and also at station 17 in the lower part of the estuary. The lowest value is observed at station 1, which increases at station 2 and then decreases at station 3. Further downstream, bottom TSM value shows an increasing trend up to station 8 with slightly lower value at station 7 and further shows a decreasing trend up to the station 11, which then shows an increasing trend up to station 14. From here TSM value decreases towards the mouth with slightly higher value at station 17.

During post-monsoon, surface and bottom water TSM concentration ranges from 5.70 to 60.0 mg/l (Avg. 24.5) and 7.9 to 224.9 mg/l (Avg. 48.4) respectively (Fig. 3.4b).

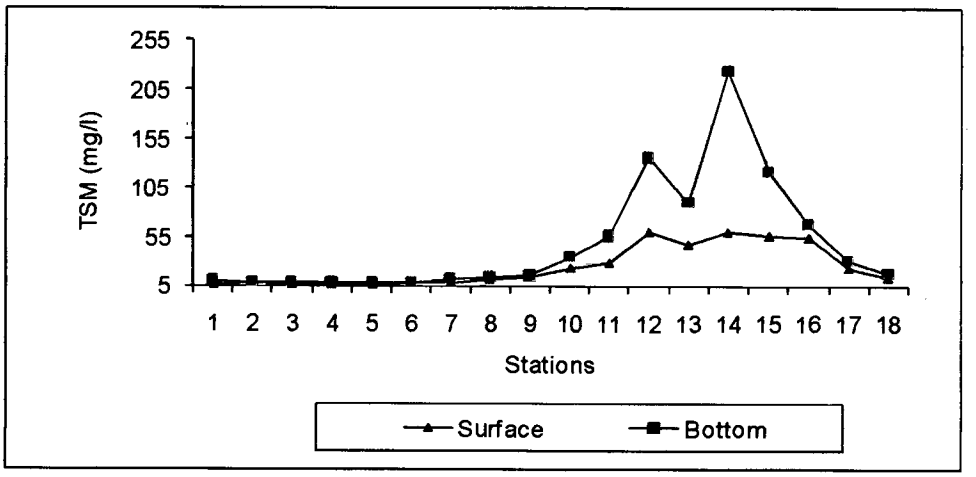


Fig. 3.4b: Distribution of total suspended matter (TSM) in surface and bottom waters of Zuari Estuary during post-monsoon.

TSM concentration in both surface and bottom waters during this season show an increasing trend up to station 12, which decreases at station 13 and then increases at station 14. Further downstream, a decreasing trend is observed towards the mouth of the estuary. Relatively higher concentrations are seen between stations 12 and 16 in both surface and bottom waters.

In case of pre-monsoon, surface and bottom TSM ranges from 8.8 to 28.6 mg/l (Avg. 20.3) and 11.6 to 100.9 mg/l (Avg. 34.7) respectively (Fig. 3.4c). Surface and bottom TSM in this season shows an increasing trend from station 1 up to station 12 with slightly higher value at station 7. TSM decreases suddenly at station 13. Further downstream, the values show an increasing trend up to station 16 and 15 in case of surface and bottom TSM respectively, followed by a decreasing trend seen towards the mouth.

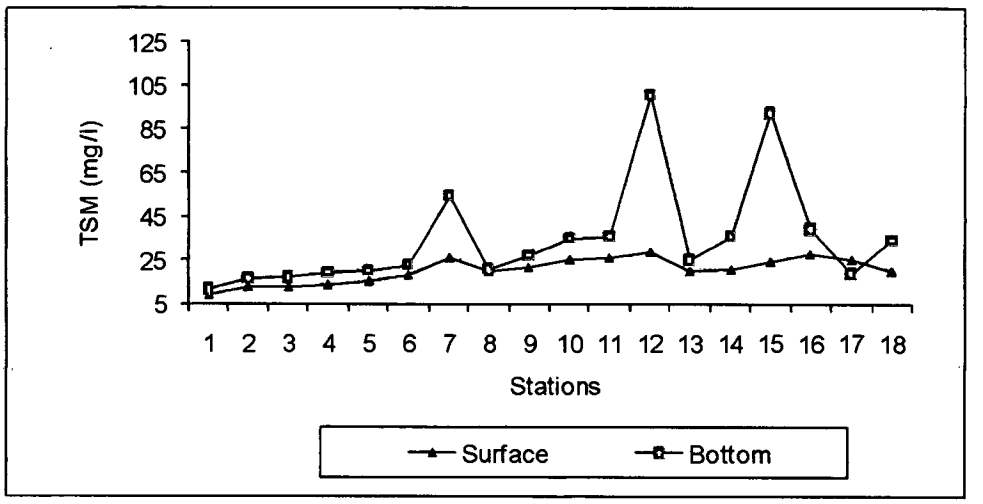


Fig. 3.4c: Distribution of total suspended matter (TSM) in surface and bottom waters of Zuari Estuary during pre-monsoon.

Relatively higher values of TSM are seen at stations 7 and 12 in case of both surface and bottom waters and also at stations 16 and 15 in surface and bottom waters respectively in pre-monsoon season.

In all the three seasons, bottom waters show relatively higher TSM than respective surface waters at all the stations. In general, TSM shows increasing trend from head to the mouth during monsoon and pre-monsoon season but with lesser value at or near the mouth region. Also, during post-monsoon, increase in TSM is seen from head towards the downstream region with decreasing trend towards the mouth. However zone of higher TSM values are observed in the lower half of the estuary roughly between stations 12 and 16. On an average higher concentrations are recorded during post-monsoon followed by pre-monsoon and monsoon for surface waters, while in case of bottom waters higher concentrations are recorded during monsoon followed by post-monsoon and pre-monsoon season.

3.2.2. Discussion

a. TSM Variation with Salinity

Three different zones of TSM concentration over entire salinity range are observed in the Zuari Estuary in surface waters during monsoon season. Relatively low amount of TSM is observed in the low salinity (0 psu) zone in

the upper estuarine region. Further downstream, it retains comparatively higher values between stations 6 and 15 where salinity ranged from 0 to 29 psu and then shows relatively higher concentration of TSM in the higher salinity zone towards the mouth region (Station 16 to 18). Similar pattern of distribution is also observed in case of bottom waters, wherein lower concentration of TSM is seen in the upstream end of the estuary which subsequently shows increase in concentration and remains high up to station 12 in the zero salinity regions. A sudden increase in concentration is seen thereafter, and maintained high concentration in the high salinity zone towards the mouth region. High concentration observed in the mid estuary or lower half of the upper estuary is in the low salinity zone, is primarily due to input from the heavy fresh water discharge. The river currents flowing with high velocity and carrying large quantity of finer sediments when come in contact with tidal waters reduce the speed. In this low velocity zone many elements which are in dissolved and in colloidal phase form fine particulate matter. This results in increase in TSM. Zone of high TSM in the high salinity zone can be attributed to resuspension of fine sediments, in addition to material brought by river, due to dynamic tidal and wave effects during this season.

In case of post-monsoon season, a steady increase in TSM concentration is observed with an increasing salinity up to station 11. A sudden increase in TSM is observed at station 12 where salinity was about 28 psu for both surface and bottom waters and higher values of TSM are seen up to station 16. Decrease in TSM concentration is observed towards the mouth region with increasing salinity in both surface and bottom waters. A conspicuous feature observed during this season is the zone of high concentration of TSM in the lower estuary. This can be the result of several processes in addition to prevailing hydrodynamic condition and topography of the area. Flocculation process is the major phenomenon in maintaining higher concentration of TSM in the higher salinity zone. Finer sediments brought during monsoon must have partly settled during post-monsoon. However increase in salinity must have resulted in mixing of saline water with fresh water creating a room for deflocculation and flocculation processes. The decrease in concentration of

TSM observed towards the mouth region indicates presence of relatively quiet tidal and wave environment following monsoon season.

In general, an increasing trend of TSM is observed with salinity, with few irregularities during pre-monsoon. The TSM concentration observed is very low between salinity ranges of 0.4 to 19.4 psu. This can be due to the eventual settling under low salinity conditions and reduced current velocities. Three apparent peaks of TSM concentration are seen at stations 7, 12 and 16 at salinities (psu) 21.9, 31.5 and 32.2 respectively in case of surface waters and in case of bottom TSM relatively higher concentrations are observed at stations 7, 12 and 15 at 21.9, 30.8 and 31.8 psu salinities. Resuspension of sediments must be responsible for higher concentration in these areas. At station 7 and 12, geomorphology and constriction must have played a dominant role. Other possibility is increase in the flocculation process. Smaller size of the floccules (Duinker, 1980) allows the current to carry the suspended matter further upstream up to the salinity 21.9 psu. The ore transport through barges especially during this season, is another factor responsible for high TSM concentration in these constricted locations. During the fair weather season estuary shows marine dominance. Substantial amount of sediment is brought into the estuary in association with the low swells of west and north west (Sankaranarayanan and Jayaraman, 1972; Murty et al., 1976; Qasim and Sen Gupta, 1981). The possibility of turbidity maxima, a characteristic feature of many estuaries, which occurs due to interaction of freshwater-saltwater, cannot be ruled out as a factor for higher concentration at station 7 and 12.

Scanning electron microscope (SEM) photographs taken for the selected samples of surface and bottom TSM during post-monsoon season are presented in the figures (Fig. 3.5 a to d). SEM photographs indicate that both biogenic and inorganic materials are contributing to the TSM (Fig. 3.5a and Fig. 3.5b). Biogenic materials include diatoms, coccolithophores, siliceous microfossils etc. Diatoms and inorganic particles are dominating in the upper as well as in the lower estuarine region. At the mouth i.e. at station 18, angular coarser particles are observed (Fig. 3.5d). Interestingly, an important

process of flocculation, which usually occurs during estuarine mixing, is observed in the lower estuarine region at station 14 (Fig. 3.5c).

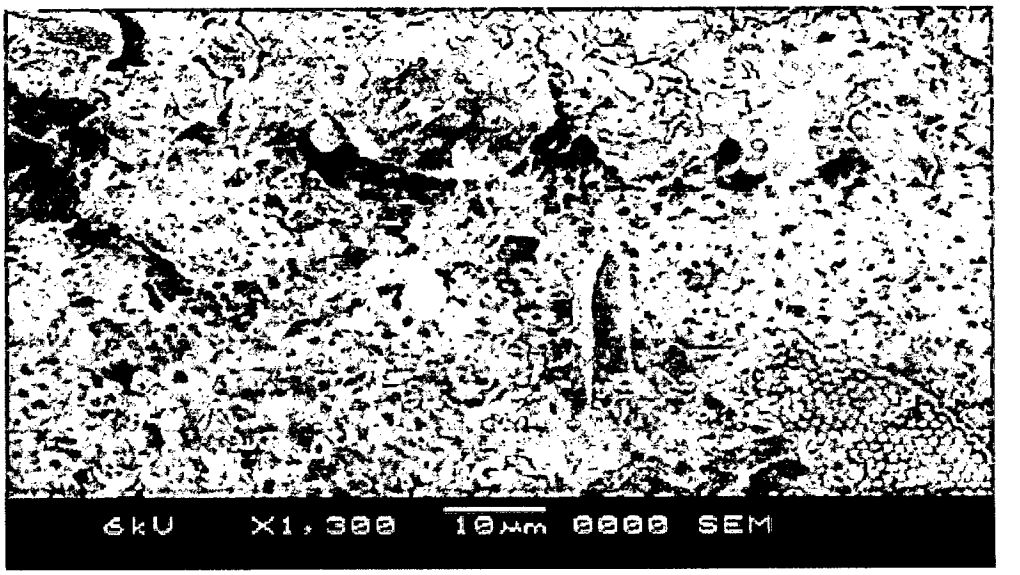


Fig. 3.5a: SEM photograph of bottom TSM at station 3.

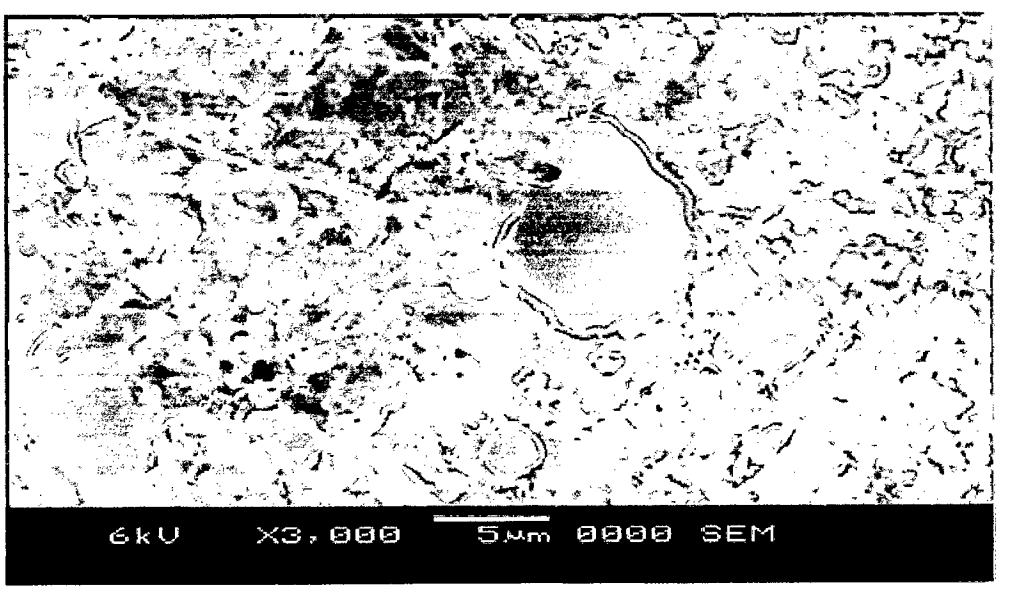


Fig. 3.5b: SEM photograph of bottom TSM at station 10.

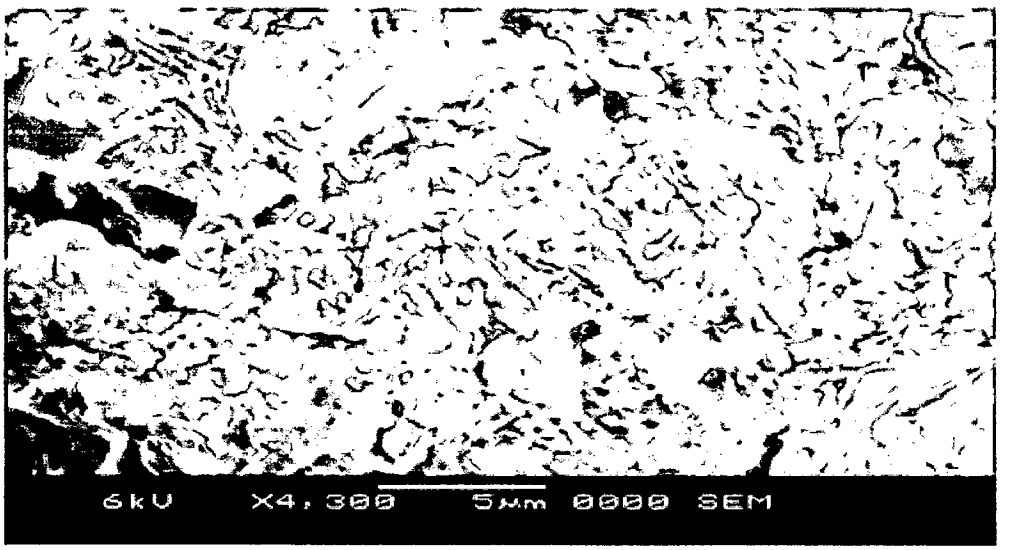


Fig. 3.5c: SEM photograph of surface TSM at station 14 indicating flocculation process.

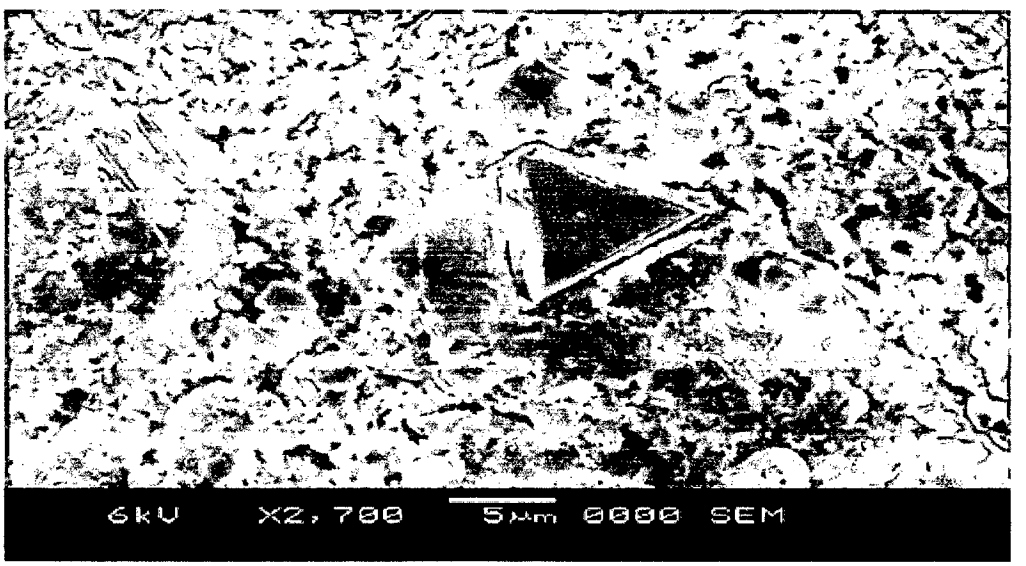


Fig. 3.5d: SEM photograph of surface TSM at station 18.

b. TSM Variation with Time

To understand the variation of TSM in Zuari Estuary over the years in Zuari Estuary, data on TSM from earlier studies has been extracted.

The 'Master plan for pollution control' (NIO, 1979) is one of the earliest studies available on this estuary. In this document, the TSM concentration recorded

for Zuari Estuary ranges from 0.8 – 143.0 mg/l. This data is based on the study carried out between October 1977 and September 1978. TSM concentration and distribution was related to the freshwater runoff. It was mentioned in the report that 112000 tones of TSM per year is added in the upper reaches of Zuari Estuary, 20 % of which gets precipitated in the estuarine and 10 % in the near shore regions. It is further stated that the major cause of maintaining higher concentration of suspended matters in the Zuari Estuary is release of material from mines in the catchment area.

Later, Nayak (1993) had studied the distribution of TSM along the Zuari Estuary during the year 1990 – 91 and reported that during monsoon (August) surface water TSM concentration was between 5.8 and 28.8 mg/l (Avg. 11.2) and bottom water was between 5.3 and 19.9 mg/l (Avg. 11.5), during post-monsoon (December) it was between 3.6 and 13.0 mg/l (Avg. 8.5) in surface waters and between 4.0 and 54.1 mg/l (Avg. 18.6) in bottom waters and during pre-monsoon season (April) surface water TSM ranges from 1.4 to 49.6 mg/l (Avg. 16.0) and bottom water ranges from 7.1 to 141.5 mg/l (Avg. 37.5). The post-monsoon and pre-monsoon data showed comparatively higher concentrations in the lower half of the estuary and decrease towards the head. In case of monsoon he had observed an increasing trend of TSM towards the head, but relatively higher concentrations are also observed in the lower half of the estuary. The surface TSM concentration reported was higher during pre-monsoon season followed by monsoon and post-monsoon, while the bottom water TSM concentration was observed to be higher during pre-monsoon followed by post-monsoon and monsoon season. Kumari et al. (2002) have made an observation only for one station in lower part of Zuari Estuary for the different seasons and reported average concentration of 48.6 mg/l in surface waters and 77.1 mg/l in bottom waters during year 1997 – 98. These values were relatively higher when compared to the values of 1977 – 78 and average TSM concentration of 1990 – 91.

As mentioned earlier, the surface TSM concentration in the present study (2004 – 05) ranges from 6.40 to 32.40 mg/l (Avg.19.98) and bottom TSM from 7.6 to 117.4 mg/l (Avg. 59.2) during monsoon season. During post-monsoon,

surface and bottom water TSM ranges from 5.7 to 60.0 mg/l (Avg. 24.5) and 7.9 to 224.9 mg/l (Avg. 48.4) respectively. In case of pre-monsoon, surface and bottom TSM concentration ranges from 8.8 to 28.6 mg/l (Avg. 20.3) and 11.6 to 100.9 mg/l (Avg. 34.7) respectively. The present study indicates a decrease in TSM concentration when compared with the average values reported for one station by Kumari et al. (2002). The study carried out during post-monsoon season in Zuari Estuary during 2007 (Nayak et al., 2008) shows that TSM concentration range from 1.4 to 47.4 mg/l (Avg. 9.4) in surface waters and from 2.4 to 119.8 (Avg. 28.5) mg/l in bottom waters. The values indicate further decrease compared to 2004 – 05. However, the distribution pattern of TSM was observed to be similar to that obtained during year 2004 – 05 for post-monsoon season.

To sum up, the present study on suspended matter distribution shows relatively higher concentration of TSM in bottom waters compared to surface waters in Zuari Estuary. Relatively higher concentrations are observed in the lower estuarine region. When the data of present study was compared with the existing data on Zuari Estuary, it is noted that the increasing trend of TSM from 1977 – 78 to 2002 has been reversed in the recent years.

c. Factors controlling TSM distribution

Estuary derives suspended matter from several sources such as land drainage, weathering, erosion, biological, chemical and physical processes and also largely by means of anthropogenic activities. Generally the concentration of TSM depends upon the sediment input and its movement within the estuary. The distribution of suspended matter in Zuari Estuary depends upon different factors which can be seen from wide fluctuations in TSM concentrations throughout the estuary. The principal factor that is mainly responsible for distribution of sediments is the circulation pattern, which depends on the tides (Petrusevics, 2005). Several other processes are involved in the distribution of suspended matter especially in case of estuarine environment since the situation becomes more complex when the fine particles discharged from the rivers encounter the salty water of an estuary. Flocculation processes which occur during estuarine mixing also play a vital

role in redistribution of suspended matter concentration. Flocculation is a reversible process. Deflocculation can occur when flocs are transported from saline water into fresh water (Postma, 1967; Duinker, 1980). In salinities above about 3 psu, fine particles in suspension are unstable and flocculate readily (Nichols and Biggs, 1985). Fine suspended particles in the estuary behave differently than those of sand grains. Clay size particles have high ratio of surface area to mass and therefore forces acting on the particles control its dynamic behavior in suspension and will flocculate most readily (Van Olphen, 1966), whereas the larger grains are not sufficiently surface-active to flocculate with other single grains but only adhere to flocs composed of many smaller grains (Nichols and Biggs, 1985). Transportation and deposition of suspended matter are not only affected by the change in particle properties and by flocculation and aggregation but also by mixing of fresh and salty water and associated estuarine circulation. Another important factor is the resuspension of finer bed sediments which is caused due to forcing functions such as disturbance caused by barge traffic etc. by which sediment is introduced back into the water column. Erosion is the dominating process, which occurs due to high currents or wave motion leading to resuspension of sediments. Changes in bed stress due to oscillation of tidal current (Alvarez and Jones, 2002) may also lead to surface erosion thereby changing the size distribution of suspended matter (Alvarez and Jones, 2002). Gauns (2000) observed the presence of rich microzooplankton community in Zuari Estuary and their abundance is relatively higher in the dry seasons than in the wet seasons indicating a key role of salinity in controlling their distribution and abundance. In addition, anthropogenic activities also contribute to the TSM concentration. Mining in Goa especially of iron and manganese ores was initiated in 1949. Since basin area of Zuari Estuary holds the considerable mining activity, the mining rejects finally end up in the estuary. The ore, after being mined at the mining sites situated in the hinterland, is transported by trucks and staked on the banks of the river, from where it is loaded on to the barges and transported through the Zuari Estuary to the Marmugao port. In addition to runoff bringing mine waste from catchment area during monsoon, the ore transport activities largely contribute to TSM concentration in the Zuari Estuary. Flocculation and resuspension processes which occur during

estuarine mixing play a vital role in redistribution of TSM concentration. Microzooplankton and phytoplankton also contribute to the TSM concentration. Coastal construction, influx of fertilizers from agricultural runoff, sewage outfalls must be also contributing to TSM in the estuary. However relative decrease in concentration of TSM from 2004 onwards can be related to decrease in contribution from mining activities. It is important to note here that though mining was started in the catchment area of Zuari River in the beginning for manganese, it was later shifted to catchment area of Mandovi in the north for iron mining. Presently Goa is known for its open cast mining and export of iron. Relatively higher concentration of TSM in bottom waters as compared to surface waters can be due to either resuspension by tidal surge that scours the finer sediments or finer particles that flocculate due to mixing of sea water and fresh water and form larger particles, which sink through the water column. This results in higher concentration in bottom water TSM.

In general, during monsoon, the surface water TSM concentration remained comparatively low up to station 6 which then shows relatively higher values up to station 15. Sudden increase is observed at station 16 and 17 and then the value decreases at station 18. Higher concentration of TSM during this season was expected in the estuary including upstream region. During monsoon Zuari Estuary behaves like a river up to the station 12 (upstream) maintaining zero salinity and comparatively low pH was recorded for stations 1 to 12. Large variation of salinity between surface and bottom waters was observed from station 13 to 18. Low concentration of TSM during this season in the upstream region could be due to heavy rainfall, which washes off the suspended material leaving behind the coarser material. The suspended matter transported by the river is mainly composed of finer particles and colloidal particles that flocculate as the salinity increases. In the zone of high sedimentation and accumulation, the optimum values of salinity for flocculation occur, leading to intense shoaling in a restricted area (Regnier and Wollast, 1993). Relatively higher concentration of TSM in the mid and lower estuary indicates hindrance by saline waters to the fast flowing river water, at this region. Wide variation in TSM concentration is observed in bottom waters than in the surface waters due to sinking of larger size

suspended matter and resuspension due to the bottom currents. Bottom waters show relatively higher concentrations between stations 5 and 8 in addition to stations 13 and 17. The River Kushawati, the tributary of Zuari Estuary, which joins at station 4, must be responsible for maintaining higher concentration of TSM between stations 5 and 8. Similarly, Cumbharjua Canal joining at the lower part must be contributing to higher TSM between stations 13 and 17. During post-monsoon, relatively higher values are observed between stations 12 and 16 in both surface and bottom waters. In case of pre-monsoon, variation between surface and bottom waters was higher and relatively higher values are seen at stations 7, 12 and 16 in both surface and bottom waters and also at station 15 in bottom waters. From the above recorded values it can be seen that higher values are observed in the lower half of the estuary roughly between stations 12 and 17 during post-monsoon and pre-monsoon seasons. During the post-monsoon and pre-monsoon higher pH values are associated with higher salinities. During post-monsoon, higher values of TSM are obtained between salinities 25 – 28 psu which further decrease up to the salinity of about 23 psu and comparatively lower values are recoded further upstream in the lower salinity with minor fluctuations. The higher concentration of TSM in lower region can be the combined effect of hydrodynamic conditions prevailing in this region, mixing of saline water with fresh water and also geomorphological setup. River Zuari has wide mouth (approximately 5.5 km), maintains almost same width up to 12 km upstream, which then narrows down to less than 0.5 km further upstream. The geomorphological constriction allows drag and lift force resulting removal of less denser material from the surface sediments leading to resuspension of sediments at this zone (Bukhari, 1994). The fair weather seasons during which currents are dominated (Das et al., 1972) are mainly due to flood and ebb tides and these are less strong in the bay region than in the constricted zone (Murty et al., 1976). The resuspended sediments are carried towards the upstream region since the water circulation pattern follows the current direction that probably carries the sediment in the same direction (Qasim and Sen Gupta, 1981). Therefore, higher TSM is maintained in the mid and lower estuary. The TSM concentration is found to be higher at station 7 during pre-monsoon season for both surface and bottom waters as saline

water intrusion is more than post-monsoon owing to very less fresh water discharge.

3.3. Particulate Metals

3.3.1. Results

a. Iron (Fe)

During monsoon Fe in surface TSM ranges from 153.8 to 5457.0 µg/l (Avg. 978.4). It shows a general increasing trend from head up to station 14 with slightly higher value recorded at station 1 and 7. Further downstream, it decreases towards the mouth region. Highest value is seen at station 14. Fe in bottom TSM ranges from 527.5 to 3732.5 µg/l (Avg. 1940.3). Fe shows an increasing trend from station 3 to 6, and then a decreasing trend up to station 14 with slightly higher values at stations 8 and 12.

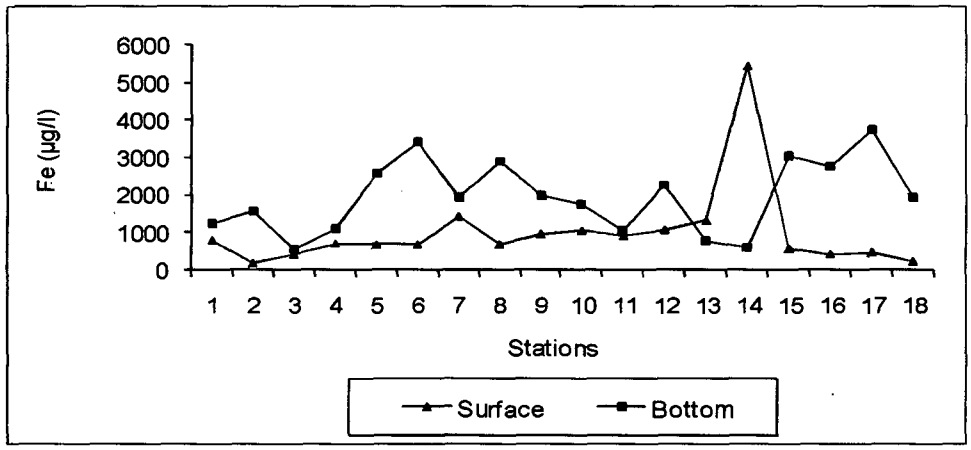


Fig. 3.6a: Distribution of Fe in surface and bottom TSM of Zuari Estuary during monsoon.

Further downstream, it increases up to station 17 with slightly lower value at station 16. Decrease in concentration is observed at station 18 (Fig. 3.6a).

Fe content during post-monsoon is very less between stations 1 and 9 in both surface and bottom waters. Between stations 9 and 18 the variation of Fe content is significant. Fe in surface TSM during this season ranges from 378.8 to 8632.0 µg/l (Avg. 2132.6).

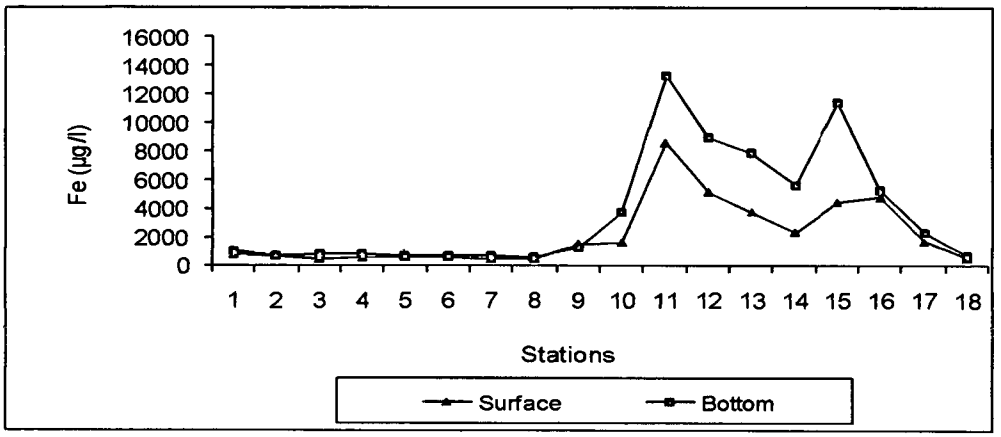


Fig. 3.6b: Distribution of Fe in surface and bottom TSM of Zuari Estuary during post-monsoon.

It shows a decreasing trend from station 1 to station 3 and then a slightly increasing trend up to station 6. Decrease in value is observed from station 6 to 8. Further downstream, large increase in value is observed up to station 11 and then Fe shows a decreasing trend up to station 14. A high value is recorded at station 15 and further then the values show a decreasing trend towards the mouth. Fe in bottom TSM ranges from 500.2 to 13365.0 µg/l (Avg. 3660.1). Fe content decreases from station 1 to 2 which then increases up to station 4 and then shows a decreasing trend up to station 8 with minor fluctuations in between. Further downstream concentration increases considerably up to station 11 and then shows a decreasing trend towards the mouth with a high value recorded at station 15, maintaining similar distribution pattern of to as that of surface waters (Fig. 3.6b).

During pre-monsoon season, Fe in surface TSM ranges from 193.8 to 1582.0 µg/l (Avg. 922.4). In general, Fe shows an increasing trend from station 1 up to station 7 with slightly higher values recorded at stations 2 and 4. Further downstream it decreases from station 7 up to station 9. Increase in values is observed from station 9 up to station 13 with lesser value at station 12 and then, it shows a decreasing trend towards the mouth region with minor fluctuations. In case of bottom TSM, Fe ranges from 537.0 to 7943.8 µg/l (Avg. 2072.1). It shows a similar distribution pattern similar to that of surface

TSM up to station 8, but with considerably higher values at stations 2, 4 and 7. Further, the value increases up to station 12.

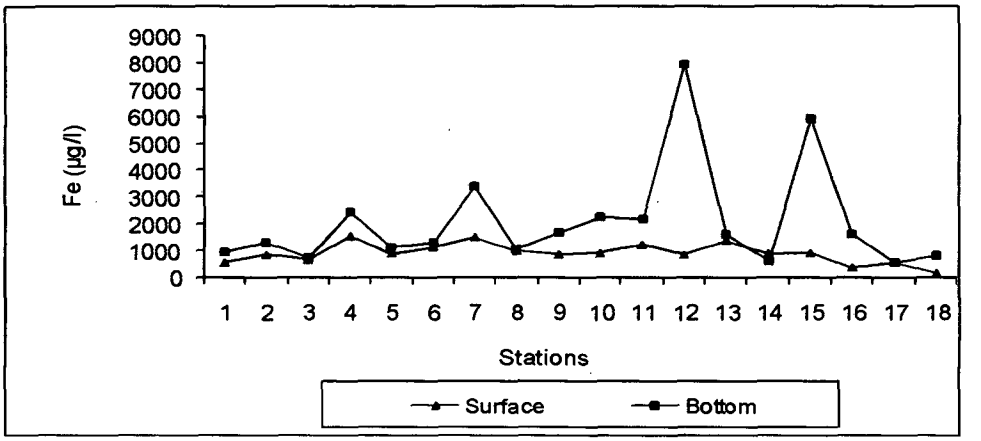


Fig. 3.6c: Distribution of Fe in surface and bottom TSM of Zuari Estuary during pre-monsoon.

Decrease in value is seen from stations 12 to 14. Very high values are recorded at stations 12 and 15, which further show a decreasing trend towards the mouth region (Fig. 3.6c).

In all the three seasons, Fe in bottom TSM shows relatively higher concentrations than in surface TSM. Fe content is observed to be higher during post-monsoon season followed by monsoon and pre-monsoon season in surface TSM while in bottom TSM it is observed to be higher during post-monsoon followed by pre-monsoon and monsoon.

b. Manganese (Mn)

During monsoon, Mn ranges from 14.7 to 525.0 µg/l (Avg. 110.1) in surface TSM and from 17.2 to 56.3 µg/l (Avg. 289.1) in bottom TSM. Mn during monsoon shows a distribution pattern similar to that of Fe in both surface and bottom TSM with slight variation in between (Fig. 3.7a).

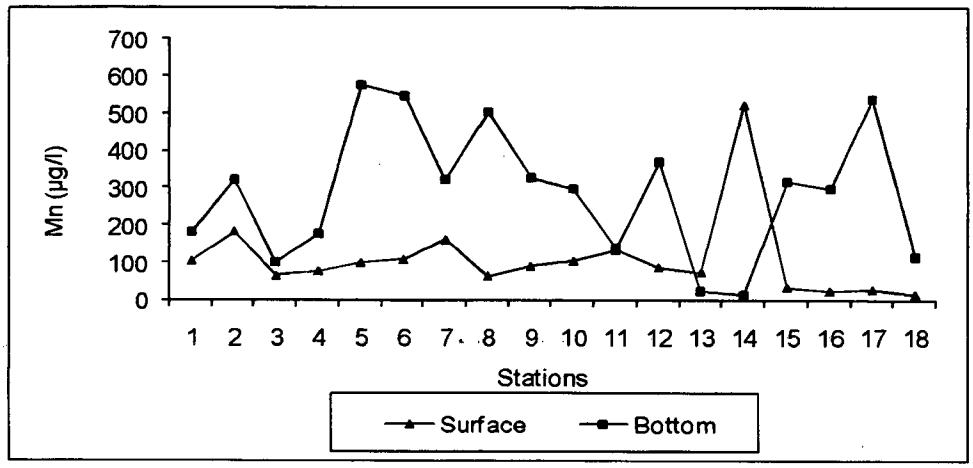


Fig. 3.7a: Distribution of Mn in surface and bottom TSM of Zuari Estuary during monsoon.

In case of post-monsoon, Mn ranges from 41.1 to 625.0 µg/l (Avg. 164.3) in surface TSM and from 42.6 to 1262.5 µg/l (Avg. 370.1) in bottom TSM. Mn in surface and bottom TSM shows an increase from station 1 to 2.

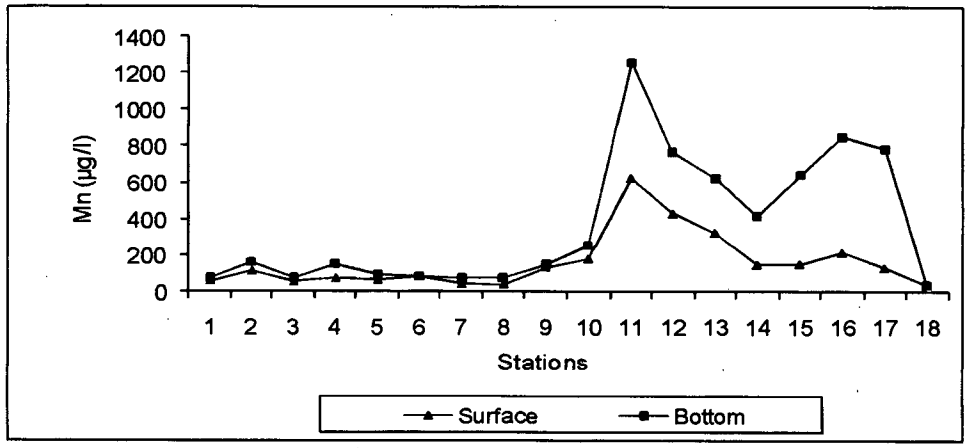


Fig. 3.7b: Distribution of Mn in surface and bottom TSM of Zuari Estuary during post-monsoon.

Decrease in value is seen at station 3 which increases at station 4 and then shows a decreasing trend up to station 8 with slightly higher value at station 6 in case of surface TSM. Further downstream Mn shows a pattern similar to that of Fe for both surface and bottom TSM with very high values at stations 11 and 16 (Fig. 3.7b).

During pre-monsoon, Mn content in surface TSM ranges from 7.3 to 189.9 µg/l (Avg. 89.6) and in bottom TSM Mn ranges from 36.90 to 645.0 µg/l (Avg. 203.2).

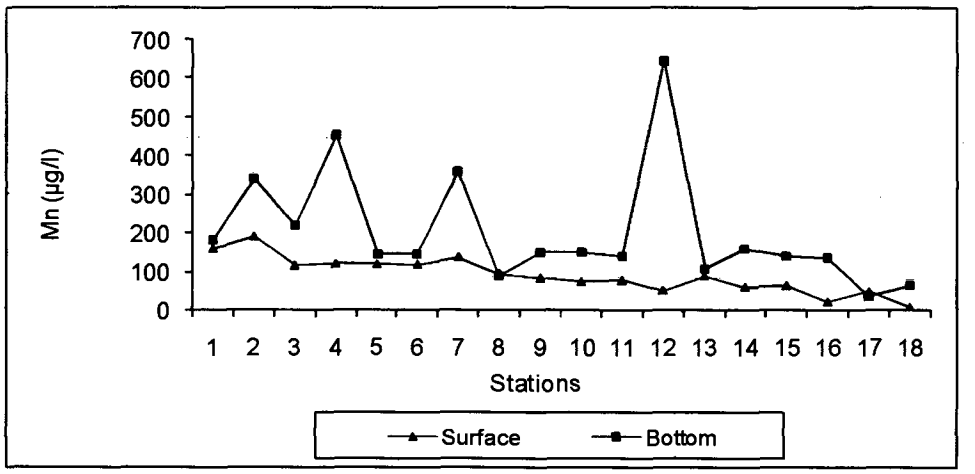


Fig. 3.7c: Distribution of Mn in surface and bottom TSM of Zuari Estuary during pre-monsoon.

In general, Mn shows a decreasing trend from head to the mouth, with some peaks obtained in between for bottom waters (Fig. 3.7c). Most of the Mn peaks are matching with the higher values of Fe during this season.

c. Chromium (Cr)

Chromium during monsoon season ranges from 1.4 to 16.0 µg/l (Avg. 9.6). It shows a decreasing trend from station 1 to 4 which then increases up to station 7 (Fig. 3.8a). Further downstream, it shows a general decreasing trend towards the mouth with slightly higher values obtained at stations 11 and 14. Cr in bottom TSM ranges from 1.9 to 33.3 µg/l (Avg. 12.0). It shows a decreasing trend from station 1 to 3 and then an increasing trend up to station 9 with some variations in between and then decreases up to station 14. An increasing trend is observed from station 14 to 17 and at station 18 a low value is recorded. Highest value is observed at station 9. Some peaks of Cr coincide with peaks of Fe.

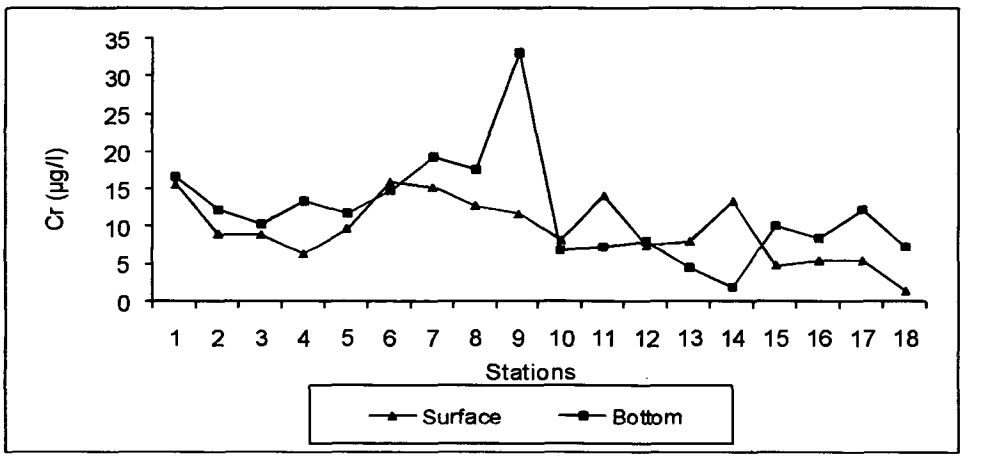


Fig. 3.8a: Distribution of Cr in surface and bottom TSM of Zuari Estuary during monsoon.

During post-monsoon Cr content in surface TSM, ranges from 3.6 – 36.9 µg/l (Avg. 12.6). Cr shows a decreasing trend from station 1 to 3 which further increases up to station 6. Decreasing trend is observed from station 6 to 8.

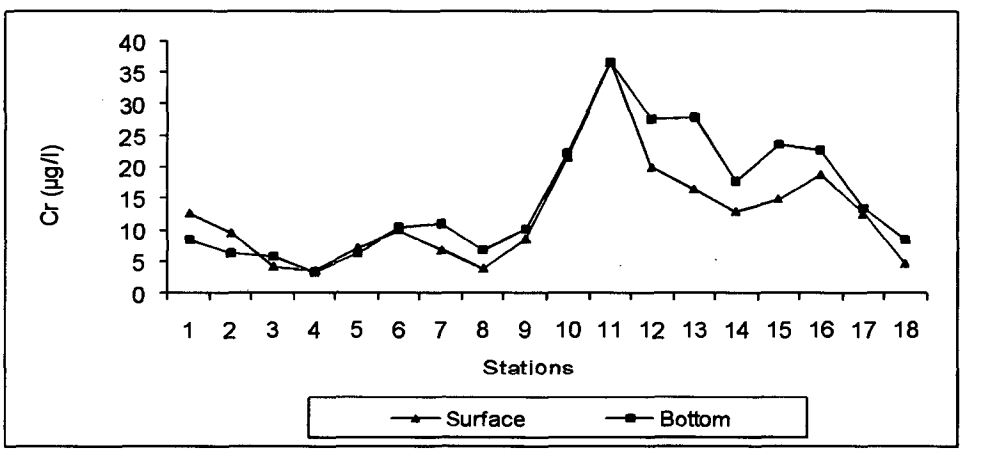


Fig. 3.8b: Distribution of Cr in surface and bottom TSM of Zuari Estuary during post-monsoon.

Further downstream, Cr shows a drastic increase up to station 11 and then shows a decreasing trend towards the mouth region with minor fluctuations in between. Distribution pattern of Cr in surface waters was similar to that of Fe and Mn. In bottom TSM, Cr varies from 3.4 to 36.9 µg/l (Avg. 15.1). Cr in bottom TSM also shows trend similar to that of surface TSM, thereby maintaining distribution pattern similar to that of Fe and Mn (Fig. 3.8b).

During pre-monsoon, Cr content in surface TSM varies from 1.9 to 13.9 µg/l (Avg. 8.3). Cr content decreases from station 1 to 2 which further increases up to station 5 and then shows a decreasing trend up to station 8 with minor fluctuations. Increase in value is observed from station 8 to 11 which then decreases at station 12. A slight peak is observed at station 13 and then values suddenly drops down at station 14.

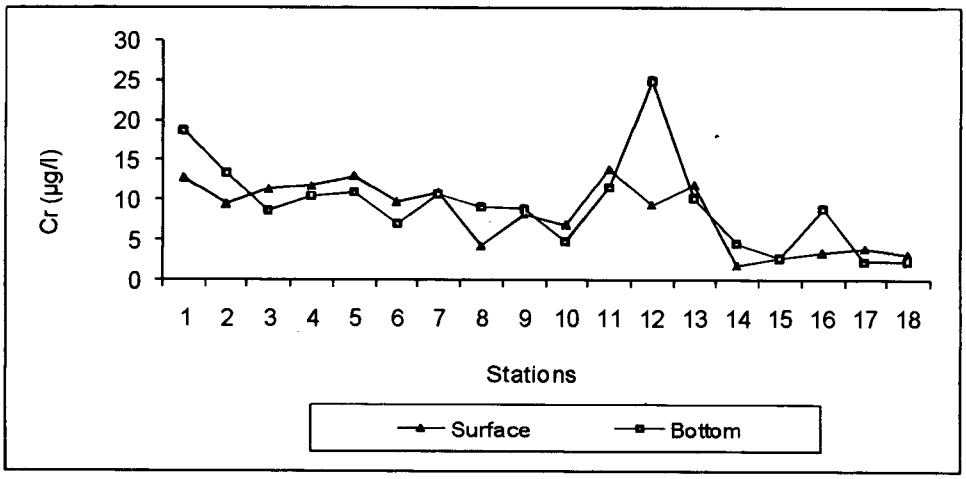


Fig. 3.8c: Distribution of Cr in surface and bottom TSM of Zuari Estuary during pre-monsoon.

Further downstream, Cr shows an increasing trend towards the mouth with slight decrease at station 18. In bottom TSM, Cr content ranges from 2.3 to 25.1 µg/l (Avg. 9.5). Cr content decreases from station 1 up to station 10 with minor fluctuation in between. Further downstream peak values are observed at stations 12 and 16 and then Cr shows a decreasing trend up to station 18 (Fig. 3.8c).

d. Copper (Cu)

Cu content in surface TSM during monsoon ranges from 1.5 to 9.5 µg/l (Avg. 3.0). In general, distribution pattern of Cu is similar to that of Fe ad Mn with some variations in between (Fig. 3.9a). Cu content decreases from station 1 to 2. It further shows an increasing trend up to station 7. Decrease in value is observed at station 8 and then Cu shows an increasing trend up to station 14 with minor variation in between. Cu shows a decreasing trend further

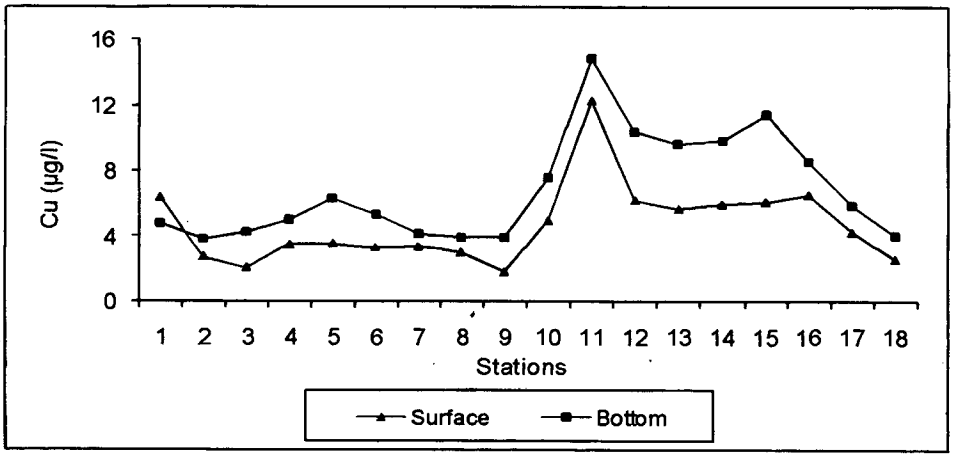


Fig. 3.9b: Distribution of Cu in surface and bottom TSM of Zuari Estuary during post-monsoon.

Between stations 9 and 18, the distribution pattern is largely similar to other elements.

In case of pre-monsoon season, Cu content varies from 1.4 to 6.0 µg/l (Avg. 2.7). Relatively higher values with peaks of Cu are observed at stations 3, 7, 11, 13 and 15. Cu in bottom TSM varies from 2.1 to 8.0 µg/l (Avg. 3.8). It is observed to be relatively higher at stations 2, 5, 7, 12 and 15 (Fig. 3.9c).

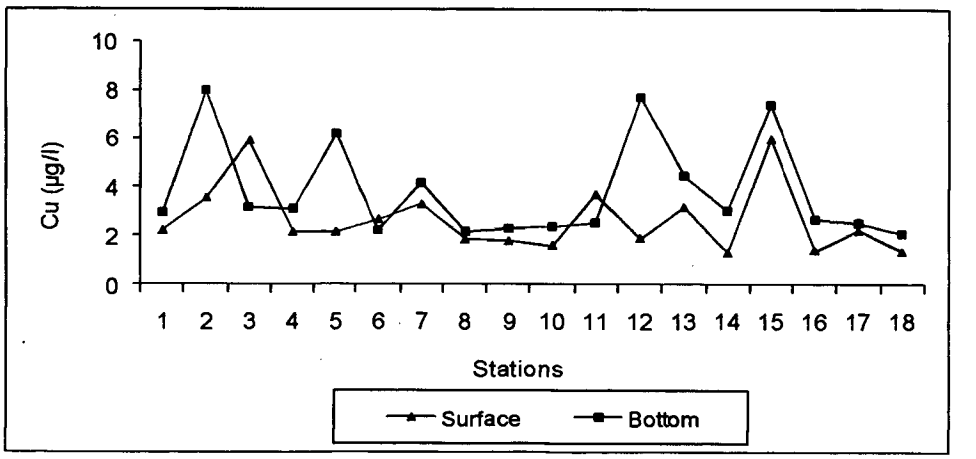


Fig. 3.9c: Distribution of Cu in surface and bottom TSM of Zuari Estuary during pre-monsoon.

e. Zinc (Zn)

Zn content from 3.0 to 26.6 µg/l (Avg. 8.2) in surface TSM ranges and varies from 4.9 to 14.9 µg/l (Avg. 9.4) in bottom TSM during monsoon. It shows a distribution pattern largely similar to that of Cu in both surface and bottom TSM with some variations in between (Fig. 3.10a).

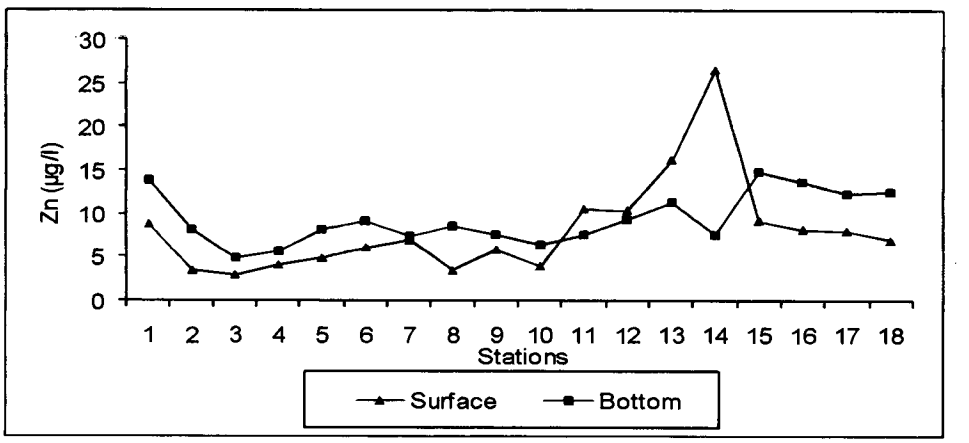


Fig. 3.10a: Distribution of Zn in surface and bottom TSM of Zuari Estuary during monsoon.

During post-monsoon Zn ranges from 2.0 to 17.0 µg/l (Avg. 7.4). It shows decreasing trend from station 1 up to station 3. Increase in value is observed at station 4, and then decreases at station 5 (Fig. 3.10b).

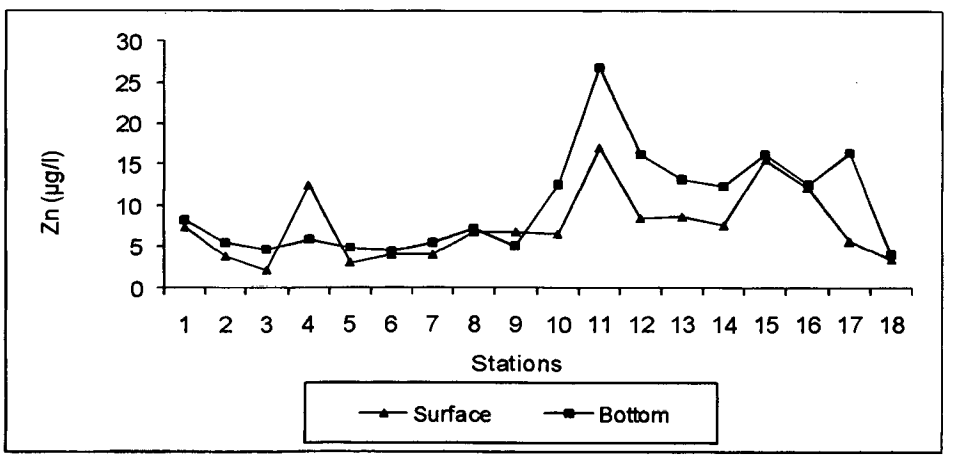


Fig. 3.10b: Distribution of Zn in surface and bottom TSM of Zuari Estuary during post-monsoon.

Further downstream, it shows an increasing trend up to station 11 with some fluctuations in between. Zn then shows decrease in values up to station 14. A peak is observed at station 15 and then it shows a decreasing trend towards the mouth. Zn content in bottom TSM ranges from 4.1 to 26.9 µg/l (Avg. 10.1). Relatively lower values are observed in the upper estuary than the lower estuary. Higher value is recorded at station 11. Distribution pattern is largely comparable to that of Cu.

Zn content in surface TSM ranges from 4.1 to 13.0 µg/l (Avg. 8.9) during pre-monsoon season. It shows a decreasing trend from head to the downstream region maintaining slightly higher values between 11 and 15.

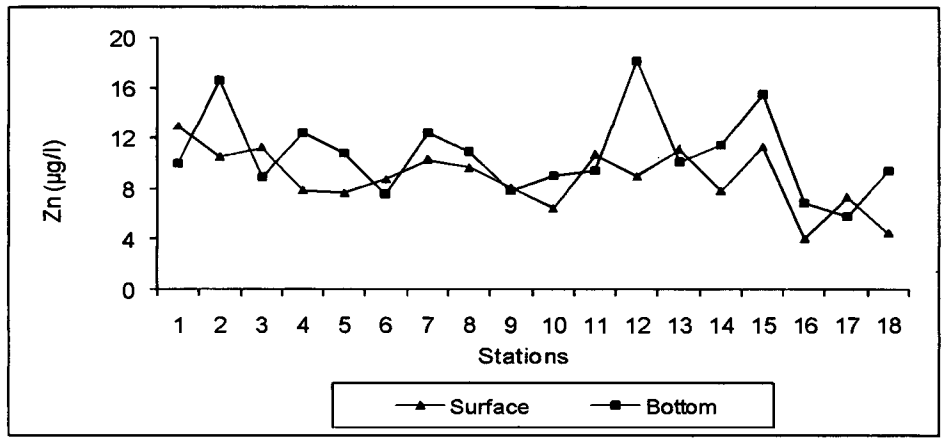


Fig. 3.10c: Distribution of Zn in surface and bottom TSM of Zuari Estuary during pre-monsoon.

In bottom TSM, Zn content ranges from 5.8 to 18.3 µg/l (Avg. 10.8). Relatively higher values are observed at stations 2, 4, 7, 12 and 15. These peak values coincide with Cu in bottom TSM (Fig. 3.10c).

f. Cobalt (Co)

During monsoon Co in surface TSM ranges from 0.7 to 3.4 µg/l (Avg. 2.1). Lower values of Co are seen between stations 1 and 5. Relatively higher values are seen between stations 6 and 16 with lower values recorded at stations 9 and 12 in between. The values then decrease towards the mouth. Co in bottom TSM ranges from 0.9 to 4.4 µg/l (Avg. 2.5).

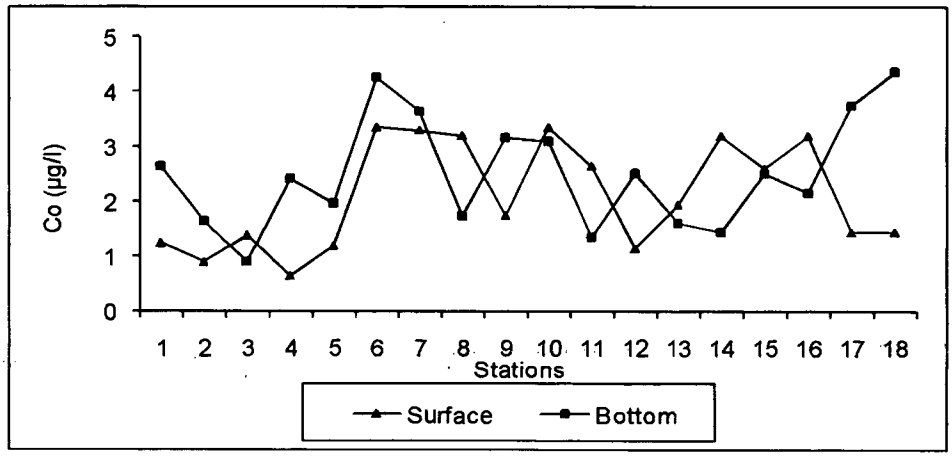


Fig. 3.11a: Distribution of Co in surface and bottom TSM of Zuari Estuary during monsoon.

Irregular distribution pattern is observed for Co but slight increase is seen towards the mouth region, which is similar to the distribution pattern of Cu in bottom TSM. Relatively higher values are observed at stations 6 and 18 (Fig. 3.11a).

In case of post-monsoon, Co content ranges from 0.3 to 4.3 µg/l (Avg. 1.7) in surface TSM. Relatively lower values are seen up to station 8 with two slightly higher values observed at stations 2 and 4. Further, an increase in values is observed up to station 11 which then decreases up to station 14

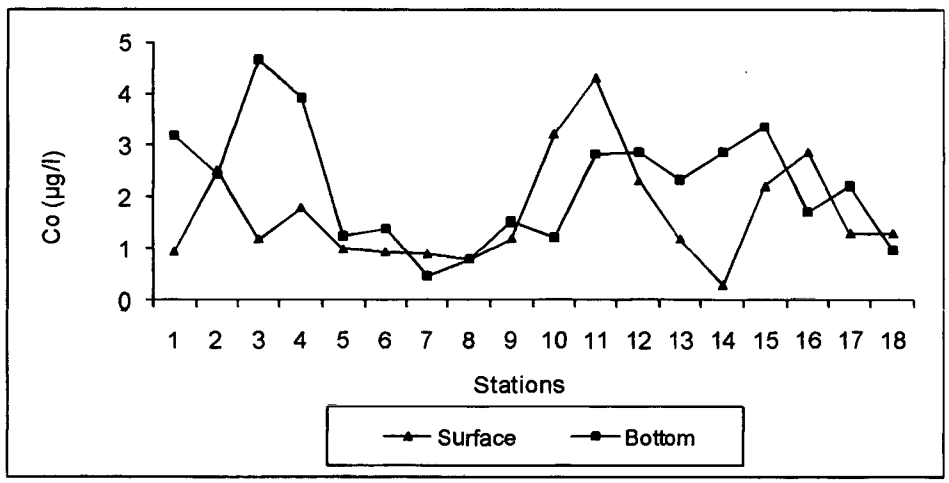


Fig. 3.11b: Distribution of Co in surface and bottom TSM of Zuari Estuary during post-monsoon.

Increase in values is observed from station 14 up to station 16. Further downstream it decreases towards the mouth region. Higher Co values are obtained for stations 10, 11, 12, 15 and 16. In bottom TSM, the Co content ranges from 0.5 to 4.7 µg/l (Avg. 2.2). Co content decreases from station 1 to 2, further an increase is observed at station 3 and then Co decreases up to station 7. Values increase from station 7 up to station 15 with minor fluctuations in between. Further Co decreases towards the mouth (Fig. 3.11b).

Co during pre-monsoon season ranges from 0.9 to 3.2 µg/l (Avg. 2.2) in surface TSM. Relatively higher values are recorded at stations 8, 12 and 15. Co in bottom TSM ranges from 0.7 to 5.0 µg/l (Avg. 2.4). In general Co shows increasing trend from head towards the mouth region. Relatively higher values are recorded at stations 7, 12, 15 and 18 (Fig. 3.11c).

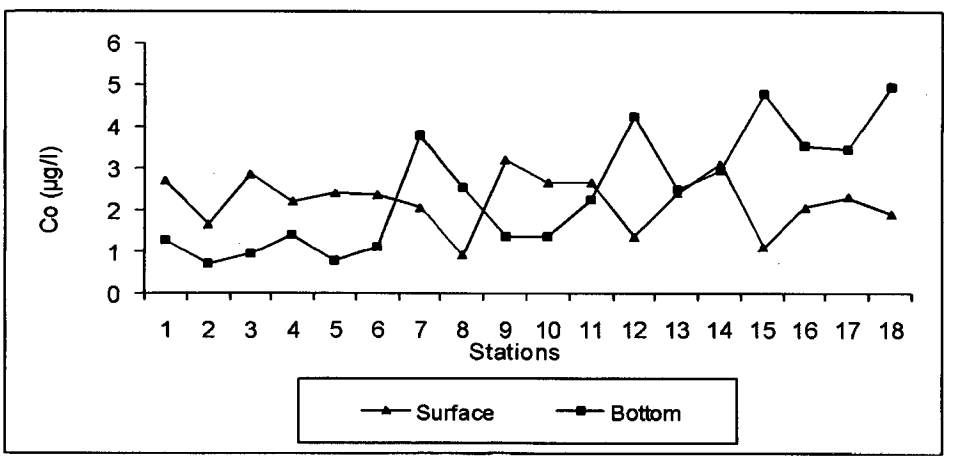


Fig. 3.11c: Distribution of Co in surface and bottom TSM of Zuari Estuary during pre-monsoon.

g. Aluminium (Al)

Al content in surface TSM during monsoon, post-monsoon and pre-monsoon ranges from 217.3 to 2747.0 µg/l (Avg. 546.9), 87.2 to 354.7 µg/l (Avg. 786.2) and 222.0 to 675.0 µg/l (Avg. 339.0) respectively, while in bottom TSM it ranges from 128.9 to 2311.2 µg/l (Avg. 877.4), 181.2 to 4418.7 µg/l (Avg. 1339.8) and from 240.5 to 3489.4 µg/l (Avg. 913.5) during the same seasons.

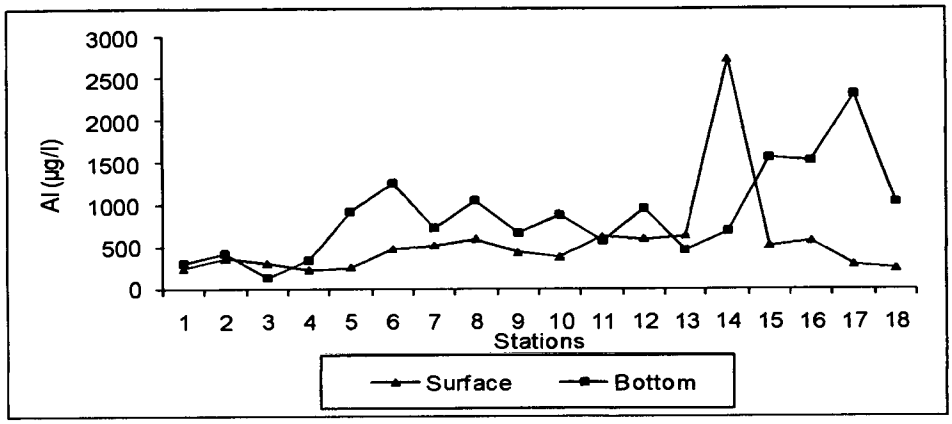


Fig. 3.12a: Distribution of Al in surface and bottom TSM of Zuari Estuary during monsoon.

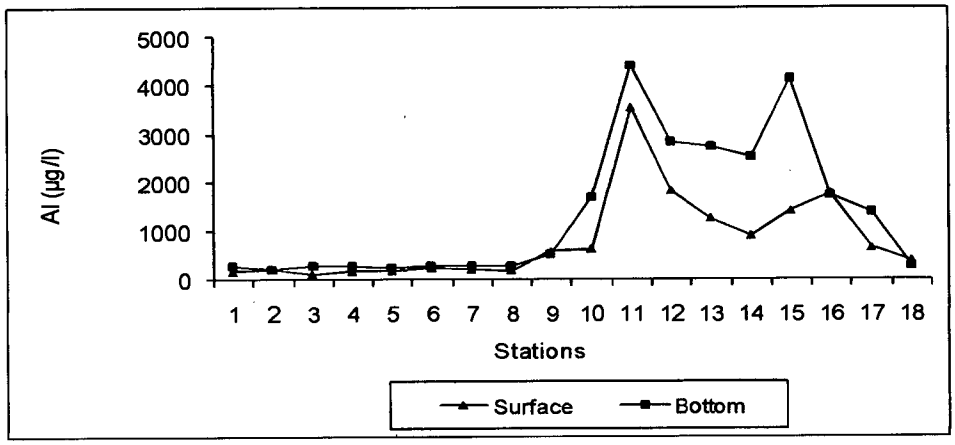


Fig. 3.12b: Distribution of Al in surface and bottom TSM of Zuari Estuary during post-monsoon.

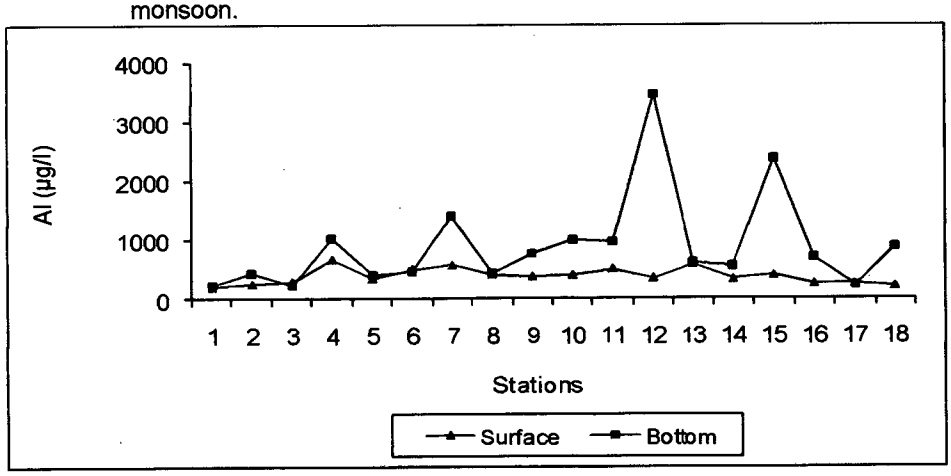


Fig. 3.12c: Distribution of Al in surface and bottom TSM of Zuari Estuary during pre-monsoon.

Distribution pattern of Al is similar to that of Fe in both surface and bottom TSM with slight variation in between, during all the seasons (Fig. 3.12 a to c).

All the metals show relatively higher concentration in bottom TSM than in surface TSM at most of the stations. Relatively higher concentrations of metals are observed during post-monsoon season compared to other two seasons.

3.3.2. Discussion

a. Relationship Between Particulate Metals and TSM Concentration

During monsoon, all the elements, except for Co ($r = 0.52$) in surface TSM and Al ($r = 0.60$) in bottom TSM, show an insignificant correlation with their respective TSM concentration. Fe ($r = 0.72$), Co ($r = 0.83$) and Al ($r = 0.80$) in surface and Fe, ($r = 0.94$), Mn ($r = 0.92$) and Al ($r = 0.92$) in bottom TSM show significant correlation ($p < 0.05$) with their respective TSM concentration while other elements show weak correlation with TSM concentration from station 1 up to station 10 when considered separately. All the elements show weak correlation with TSM concentration in the downstream region (station 11 to 18) in both surface and bottom waters.

During post-monsoon, all the elements show positive correlation with the TSM concentration in both surface and bottom waters when the whole estuary is considered. Fe ($r = 0.81$), Mn ($r = 0.76$), Cr ($r = 0.70$), Co ($r = 0.60$), and Al ($r = 0.89$) in surface TSM exhibits significant correlation ($p < 0.05$) with surface TSM concentration from station 1 up to station 10, while in case of bottom TSM, Fe ($r = 0.95$), Mn ($r = 0.75$), Cr ($r = 0.90$), Zn ($r = 0.87$), Cu ($r = 0.63$) and Al ($r = 0.97$) exhibit significant correlation with respective TSM concentration in the same region. From station 12 to 18 all the elements except for Co in surface TSM, viz. Fe ($r = 0.83$), Mn ($r = 0.60$), Cr ($r = 0.79$), Cu ($r = 0.95$), Zn ($r = 0.71$) and Al ($r = 0.81$) are significantly correlated with the surface TSM concentration, while Cu ($r = 0.75$) and Co ($r = 0.71$) in bottom TSM are significantly correlated with their respective TSM

concentration. Also Al ($r = 0.63$) and Fe ($r = 0.56$) shows good correlation ($p < 0.1$).

During pre-monsoon, all the elements except for Fe ($r = 0.45$) and Al ($r = 0.48$) in surface TSM and Fe ($r = 0.85$), Co ($r = 0.77$) and Al ($r = 0.87$) in bottom TSM are inversely correlated with the respective TSM concentration from station 1 to 12. In lower estuarine region from station 11 to 18 all the elements shows weak correlation with the surface TSM concentration, while metals in bottom TSM exhibit significant correlation ($p < 0.05$, $p < 0.1$) with the bottom TSM concentration (Fe ($r = 0.96$), Mn ($r = 0.75$), Cr ($r = 0.51$), Cu ($r = 0.91$), Zn ($r = 0.91$), Co ($r = 0.56$) and Al ($r = 0.97$)).

Estuaries are traps of suspended matters received from rivers (Turner and Millward, 2002). Metals are primarily associated with the suspended particulate matter in the estuarine system due to the processes of adsorption onto hydrous iron, aluminium and manganese oxides, organic substrates, silicates such as clays and salting-out effects (Webster, 1995; Turner and Millward, 2002). Therefore, suspended sediments provide a pathway for transport of associated metals. Deposition of suspended sediments on the bottom creates reservoirs of metals in many estuaries over the time (Ridgeway and Shimmield, 2002; Taylor et al., 2004). Subsequent erosion and resuspension of bottom sediments can remobilize previously buried contaminants (Arzayus et al., 2002; Hornberger et al., 1999; Lee and Cundy, 2001) which potentially contributes to contamination of the overlying water column (Turner and Millward, 2002; Conaway et al., 2003) leading to deleterious effects to the environment. Tracing sources and pattern of transport of contaminant suspended matter in the estuarine environment is complicated for a number of reasons, but very essential. Several researchers have commented on profound effect of the estuarine turbidity maximum zone, located where riverine and tidal flows meets, on trace metal distribution (Yeats and Loring 1991).

In most of the cases, metals are significantly correlated with the TSM concentration except for surface TSM during pre-monsoon and surface and

bottom TSM during monsoon. Elemental distribution as well as suspended matter concentration in the estuary varies spatially due to proximity to source and spatial variability in physical processes that suspend or remove contaminant from the water column (Brown et al., 2003; Linville et al., 2002; Squire et al., 2002). Zuari Estuary is divided into two halves to understand the terrestrial and marine dominance of metals in TSM in the estuary. A distinct distribution pattern of TSM is obtained during post-monsoon, which is quite different from monsoon and pre-monsoon. Higher concentration of metals is observed in the lower half of the estuary roughly between stations 11 and 16 or 17 except Co in surface TSM. TSM concentration is also observed to be higher at these stations during this season. The clay particles and hydroxides which are generally the fine sediments are expected to flocculate at prevailing salinity conditions and remain in suspension resulting in high zone of TSM concentration along with relatively higher concentrations of metals. During post-monsoon the concentration of metals as well as TSM decreases at the mouth. This can be explained considering desorption of metals from particles by complextion or by dilution of the polluted fluvial sediments by mixing with less polluted marine solid matter (De Groot et al., 1971; Forstner and Muller, 1975).

During monsoon there is an increase in concentration of TSM towards the downstream region and is due to strong river currents carrying the suspended sediments towards the downstream region. During episodic events of pronounced freshwater discharges, large quantities of water and freshly eroded material, eventually containing mobilized contaminants, enter the estuary (Makepeace et al., 1995). Negative correlation obtained between TSM concentration and metals especially in lower estuarine region during this season can be due to desorption of metals in the high salinity region. Also, low metal content in the high TSM can be due to the dominance of detrital finer coarse fractions which are generally depleted in metals and hence contribute more mass but less metals to TSM (Biskam et al., 1991; Houba et al., 1983; Jain and Sharma 2001). Significant correlation obtained in the upper half of the estuary during monsoon supports catchment area as a major source. Also, during pre-monsoon similar pattern of general increasing trend

of TSM towards the downstream region was observed, which can be due to resuspension by tidal surge at this region. Metals in surface TSM generally did not show increase with TSM concentration. But in bottom TSM metal concentration was high. Fe and Al are positively correlated with surface TSM in the upper estuarine region and all other elements show negative correlation. Bottom water TSM generally shows significant correlation with metal concentrations than the surface waters. Several factors such as mixing of riverine suspended matter and particles of marine origin (Nolting et al., 1990); resuspension of sediments (Turner et al., 1991); mobilization of Fe and Mn in reducing sediments (Feely et al., 1986); flocculation of colloidal material (Turner and Millward, 2002); sorption in low salinity and high turbidity zones (Gobeil et al., 1981); production of organic matter (Collier and Edmond, 1984) and industrial and urban waste water discharges (Nolting et al., 1999) contribute to the distribution of elements. Some of these if not all must have played a role in distribution of sediments in Zuari Estuary.

Metals in suspended matter are significantly correlated with aluminium which is generally associated with the finer fractions of the sediments. This suggests that granulometry must have also played a role in metal concentrations in the Zuari estuarine sediments. Elements show significant correlation with Fe and Mn which are the major metals in the estuary indicating that either hydroxides of Fe or Mn or both must be also controlling the distribution of other elements.

b. Normalization with Aluminium

To evaluate the grain size effect on metal concentrations in sediments, the elements are normalized with Al. Aluminium is the most commonly used normalizing element due to its abundance, immobility, association with finer size, natural origin in most cases and a metal of sediment constituent (Zhang and Liu, 2002; Feng et al., 2004; Mil-Homens et al., 2006; Qiao et al., 2007;). Aluminium was used as reference element in the present study as its presence in the marine environment is generally related to crustal origin. The positive correlation of Aluminium with the studied metals (Table 3.1 to 3.3) confirms that Al can be an ideal element for normalization. The enrichment of

Al in the low salinity zone can be due to settling of coarse particles when current velocity is relatively high (Wartel, 1977). It is also noted that in general, Al in the estuary has positive correlation with TSM.

Table 3.1a: Correlation between metals in surface TSM during monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al
Fe	1.00						
Mn	**0.92**	1.00					
Cr	0.34	0.47	1.00				
Cu	**0.90**	**0.82**	0.31	1.00			
Zn	**0.85**	**0.70**	0.14	**0.91**	1.00		
Co	0.36	0.26	0.37	0.23	0.25	1.00	
Al	**0.96**	**0.89**	0.27	**0.88**	**0.86**	0.42	1.00

Table 3.1b: Correlation between metals in bottom TSM during monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al	TSM
Fe	1							
Mn	**0.87**	1.00						
Cr	0.26	0.41	1.00					
Cu	**0.59**	0.25	0.06	1.00				
Zn	0.45	0.07	-0.12	**0.79**	1.00			
Co	**0.55**	0.38	0.32	**0.62**	0.30	1.00		
Al	**0.87**	**0.59**	-0.05	**0.65**	**0.56**	0.49	1.00	

Table 3.2a: Correlation between metals in surface TSM during post-monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al	TSM
Fe	1.00							
Mn	**0.93**	1.00						
Cr	**0.89**	**0.90**	1.00					
Cu	**0.88**	**0.83**	**0.91**	1.00				
Zn	**0.79**	**0.63**	**0.64**	**0.76**	1.00			
Co	**0.70**	**0.70**	**0.77**	**0.63**	**0.60**	1.00		
Al	**0.99**	**0.94**	**0.90**	**0.89**	**0.76**	**0.72**	1.00	

Table 3.2b: Correlation between metals in bottom TSM during post-monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al	TSM
Fe	1.00							
Mn	**0.86**	1.00						
Cr	**0.93**	**0.87**	1.00					
Cu	**0.97**	**0.86**	**0.92**	1.00				
Zn	**0.89**	**0.94**	**0.89**	**0.90**	1.00			
Co	0.30	0.23	0.08	0.28	0.24	1.00		
Al	**0.99**	**0.85**	**0.92**	**0.96**	**0.90**	0.29	1.00	

Table 3.3a: Correlation between metals in surface TSM during pre-monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al	TSM
Fe	1.00							
Mn	0.42	1.00						
Cr	0.49	**0.64**	1.00					
Cu	0.20	0.31	0.24	1.00				
Zn	0.41	**0.66**	**0.52**	**0.65**	1.00			
Co	0.00	0.08	0.30	-0.14	-0.05	1.00		
Al	**0.94**	0.18	0.40	0.14	0.21	0.00	1.00	

Table 3.3b: Correlation between metals in bottom TSM during pre-monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al	TSM
Fe	1.00							
Mn	**0.66**	1.00						
Cr	0.44	**0.72**	1.00					
Cu	**0.62**	**0.53**	0.44	1.00				
Zn	**0.70**	**0.72**	**0.51**	**0.84**	1.00			
Co	0.48	0.01	-0.18	0.11	0.20	1.00		
Al	**0.98**	**0.64**	0.38	**0.56**	**0.68**	**0.58**	1.00	

* Bold values are statistically significant at $p < 0.05$.

The distribution of normalized metal concentrations in the both surface and bottom TSM is presented in the figures (Fig. 3.13 to 3.15). From the plots it is seen that the concentrations of most of the metals are greatly affected by the grain size. Seasonal differences of metal concentration in suspended matter due to grain size have been reported earlier by Qiao et al. (2007).

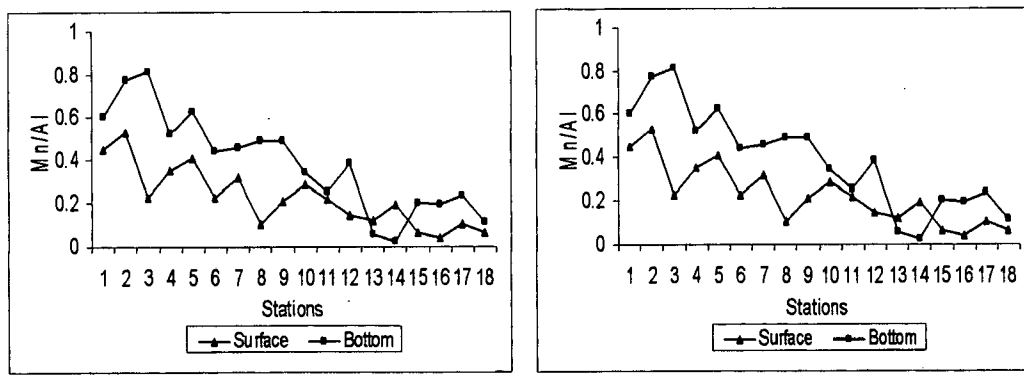


Fig. 3.13a: Al normalized plots of Fe and Mn in surface and bottom TSM during monsoon.

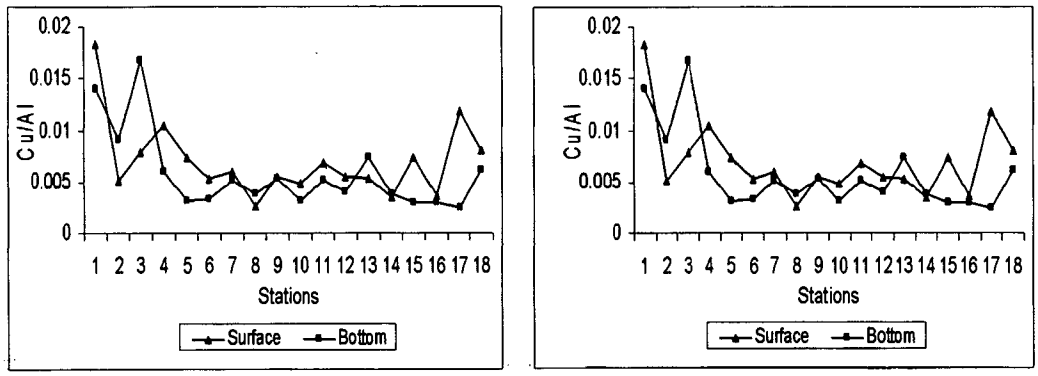


Fig. 3.13b: Al normalized plots of Cr and Cu in surface and bottom TSM during monsoon.

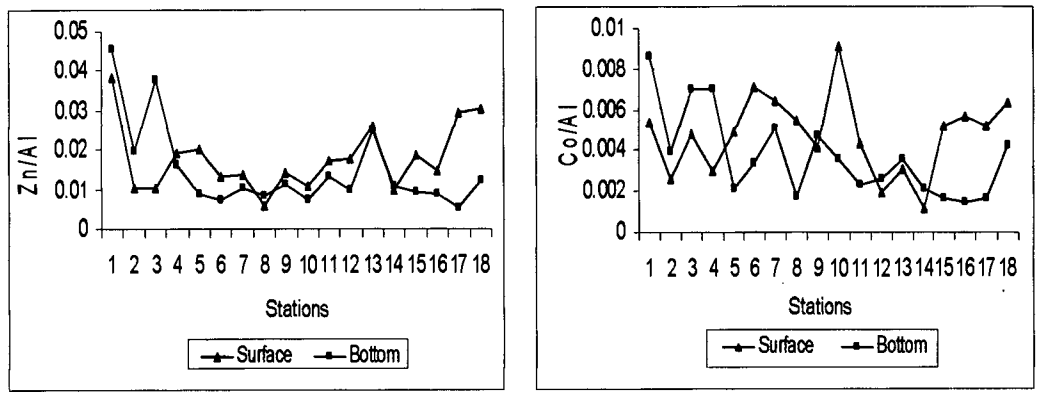


Fig. 3.13c: Al normalized plots of Zn and Co in surface and bottom TSM during monsoon.

During monsoon, normalized values of all the metals show higher concentrations in the upper estuarine region, which, further downstream shows a decreasing trend with some fluctuations in between towards the mouth. However, Co/Al and Zn/Al show an increase towards the mouth in both surface and bottom TSM. Bottom TSM holds comparatively higher concentration of most of the metals with few exceptions. Relatively higher values are seen at stations 1, 4, 5, 7 and 10 for Fe/Al, stations 1 and 2 for Mn/Al, station 1 for Cr/Al, stations 1 and 17 for Cu/Al, stations 1, 16 and 17 for Zn/Al and stations 10 and 17 for Co/Al in surface TSM. While in bottom, TSM higher values are seen at stations 1 and 3 for Fe/Al, 2 and 3 for Mn/Al, 3 and 9 for Cr/Al, 1 and 3 for Cu/Al and Zn/Al and 1, 3 and 4 for Co (Fig. 3.13 a to c).

In case of post-monsoon season also, in general, decrease in values of the normalized metals towards the downstream region is seen with minor fluctuations. However, distinctly higher concentrations are seen in the upper half of the estuary than the lower estuary (Fig. 3.14 a to c).

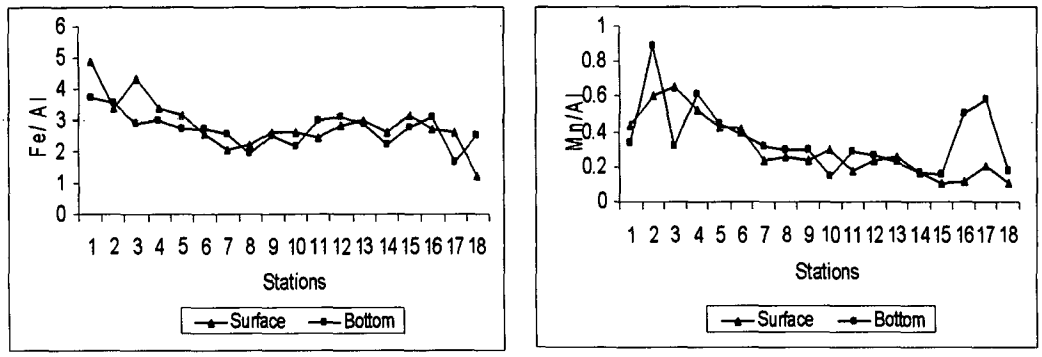


Fig. 3.14a: Al normalized plots of Fe and Mn in surface and bottom TSM during post-monsoon.

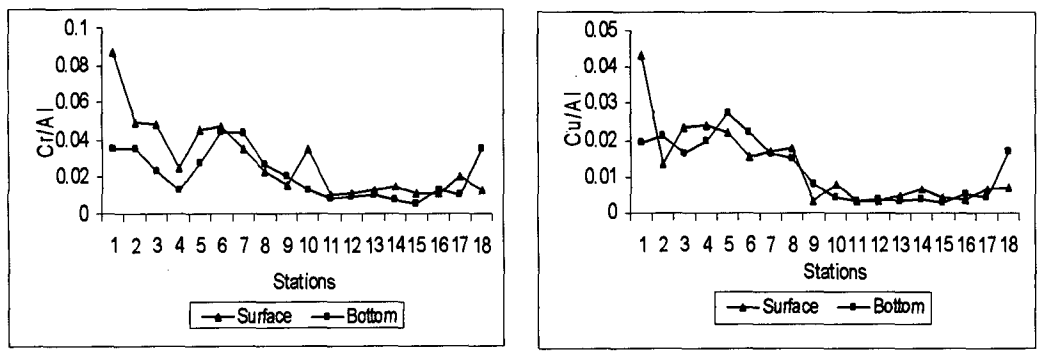


Fig. 3.14b: Al normalized plots of Cr and Cu in surface and bottom TSM during post-monsoon.

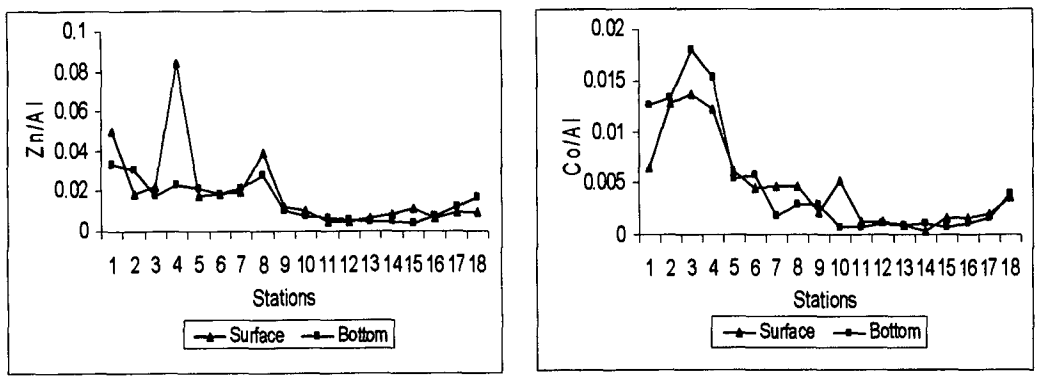


Fig. 3.14c: Al normalized plots of Zn and Co in surface and bottom TSM during post-monsoon.

Relatively higher values are recorded at stations 1 and 3 for Fe/Al, 3 for Mn/Al and Co/Al, 1 for Cr/Al and Cu/Al and 4 for Zn/Al in surface TSM. In case of Mn/Al, slightly higher values are seen at stations 2, 16 and 17 in bottom TSM. Further, higher values are seen at station 1 and 2 for Fe/Al, 6 and 7 for Cr/Al, 5 for Cu/Al, 1 and 8 for Zn/Al and 3 and 4 for Co/Al.

During pre-monsoon also, all the normalized values, show higher concentration in the upstream end which decrease towards the downstream region except for Co, which shows an increase towards the mouth region. Relatively higher values are recorded at station 2 for Fe/Al, 3 for Cu/Al, 1 for Cr/Al, Zn/Al and Co/Al and stations 1 and 2 for Mn/Al, in surface TSM. In bottom TSM, relatively higher concentrations are seen at station 1 for Fe/Al, Cr/Al and Zn/Al, 3 for Mn/Al, 2 for Cu/Al and 17 for Co/Al (Fig. 3.15 a to c).

Most of the metal concentrations are found to be higher in the upper estuary in all the three seasons. Comparatively higher concentrations of metals are observed during post-monsoon season, which is then followed by monsoon and pre-monsoon. Seasonal shift of metal concentrations is observed in the present study.

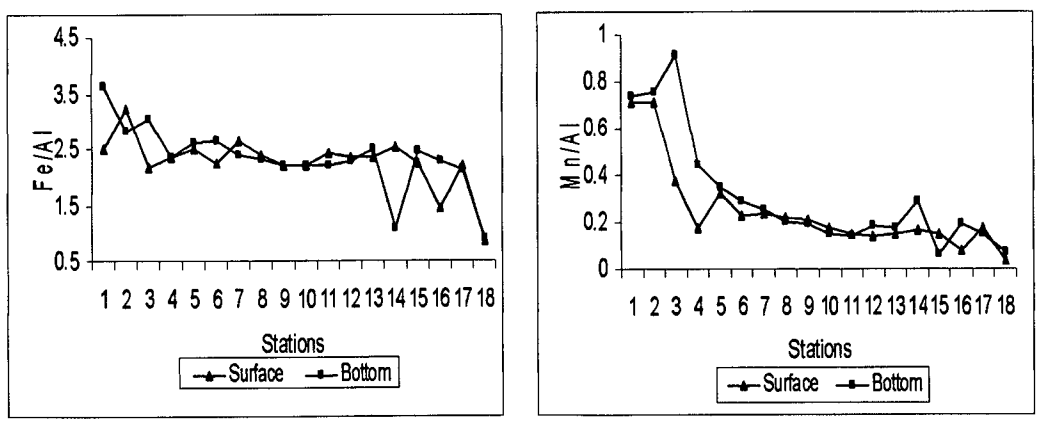


Fig. 3.15a: Al normalized plots of Fe and Mn in surface and bottom TSM during pre-monsoon.

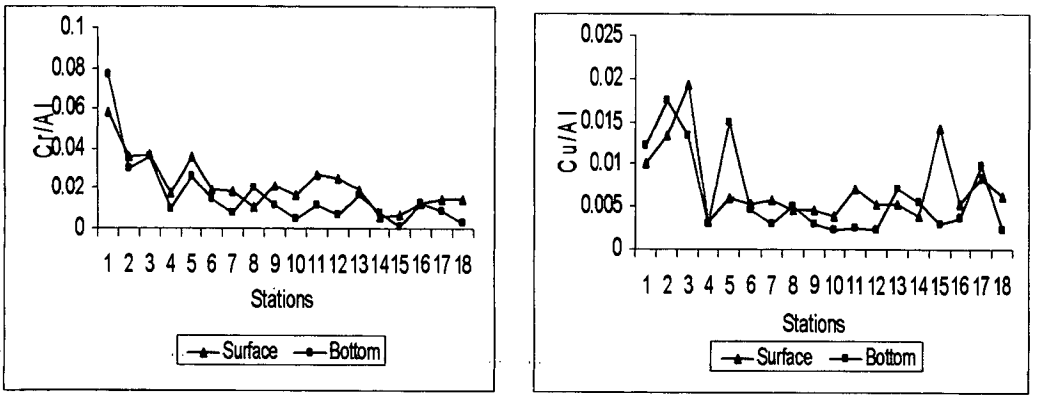


Fig. 3.15b: Al normalized plots of Cr and Cu in surface and bottom TSM during pre-monsoon.

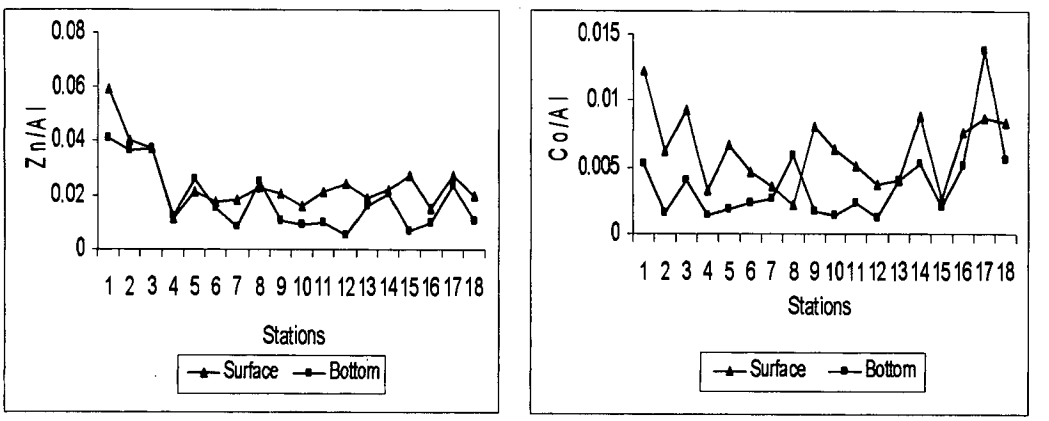


Fig. 3.15c: Al normalized plots of Zn and Co in surface and bottom TSM during pre-monsoon.

During pre-monsoon, in general, concentration of metals remained more or less high up to station 5 for most of the metals, while during post-monsoon it remained high up to station 8 and during monsoon it was up to station 12 which indicates that the fluxes of the trace metals in the estuary are essentially controlled by river discharge. However, Stecko and Bendell-Young (2000) observed seasonality in geochemistry of TSM with reference to metal bioavailability by sediment ingesting organisms. Metals on suspended sediments represent a more temporally and spatially integrated picture of metal contamination (Niencheski and Baumgarten, 2000). Therefore, they provide best matrix for assessing metal contamination in estuarine environment. Normalized metal content expect for Co during monsoon and pre-monsoon, show higher concentrations in the upstream region, which then

shows exponential decrease towards the downstream region with minor variations. The higher content of metals in the upper estuarine region confirms that the source is largely the catchment area geology. Mining activities in the catchment area must have played an important role in maintaining relatively higher concentration. Fresh water discharge brings the mining material along with other waste to the Zuari Estuary. Mesquita and Kaisary (2007) stated that the wind-borne dust and water-borne material both arising from mining operations are responsible for metal concentrations in the Zuari Estuary. Kushawati, a main tributary of Zuari Estuary which joins between stations 3 and 4 must be responsible for higher concentration of metals at station 3 especially during monsoon. The decrease in concentration of metals observed towards the downstream can be directly related to the dilution process. Regular generation of suspended matter and their cyclic deposition-resuspension transfers chemical constituents between water, foodchain and bed sediments.

Normalized metals show decrease in concentration as salinity increases. This indicates that the grain size plays an important role in controlling the distribution of metals although salinity and other factors played a role in distribution of metals in the suspended matters in Zuari Estuary. Cenci and Martin (2004) have reported decrease in metal concentration with increasing salinity elsewhere.

c. Factor Analysis

In order to understand source and relationship between different variables studied, Varimax normalized R-mode factor rotation using principal component analysis was applied to the data set of three seasons (Fig. 3.16 to 3.18).

Three significant factors were obtained for both surface and bottom TSM in case of monsoon season. F1 for surface TSM accounts for 49.2 % of total variance and is dominated by Fe, Mn, Cr, Cu, Zn and Al. Grouping of these metals in the same factor indicates their similar geochemical behaviour and their association with Al, indicates their affinity to clay fraction.

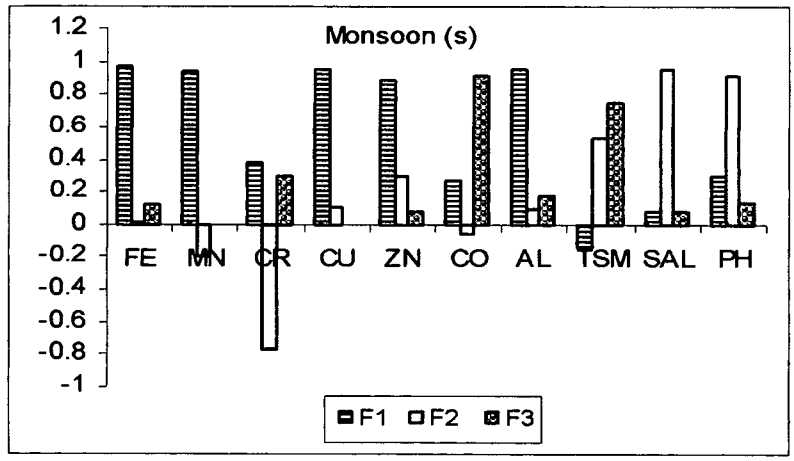


Fig. 3.16a: R – mode factor analysis for surface (s) TSM during monsoon.

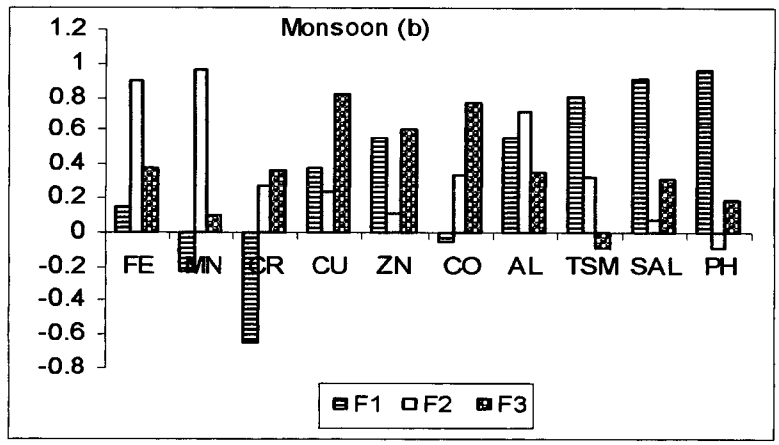


Fig. 3.16b: R – mode factor analysis for bottom (b) TSM during monsoon.

Negative loading of TSM and very poor loading of pH and salinity indicates that these metals in TSM are independent of pH and salinity during monsoon season. F2 accounts for 28.6 % of total variance and dominated by pH and salinity, while the third factor, F3 accounts for 13.6 % of total variance wherein there is high loading of Co and TSM (Fig. 3.16a). In case of bottom TSM, F1 accounts for 47.7 % of total variance, which is dominated by TSM, salinity, pH and to some extent with Al (0.5) and Zn (0.5). So, this factor probably suggests that the distribution of Zn and Al is controlled by salinity and pH in bottom TSM. F2 accounts for 27.5 % of total variance where high loading of Fe and Mn along with Al is seen. This factor shows the association of Fe, Mn

and Al and may represent the common source. High loading of Cu, Zn and Co is seen in F3, which accounts for 10.3 % of total variance. Al and salinity also show moderate loading with these metals suggesting their control on them (Fig. 3.16b).

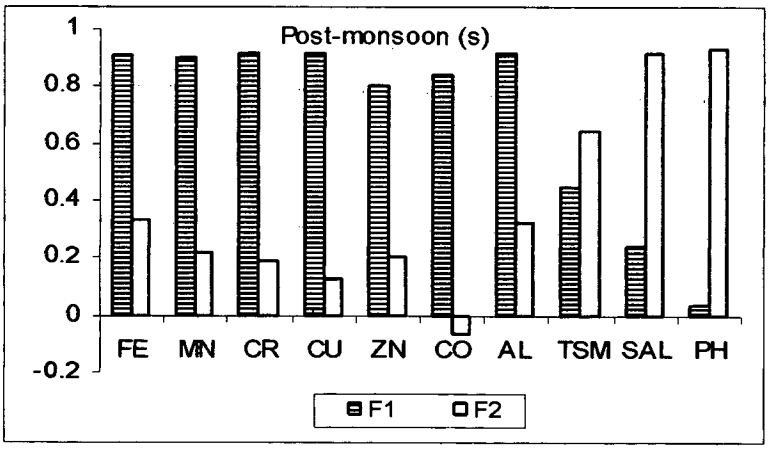


Fig. 3.17a: R – mode factor analysis for surface (s) TSM during post-monsoon.

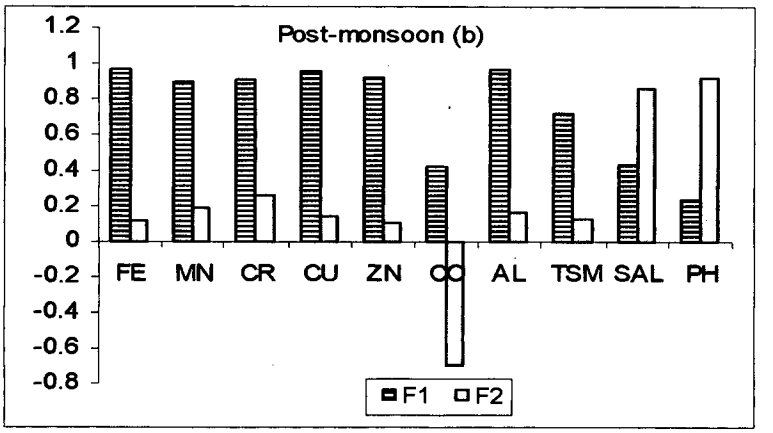


Fig. 3.17b: R – mode factor analysis for bottom (b) TSM during post-monsoon.

Two significant factors were obtained for both surface and bottom TSM during post-monsoon season. F1 accounts for 65.9 % of total variance, which is dominated by Fe, Mn, Cr, Cu, Zn, Al and to some extent with TSM concentration indicating their similar geochemical behaviour in surface TSM. F2 accounts for 18.3 % of total variance and is dominated by salinity, pH and

to some extent with TSM concentration (Fig. 3.17a). In case of bottom TSM, F1 accounts for 66.1 % of total variance. High loading of Fe, Mn, Cr, Cu, Al along with TSM is seen in this factor indicating their common source where salinity, to some extent, plays the role in distribution of these elements. F2 accounts for 19.7 % of total variance and represents the group of metals controlled by salinity and pH (Fig. 3.17b).

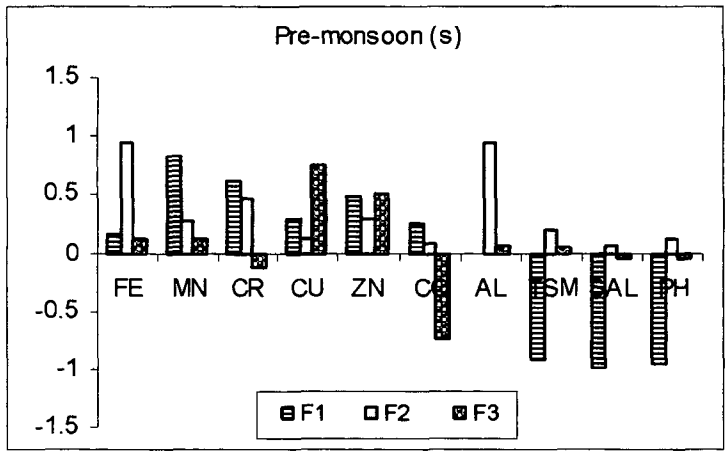


Fig. 3.18a: R – mode factor analysis for surface (s) TSM during pre-monsoon.

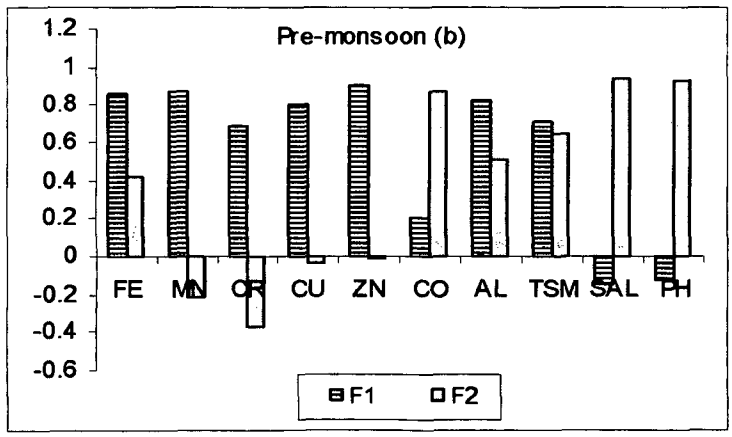


Fig. 3.18b: R – mode factor analysis for bottom (b) TSM during pre-monsoon.

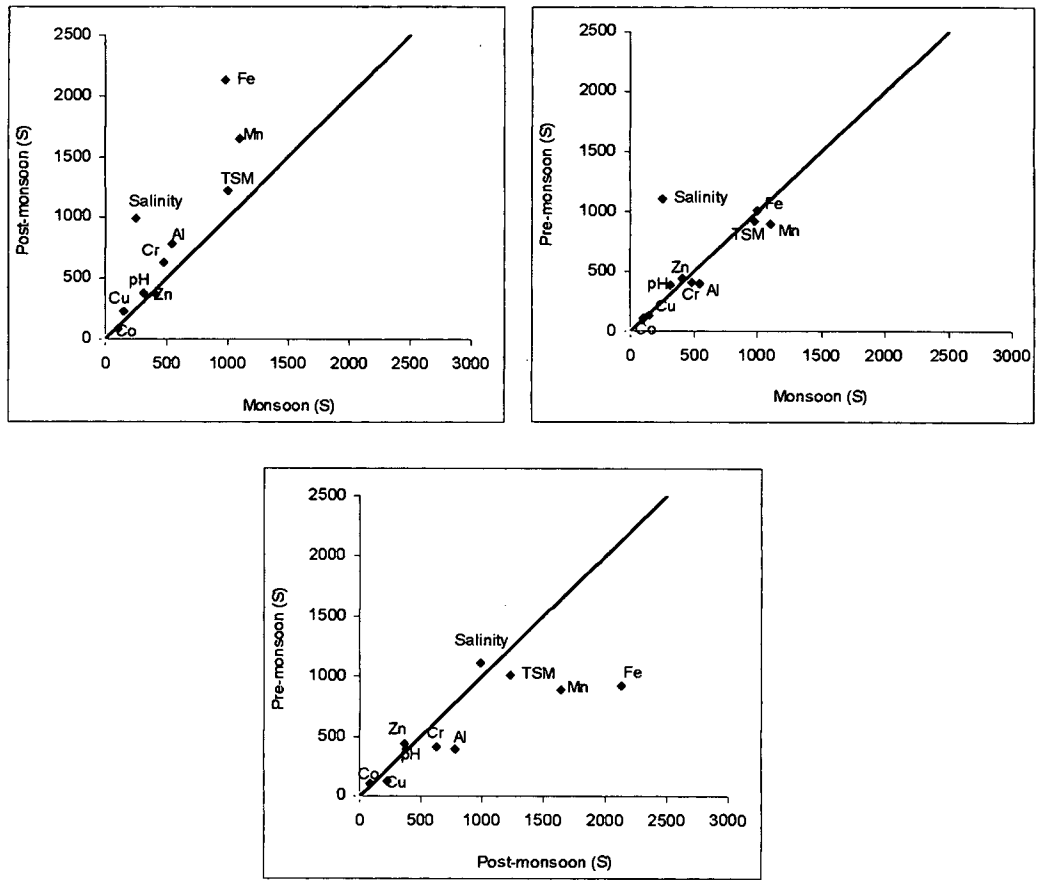
During pre-monsoon, F1 accounts for 46.2 % of total variance for surface water. Mn is highly loaded in this factor and Cr and Zn are also loaded to some extent suggesting a common source probably of anthropogenic origin.

F2 accounts for 22.9 % of total variance wherein high loading of Fe and Al and to some extent Cr is seen indicating their association with clay fraction. Factor F3 accounts for 13.2 % and characterized by high positive loadings of Cu and Zn and negative loading of Co indicating their different source (Fig. 3.18a) In case of bottom TSM two significant factors are obtained where F1 accounts for 50.4 % of total variance wherein high loading of Fe, Mn, Cr, Cu, Zn, Al and TSM concentration represent the common origin whereas F2 accounts for 32.6 % of total variance which is dominated by Co, salinity, pH, TSM concentration and to some extent by Al indicating a role played by salinity and pH in distribution of TSM and associated Co (Fig. 3.18b).

d. Inter-Seasonal Variation

In order to understand the seasonal variations of different parameters associated with TSM, data is plotted on isocon diagram. Isocon plots allow an easy visual comparison of the average composition of each parameter studied in every season (Grant, 1986; Cundy et al., 1997; Rosales-Hoz et al., 2003). Average concentrations of metals in surface and bottom water TSM were plotted separately along with their respective salinity, pH and TSM concentration (Fig. 3.19 a to b).

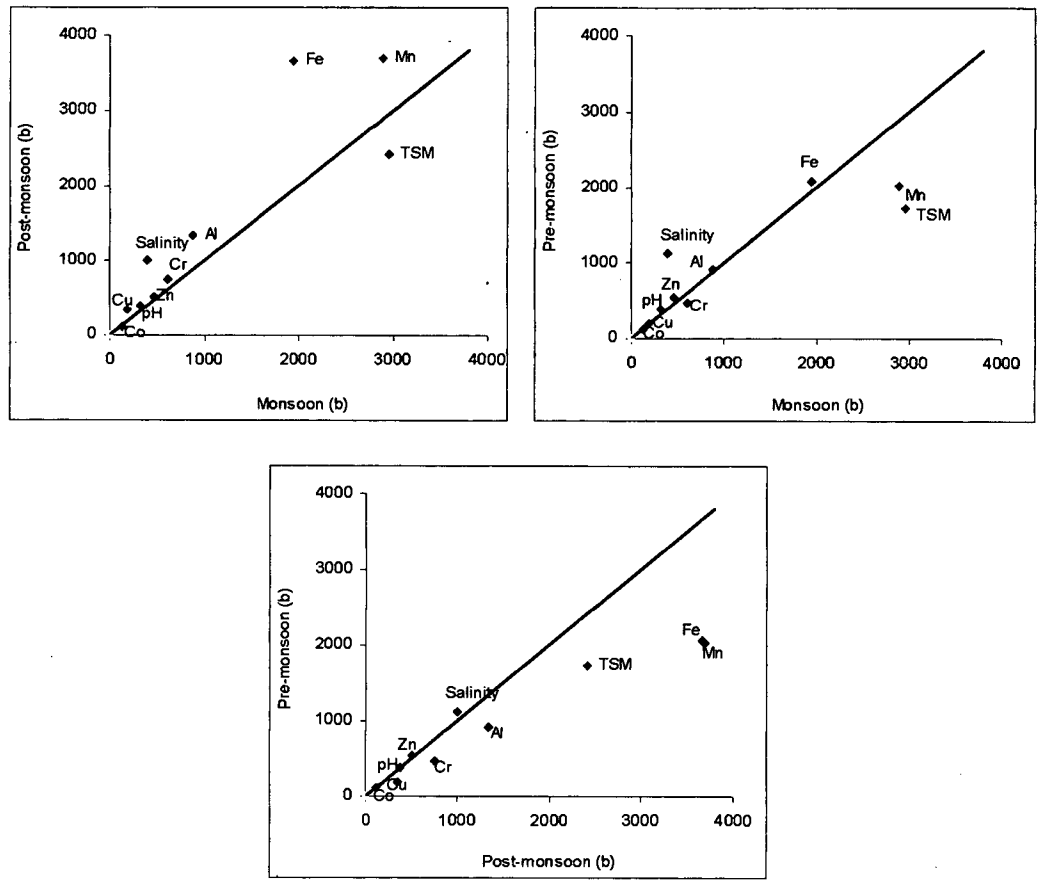
Comparison of the data of monsoon and post-monsoon indicates that Cu and Zn fall on or near the isocon line in both surface and bottom TSM representing little inter-seasonal variations. Other metals along with salinity are deviating from the isocon line maintaining higher concentrations in the post-monsoon season in both surface and bottom TSM indicating the role of salinity in distribution of these metals during this season. Also TSM concentration must have played a role in maintaining higher concentration of metals in surface TSM which was observed to be higher during post-monsoon than in monsoon. Bottom TSM concentration registered higher values during monsoon season than in post-monsoon.



* s - Surface

Fig. 3.19a: Isocon diagram (after Grant, 1986) for surface TSM. Individual points represent average concentration of different parameters in different seasons multiplied by different factors to ensure all parameters plot on the same scale.

When the data of monsoon is plotted with that of pre-monsoon season, Fe, Zn, Cu and Co in surface TSM and Al, Zn, Co and Al in bottom TSM, fall on or near the isocon line indicating that there is not much variation in these metals during these two seasons. Mn and to some extent Cr, Al and TSM, are observed to be higher during monsoon than in pre-monsoon indicating the role of TSM in distribution of these metals. Concentration of Mn and TSM and to some extent Cr is apparent during monsoon season. In this season, high runoff must be carrying large amount of material along with associated metals from the catchment area into the estuary especially Mn, since Mn mining is carried out on large scale in the catchment area of Zuari Estuary. Fe and salinity are high during towards the pre-monsoon season indicating the role of salinity in distribution of Fe.



* b - Bottom

Fig. 3.19b: Isocon diagram (after Grant, 1986) for bottom TSM. Individual points represent average concentration of different parameters in different seasons multiplied by different factors to ensure all parameters plot on the same scale.

Comparison of the data of post-monsoon and pre-monsoon showed little variation of Co, Zn and pH which fall on or near the isocon line while metals are observed to be relatively higher during post-monsoon season along with TSM concentration.

Isocon plots indicated that most of the metals are highly concentrated in the post-monsoon in both surface and bottom TSM as compared to other two seasons.

Chapter IV

BED LOAD - SURFACE SEDIMENTS

4.1 Introduction

An estuary derives sediments from multiple sources. The primary sediment input into an estuary generally comes from the river, offshore, littoral areas and shoreline of estuaries (Meade, 1972; Burton, 1988). Sediment dynamics in the estuaries is largely controlled by the hydraulic system wherein tides, waves and river currents play a significant role in transportation of the sediments. The sediment transport processes vary from hourly to seasonally, depending on the stage of the tide and river discharge. During its transport from land to ocean, the mineralogy, texture and chemistry of sediments is considerably modified and these changes are more pronounced and complex when the river carries the load through the estuaries. The dependence of the mobility of the sediments on the hydraulic conditions leads to a progressive sorting of the sediments with respect to composition and size. The most significant sorting is the coarse (sand and gravel) and fine (silt and clay) sediments. The coarse sediments are found in high energy areas such as steep rivers, strong tidal currents and along the exposed coast, while fine sediments accumulate in more quiet waters such as tidal flats. Fine sedimentary deposits or muds are characteristic features of most of the estuaries (Hedgpeth, 1967). A change in surface sediment composition gives an indication to changes in patterns of sedimentation within an estuary and provides information on relative inputs from marine and terrestrial sources. Riverine sediments generally consist of grain size potentially ranging from gravel through sand, to fine silt and clay; while sand is carried into the estuary from the marine environment by tidal currents flowing through the inlet (Komar, 1997). The sediments in an estuary undergo a repetitive cycle of erosion, transport and deposition by ebb and flood tidal currents and are thrown into suspension many times before final accumulation (Nichols, 1986). Flocculation process occurring at low as well as high salinity is also responsible in the sediment distribution. Biological and chemical processes also contribute in the sedimentation. Human activities such as dredging, construction of dams, deforestation, navigation channels, harbour basins etc., alter the sediment delivery to the estuary (Komar, 1997). The supply and removal of sediment in the estuaries is presented in the figure 4.1.

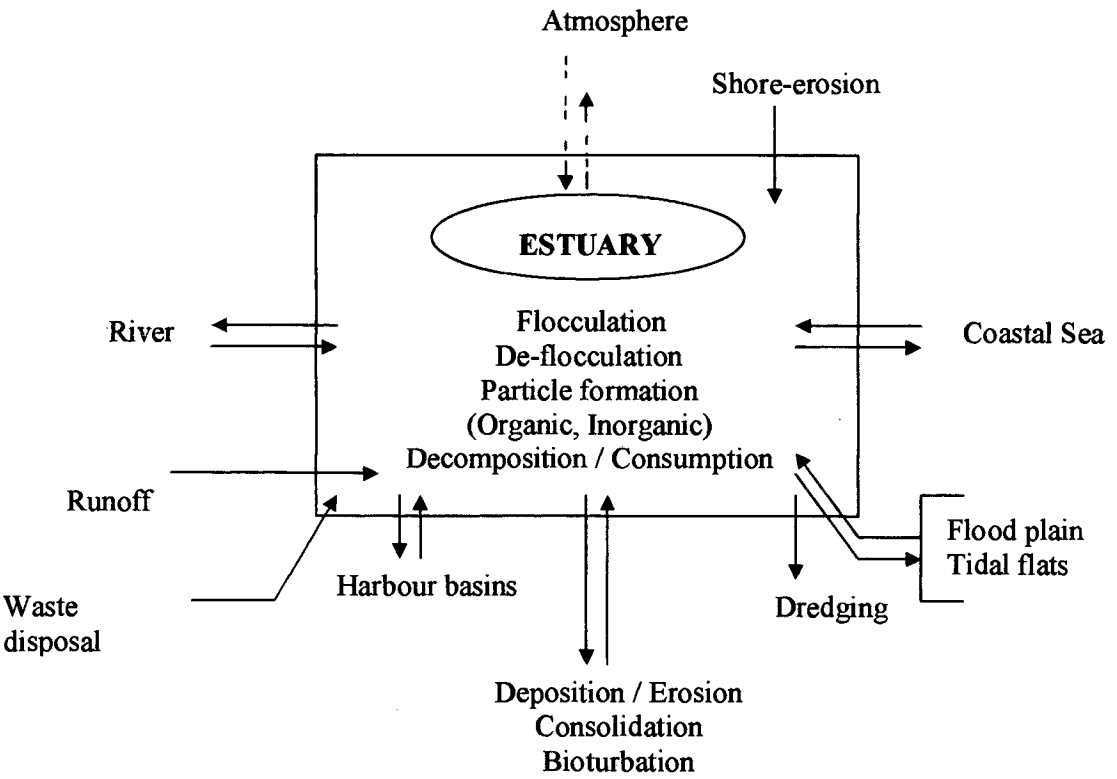


Fig. 4.1: Diagram displaying supply and removal of sediments in estuaries (After Eisma and Burg, 1988).

The adsorption of metals on sediments depends on the composition of the sediments. In estuaries, metals are mainly adsorbed on the fine sized sediments (clays) and organic matter because of their large adsorption capability. The geochemical characteristics of the sediments can therefore be used to infer the weathering trends and the sources of pollutants (Forstner and Salomons, 1980; Fedo et al., 1996; Nath et al., 2000). As sediments are major carriers of trace metals in the hydrological cycle and because metals are partitioned with the surrounding waters, the sediments reflect the quality of an aquatic system (Chatterjee et al., 2007). The degree to which metals content in the sediment is harmful to the environment depends on the geochemical conditions existing in the sediment (Adamo et al., 2005).

4.2 Sediment Components

4.2.1 Results

The distribution and abundance of sand, silt, clay and organic carbon in the surface sediments for three different seasons of Zuari Estuary are presented in the figures (Fig. 4.2 to 4.5).

a. Sand

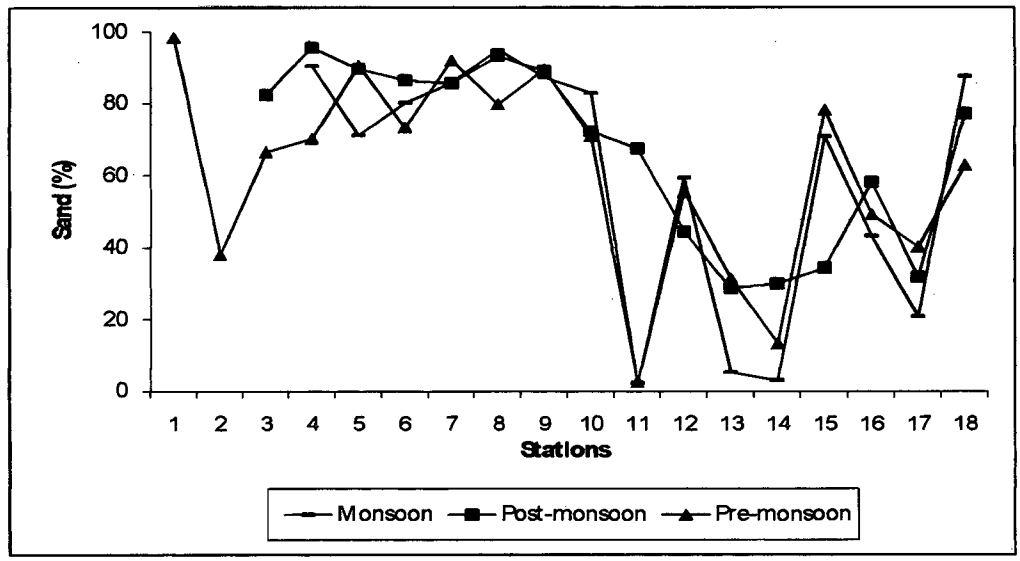


Fig. 4.2: Spatial distribution of sand content of surface sediments from Zuari Estuary.

Sand content during monsoon ranges from 2.3 to 94.8 %. During this season, sand content is observed to be high (Avg. 84.5 %) in the upper estuary and comparatively low (Avg. 36.5%) in the lower estuary with peaks at few stations. An increasing trend is seen from station 4 to 8 and then the values decreases gradually up to station 10 in the upper estuary. In the lower estuary, large variation of sand content is observed between different stations. A sharp decrease is observed from station 10 to station 11. Low values are also observed at stations 13, 14 and 17. However high values have been recorded at stations 12, 15 and 18. During post-monsoon, sand content ranges from 28.8 to 95.4 %. In this season also sand content is observed to be high (Avg. 86.6 %) in the upper estuarine region. The decreasing trend is seen from station 1 to station 10 with minor variations in between. Decreasing trend noted in the upper estuary continues up to the station 13 in

the lower estuary. Further downstream, it shows a gradual increasing trend up to station 18 with slightly lesser value at station 17. Sand content during pre-monsoon ranges from 2.5 to 98.4 %. Similar to monsoon and post-monsoon, during pre-monsoon season also high (Avg. 76.8 %) sand content was recorded in the upper estuary compared to lower estuary (Avg. 41.6 %). Sand shows an increasing trend from station 2 to station 9 with some fluctuations in between and then it decreases up to station 11. High values have been recorded at stations 12, 15 and 18 with lower values in between.

b. Silt

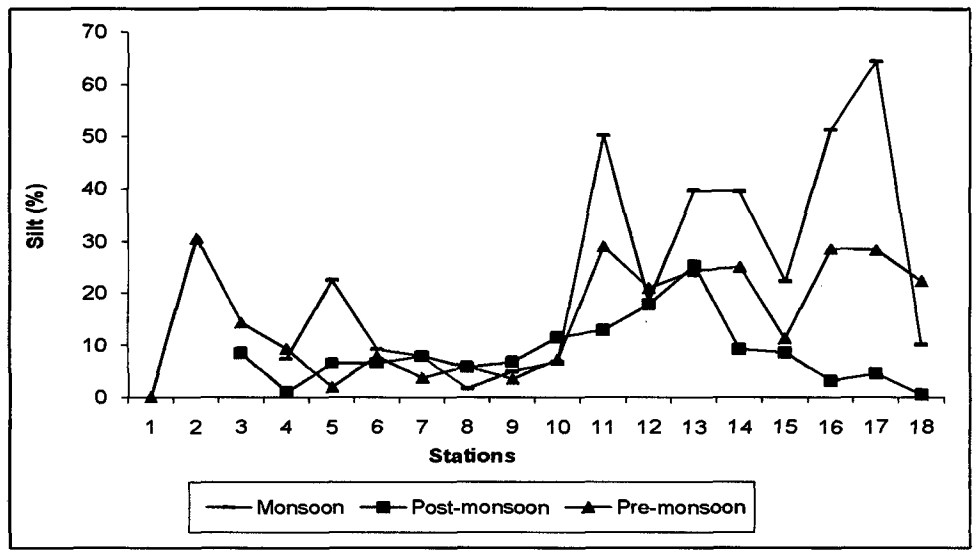


Fig. 4.3: Spatial distribution of silt content of surface sediments from Zuari Estuary.

Silt content ranges from 1.7 to 64.4 % during monsoon season. Comparatively low values of silt are recorded in the upper estuarine region i.e. up to the station 10 during this season. However, within the upper estuary a high value is recorded at station 5. In the lower estuary, silt shows higher values at stations 11, 13, 14 and 17 and lower values at other stations. Higher silt values compensate lower sand values in the lower estuary. During post-monsoon, the value ranges from 0.5 to 25.3 %. Lower silt values are recorded in the upper estuarine region with an increasing trend from station 4 to 10. Increasing trend continues up to station 13 in the lower estuarine region. Further downstream, it shows a decreasing trend with minor variations up to

the mouth. During pre-monsoon, silt content ranges from 0.1 to 30.6 %. It is observed to be relatively lower in the upper estuary than the lower estuary. In the upper estuary, silt increases from station 1 to 2, this decreases further up to station 5 and then increases up to station 11 with minor variations. In the lower estuary, it shows a decreasing trend from station 11 up to station 15 and then increases at station 16, which further decreases gradually up to station 18.

c. Clay

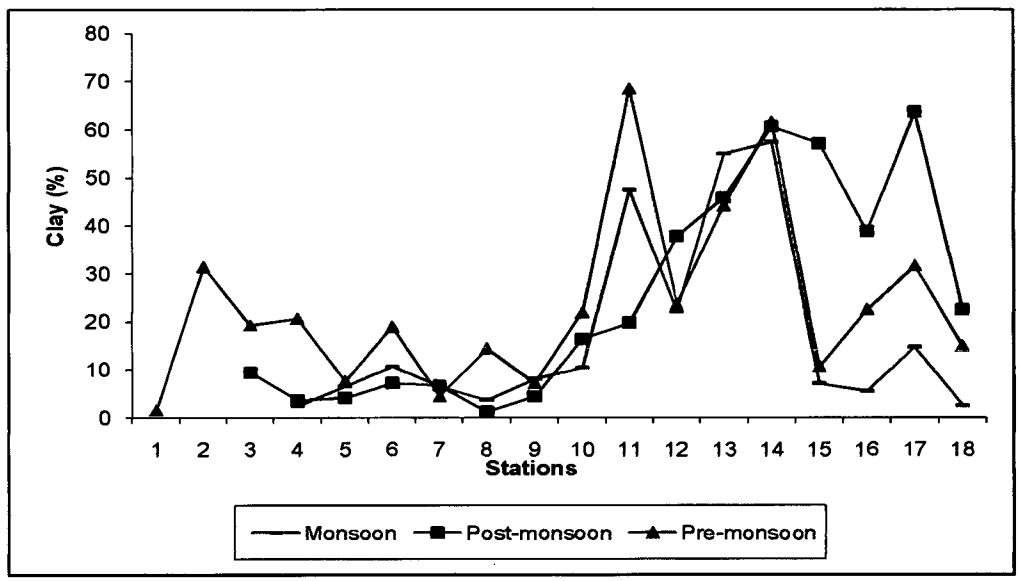


Fig. 4.4: Spatial distribution of clay content of surface sediments from Zuari Estuary.

During monsoon, clay content ranges from 2.4 to 57.4 %. Low clay content is recorded in the upper estuarine region. The percentage of clay increases gradually from station 4 to 10 with minor fluctuations in between. In the lower estuary, clay is seen to be high at most of the stations with peak values at stations 11, 14 and 17. During post monsoon, lower values of clay content are recorded in the upper estuarine region and higher values are noted in the lower estuary with minor variations. In this season it varies from 1.2 to 63.7 % within the estuary. During pre-monsoon, it varies from 1.6 to 68.5 %. Lower values of clay are noticed in the upper estuarine region. Clay shows a decreasing trend from station 2 up to the station 9 with minor fluctuations. From station 9, the value increases up to the station 11 in the lower estuary.

Higher values are also seen at stations 14 and 17 with lower clay values in between.

d. Organic Carbon

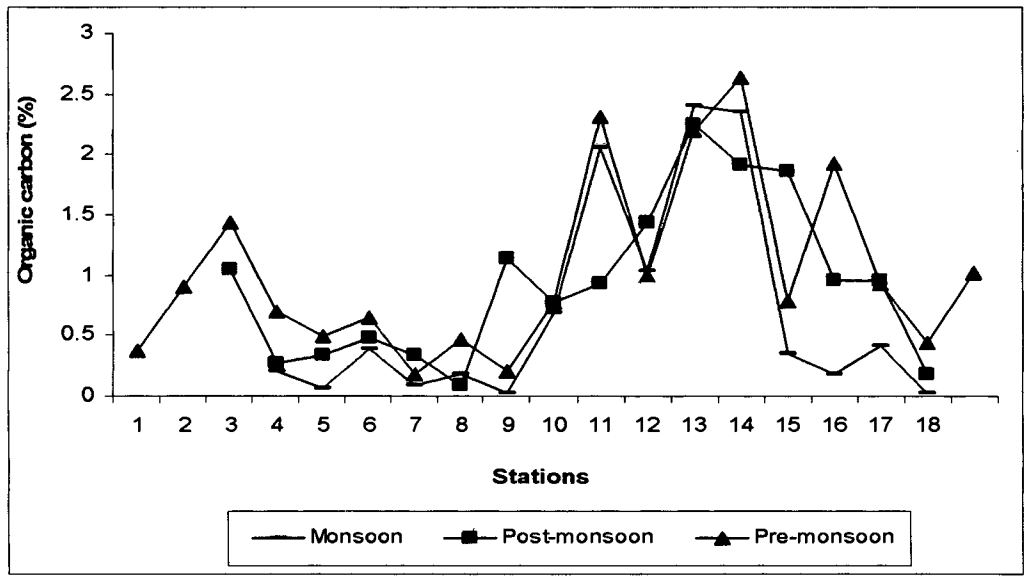


Fig. 4.5: Spatial distribution of organic carbon content of surface sediments from Zuari Estuary.

During all the three seasons viz. monsoon, post-monsoon and pre-monsoon, organic carbon maintains comparatively higher concentration in the lower estuarine region than the upper estuarine region at most of the stations even though few peaks are observed at some stations in the upper part of the estuary. Relatively higher organic carbon values have been recorded at stations 11, 13 and 14 during monsoon, 13, 14 and 15 during post-monsoon and 11, 13, 14 and 16 during pre-monsoon in the lower estuary. In the upper estuary higher values of organic carbon are recorded at stations 2 and 3 in pre-monsoon season and at station 3 in post-monsoon season.

4.2.2 Discussion

The processes that influence the grain size variation of sediments are primarily the supply or source of material, transportation, deposition and redistribution of sediments within an estuary. In addition, geomorphology of the estuary and water movements due to tidal cycles also contributes to the

distribution of sediment components. Significant variations in sediment components have been observed all along the Zuari Estuary in the different seasons (Dessai and Nayak, 2008). In general, sand is dominating in upper estuary in all the three seasons. Upper estuarine region is narrow and except during highest high tide, water generally flows in the downstream direction. Depending on the competency of flow, finer material gets entrained in the water leaving behind coarser sediments as lag deposits (Nair and Ramachandran, 2002). This must have resulted in the enrichment of coarser sandy material in the upper reaches. High sand content noted at some stations in the lower estuary especially at the mouth can be due to the strong hydrodynamic condition prevailing at this location as well as geomorphology of the region. Zuari Estuary maintains almost same width from mouth up to station 11 allowing the tidal surge to enter with considerable energy. Also, water and sediments get transported to the Zuari Estuary from Mandovi Estuary through Cumbharjua Canal during monsoon and also during ebb tide (Nayak, 1993). It is also important to note here that the Cumbharjua Canal, which connects Mandovi and Zuari estuaries, joins at station 12, which is responsible for bringing additional material, contributing largely to the redistribution of sediments. At the mouth i.e. station 18 high sand content has been observed in all the three seasons. The sediment distribution becomes more complex near the estuarine mouth since the sediment in this zone is under the influence of intense tidal activities. The high energy levels permit deposition of coarser sediments as well as transportation of wide range of finer sediments (Bryant, 1982). Comparatively high values of clay and silt content are noticed in the lower estuarine regions in all the three seasons. Lower sand values are systematically compensated by higher silt and clay values in the lower estuary. Higher concentration of silt and clay in the lower estuary may be due to settling of these particles in low energy conditions. The flocculation process during estuarine mixing helps in faster settling of fine colloidal aggregates in this region. Near the mouth, due to high-energy turbulent conditions, finer grains do not settle instead they are carried away to far distances, which then settle down, at low energy conditions (Nayak, 1996). For this reason coarser grain size is seen near the river mouth and finer in the interior of the lower estuary.

Organic carbon is observed to be comparatively less in the upper estuary than lower estuary in all the three seasons. Slightly higher values of organic carbon observed at stations 2 and 3 during pre-monsoon and at station 3 during post-monsoon coincide with higher values of silt and clay content. Kushawati tributary that joins the Zuari Estuary between stations 3 and 4 may be responsible for bringing large quantity of fine sediments and organic matter as the agricultural activity is higher in its catchment area. In the lower estuary, organic carbon content is high except at the mouth region. A comparison of data on grain size distribution and organic carbon distribution revealed that the organic carbon content increases with increasing finer fractions and decreases with the increasing coarser fractions in sediments (Fig. 4.2 to 4.5). The main reason for more organic carbon in finer particles is the similarity in settling velocity of both organic constituents and finer particles (Trask, 1939). It has been also established that organic carbon gets selectively enriched in fine particles of estuarine sediments (Hunt, 1981). The ratio C-org / surface is higher for finer sediments than for coarser, such as sand particles (Hedges, 2002; Wakeham, 2002). Fine (clay + silt) particles having larger surface to volume ratio (Williams et al., 1994; Rae, 1997) tend to be associated with negative charges. Therefore, on entering the seawater their surfaces are quickly coated with a layer of organic materials. This results in stronger association of finer sediments with organic matter. On an average high organic carbon was obtained during pre-monsoon (1.0 %) followed by post-monsoon (0.9 %) and monsoon (0.6 %). From this it can be inferred that the adsorption of organic compounds onto clay minerals is promoted under saline conditions (Nair et al., 1993) during pre-monsoon season. Organic coatings on clay minerals affect the settling rates of inorganic particles and thus contribute to increase in both clay-size particles and organic matter during this period. Correlation obtained of organic carbon with sand, silt, clay and also with mud (silt + clay) show positive with silt, clay and mud and negative with sand in all three seasons (Fig. 4.6 a to c).

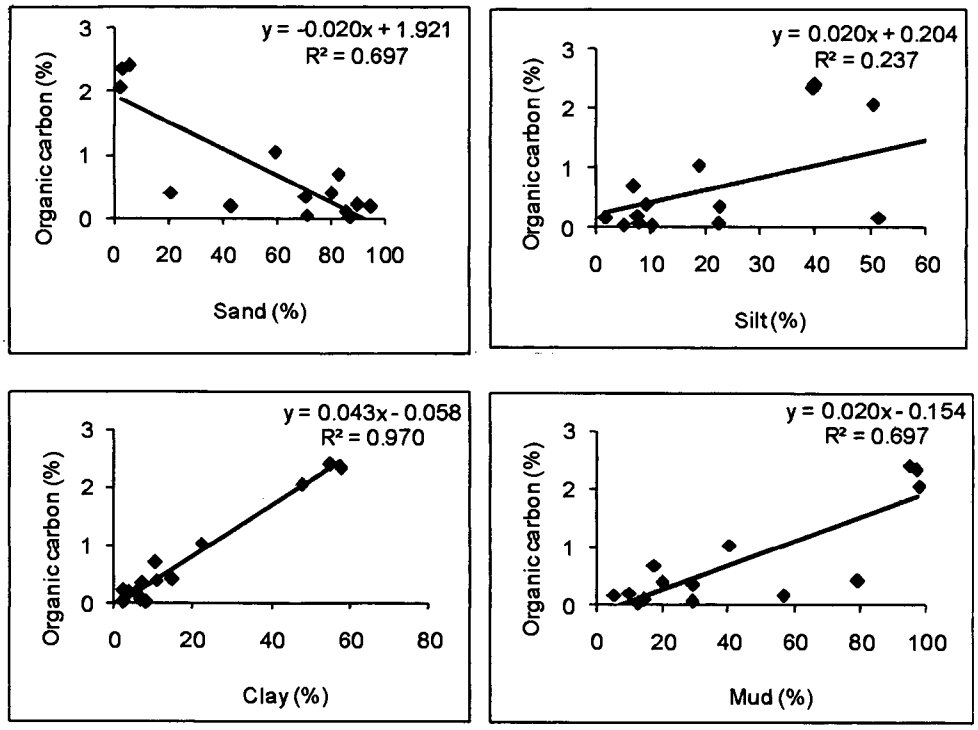


Fig. 4.6a: Relationship between organic carbon and different sediment components from Zuari Estuary during monsoon season.

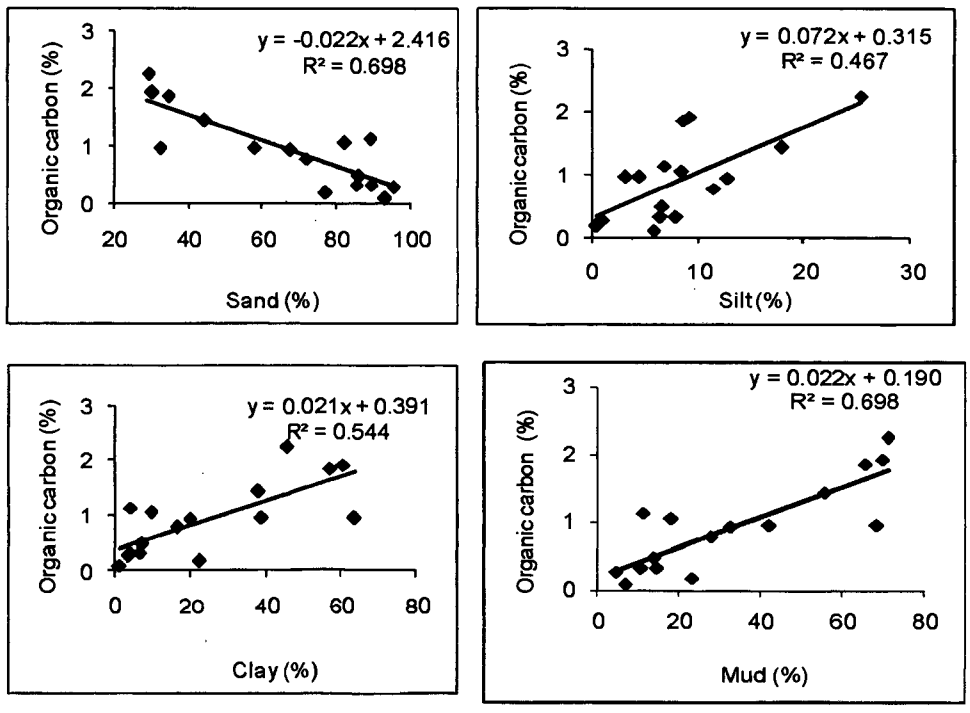


Fig. 4.6b: Relationship between organic carbon and different sediment components from Zuari Estuary during post-monsoon season.

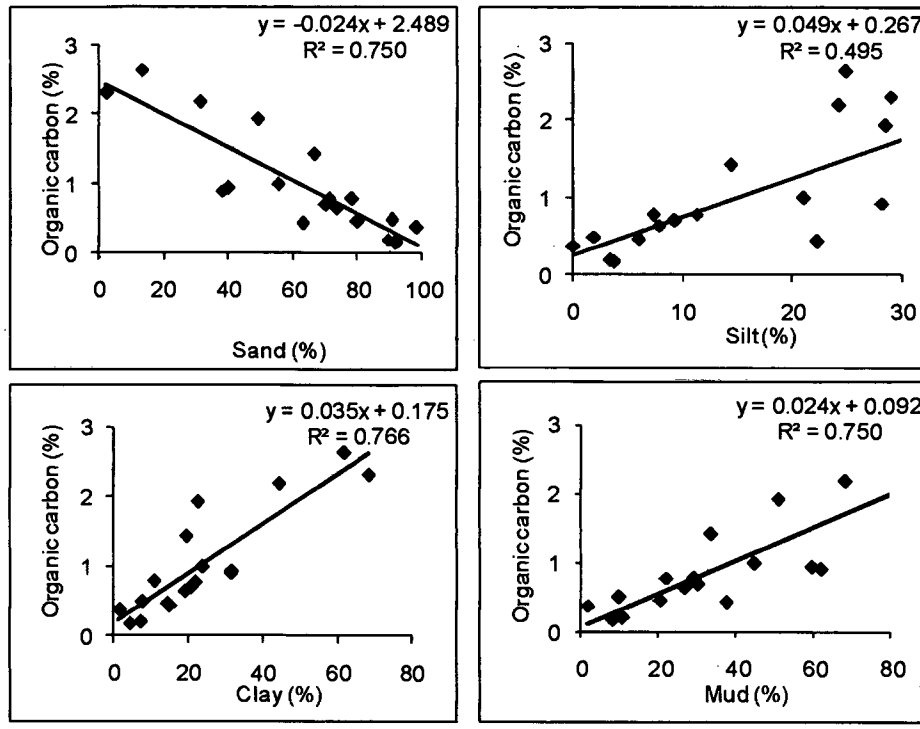


Fig. 4.6c: Relationship between organic carbon and different sediment components from Zuari Estuary during pre-monsoon season.

A significant correlation observed between organic carbon and mud as well as clay in all the three seasons strongly supports their association and settling in a similar depositional environment.

Zuari Estuary can be classified as a tide-dominated coastal plain estuary, which exhibits homogenous vertically, but has lateral variations in salinity (Qasim and Sen Gupta, 1981). The average current speed was observed to be stronger during the flood tide in the pre-monsoon and post-monsoon months whereas during the monsoon months the current become stronger during ebb tides as the river runoff accelerates the flow (Varma et al., 1975). Qasim and Sen Gupta (1980) observed that the current velocity in Zuari Estuary, during the flood tide is maximum and the currents are directed upstream and largely towards the left side of the river. Further they have also observed that the speed of the current varies at different places within the estuary with the state of tide.

Various approaches to understand the hydrodynamic conditions of Zuari Estuary using the distribution of various parameters like salinity and its gradients (Shetye and Murty, 1987), river runoff and tidal propagation (Shetye, 1999; Unnikrishnan et al., 1997) have been tried. In the present study however, an attempt has been made to understand the hydrodynamics using sediment components namely sand, silt and clay with the help of ternary diagram proposed by Pejrup (1988). The diagram has four sections labelled I to IV. Section I indicates very calm hydrodynamic conditions and section II to IV indicate increasingly violent hydrodynamic conditions. During monsoon (Fig. 4.7a), stations 6, 8, 9, 10, 12, 13 and 14 fall under section II, stations 4, 5, 7, 11 and 15 fall under section III and stations 16, 17 and 18 which are near the mouth fall under section IV. During monsoon all the stations fall under sections II, III and IV, indicating strong hydrodynamic conditions prevailed during this season.

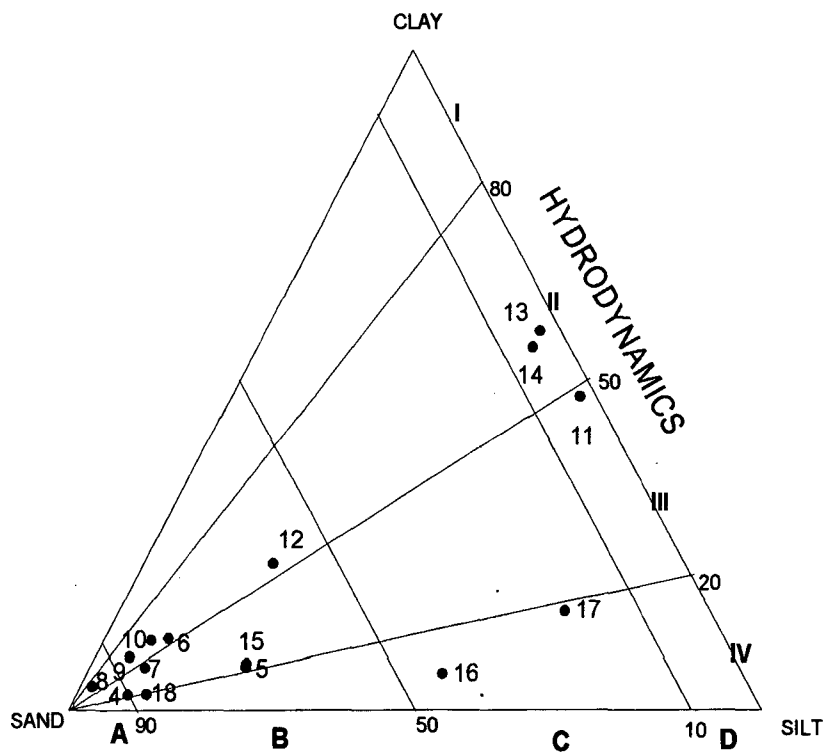


Fig. 4.7a: Ternary diagram for classification of hydrodynamic conditions during monsoon season, after Pejrup (1988).

Stations 4, 5 and 7 of the upper estuary, that fall within section III, indicate relatively violent hydrodynamic conditions available at this region. Probably due to this more percentage of sand was retained in the upper estuarine region removing finer sediments. Intense tidal activity near the mouth is represented by section IV, which is an indicative of very violent hydrodynamic condition and is mainly responsible for the presence of coarser size particles at this location. In general, estuary maintains relatively strong hydrodynamic conditions during monsoon.

During post-monsoon (Fig. 4.7b), stations 14, 15, 16, 17 and 18 fall under section I indicating very calm hydrodynamic conditions which facilitated the deposition of finer sediments along with organic matter except at station 18, wherein higher sediment size is recorded.

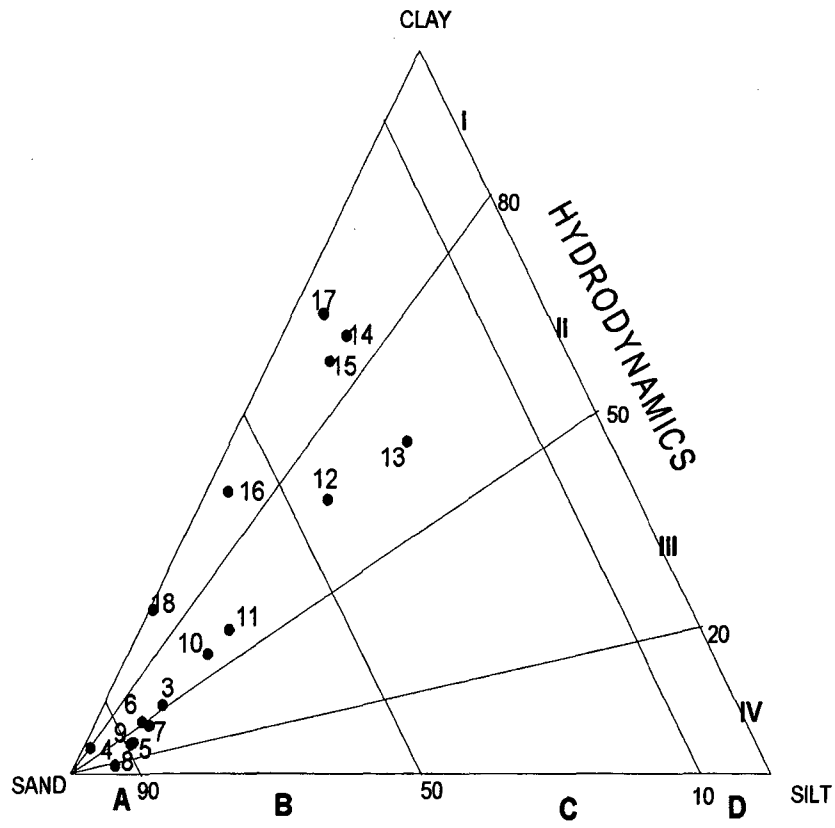


Fig. 4.7b: Ternary diagram for classification of hydrodynamic conditions during post-monsoon season, after Pejrup (1988).

Further, stations 3, 4, 6, 10, 11, 12 and 13 fall under section II, which indicates relatively less violent condition, at these stations during this season, responsible for deposition of finer sediments at these locations compared to monsoon season. Stations 5, 7 and 9 fall under section III and station 8 under section IV indicating relatively violent and very violent conditions respectively at these stations.

While during pre-monsoon (Fig. 4.7c), stations from 1 to 14 and 17 fall under section II which represents relatively less violent hydrodynamic condition, thus allowing finer sediments to settle.

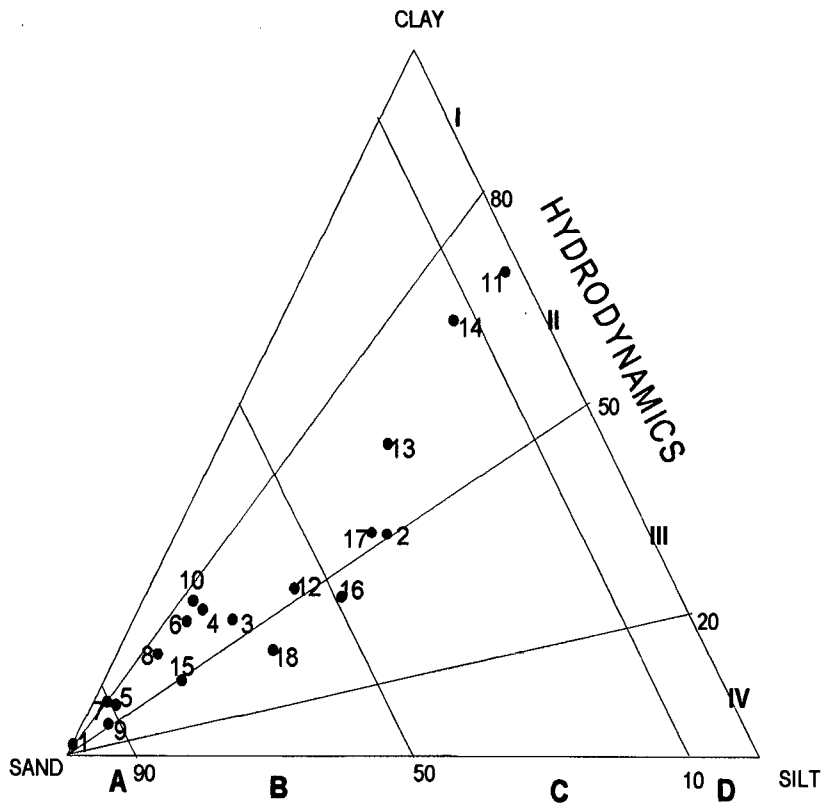


Fig. 4.7c: Ternary diagram for classification of hydrodynamic conditions during pre-monsoon Season, after Pejrup (1988).

Stations 15, 16 and 18 (near mouth region) fall under section III indicate rather violent conditions thereby retaining comparatively higher percentage of sand through tidal influence.

4.3 Clay Mineralogy

4.3.1. Results

Clay minerals are hydrous aluminium phyllo-silicates, produced from weathering of rocks which have variable amount of iron, magnesium and other cations. Depending upon the source, clay minerals are classified as kaolinite, montmorillonite-smectite, illite and chlorite.

The clay minerals identified in the Zuari Estuary are kaolinite, illite, chlorite and smectite. The percentage distributions of clay minerals for the three different seasons are presented in the figures (Fig. 4. 8).

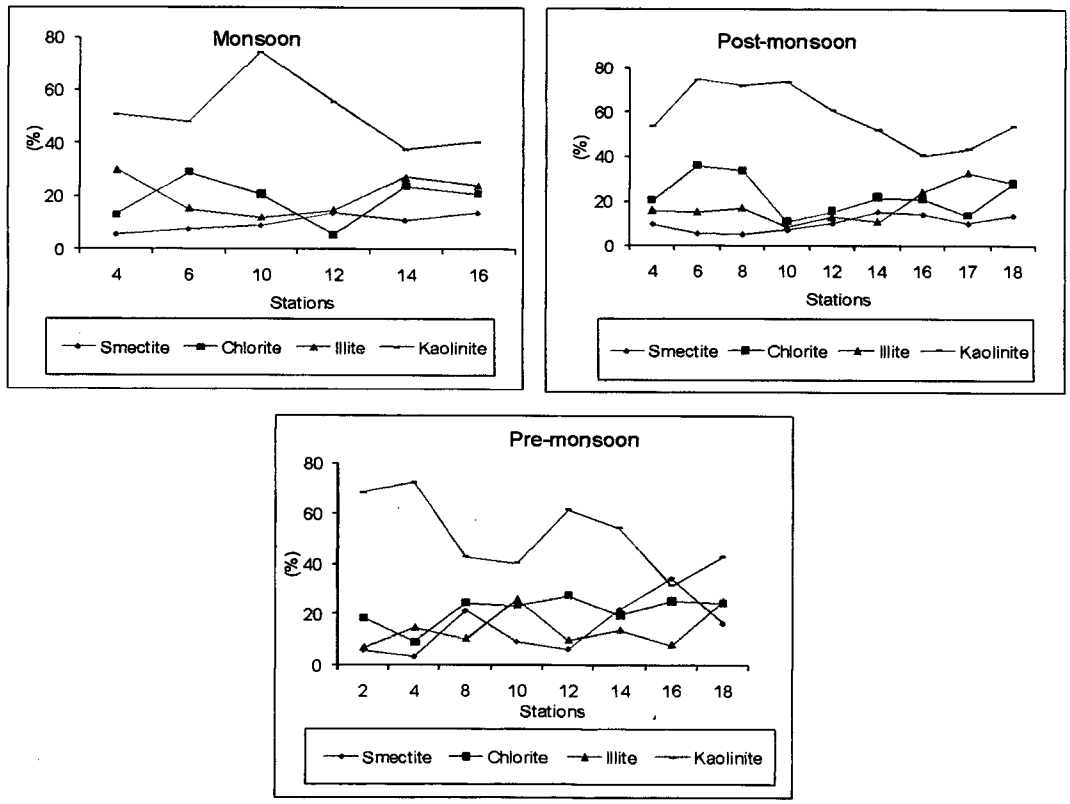


Fig. 4.8: Spatial distribution of different clay minerals in surface sediments from Zuari Estuary.

a. Kaolinite

During monsoon, kaolinite content ranges from 37.9 to 74. 4 % (Avg. 51.3). It shows a slight decrease from station 4 to 6. An increase is observed at

station 10 and then shows a decreasing trend up to station 14. However, a slight increase in value is observed at station 16. Highest concentration is observed at station 10. Kaolinite content ranges from 40.7 to 74.8 % (Avg. 58.3) during post-monsoon season. It shows an increasing trend from station 4 to 6 then shows a decreasing trend up to station 16 and then shows an increasing trend towards the mouth. Comparatively higher values are observed in the upper estuary than in lower estuary. In case of pre-monsoon, it ranges from 31.8 to 72.4 % (Avg. 52.0). The percentage of kaolinite increases from station 2 to 4 which further decreases up to station 10, followed by increase at station 12. Further downstream, the value decreases up to station 16. An increase in value is recorded near mouth region i.e. at station 18. In general, kaolinite content is observed to be relatively higher in the upper estuary. On an average relatively higher percentage of kaolinite is observed during post-monsoon followed by pre-monsoon and then by monsoon season.

b. Illite

During monsoon, illite content ranges from 12.0 to 30.2 % (Avg. 20.6). It shows a decreasing trend from station 4 to 10 which further downstream increases up to station 14. Slight decrease is observed at station 16. In case of post-monsoon, it ranges from 8.5 to 32.8 % (Avg. 18.5). In this season, illite content decreases from station 4 to 6 which further increases at station 8. Decrease in value is observed at station 10. It then shows an increasing trend up to station 17 with slightly lower value at station 14. Decrease in value is recorded at station 18 which is near mouth region. During pre-monsoon, illite content ranges from 7.1 to 26.3 % (Avg. 14.6). An increasing trend of illite is observed from station 2 to 10 with slightly lower value at station 8 and then decreases at station 12. Increase in value is observed at station 14. The value decreases at station 16 and then increases up to station 18.

c. Chlorite

Chlorite content ranges from 5.7 to 29.0 % (Avg. 18.9) during monsoon. An increasing trend is observed from station 4 to 6 which later decreases up to

station 12. An increase in value is seen at station 14 which then slightly decreases at station 16. The chlorite content during post-monsoon season ranges from 11.0 to 36.4 % (Avg. 22.5). It shows an increasing trend from station 4 to 6 and then the value decreases up to station 10. An increasing trend is observed from station 10 to 16 with minor fluctuations. The value decreases at station 17 which further shows an increase at station 18. Like kaolinite, the values are observed to be higher in the upper estuarine region than in the lower estuarine region. During pre-monsoon, the chlorite content ranges from 9.4 to 27.6 % (Avg. 21.7). A decrease in value is observed from station 2 to 4 and then shows an increasing trend up to station 12. The value decreases at station 14, which then shows an increasing trend towards the mouth.

d. Smectite

The smectite content during monsoon ranges from 5.7 to 14.0 % (Avg. 10.2). It shows an increasing trend from station 4 up to station 12. A decrease in value is observed at station 14. The value further increases at station 16. In general, it shows an increasing trend from head to the mouth of the estuary during this season. During post-monsoon, it ranges from 5.0 to 15.2 % (Avg. 10.0). In general, it shows a decreasing trend from station 4 to 8 which further shows an increasing trend up to station 14 and then shows a decreasing trend up to station 17. A slight increase is observed at station 18. In case of pre-monsoon season, the smectite content ranges from 3.3 to 34.7 % (Avg. 15.0). A slight decrease is observed from station 2 to 4, which further downstream shows an increase up to station 8. Decreasing trend is observed from station 8 to 12 followed by an increasing trend up to station 16. Decrease in value is observed at station 18. On an average smectite is found to be relatively higher during pre-monsoon followed by monsoon and then by post-monsoon season.

4.3.2 Discussion

Kaolinite is the dominant mineral observed in the Zuari estuarine sediments in all the three seasons. On an average kaolinite content is observed to be high during post-monsoon followed by pre-monsoon and then monsoon season.

Kaolinite is produced by intensive weathering under humid tropical climatic conditions (Millot, 1970; Chamley, 1989; Pandarinath and Narayana, 1992). One of the most important factors responsible for maintaining high concentration of the mineral is its source. The type of soil and rocks and weathering conditions in the region mainly contribute to abundance and composition of mineral. Silicate alteration in laterites and lateritic soils wherein strong leaching produces moderate dislocation must have resulted in the formation of kaolinite as laterite is a common rock in the catchment area of Zuari Estuary. The relatively higher content of kaolinite is observed in the upper estuarine region i.e. the low salinity zone and it generally decreases towards the downstream region. High content of kaolinite in the low salinity zone can be due to the attraction between the positive charges on the edges of the particles and negative charges on the planar surfaces of other particles which leads to flocculation of this clay mineral at low salinity and even in the absence of salt (Schofield and Samson, 1954). The flocculation of kaolinite at low pH and salinity is reported earlier by many researchers (Schofield and Samson, 1954; Edzwald and O'Melia, 1975; Suraj et al., 1996; Patchineelam and de Figueiredo, 2000). Slightly higher kaolinite content is observed in the lower half of the Zuari Estuary at stations 12 and 14 during pre-monsoon season. The rate of flocculation of kaolinite increases rapidly with small changes in salinity (Patchineelam and de Figueiredo, 2000). Bukhari and Nayak (1996) had studied the clay mineralogy in surface sediments of adjacent Mandovi Estuary. Observations made by them are somewhat similar to those made in the present study. The range of kaolinite recorded by them is from 44.0 to 85.7 %. In the present study, kaolinite shows good correlation with the sand content during monsoon ($r = 0.65$) and post-monsoon ($r = 0.55$). It shows negative correlation with the other minerals except with chlorite, with which it shows less significant correlation ($r = 0.37$). Kaolinite shows good correlation with Cr ($r = 0.77$) and weak positive correlation with Fe ($r = 0.45$) during monsoon season while, it shows good correlation with Fe ($r = 0.59$) and Cr ($r = 0.60$) during pre-monsoon season. Significant amount of Fe-oxides are observed in association with kaolinite although generally it has very little structural Fe (Malden and Meads, 1967; Jefferson et al., 1975).

The next abundant clay minerals are chlorite (21.1 %) and illite (17.9 %). The least one is the smectite (11.7 %). Illite can be a product of intense weathering or a stable product under intermediate conditions (Jackson, 1959; Meunier, 1980; Edzwald and O'Melia, 1975). During monsoon, illite content is observed to be relatively higher in the upstream i.e. at station 4 and also in the lower estuarine region. Similar distribution is observed during post-monsoon season with relatively higher concentration in the downstream region. During pre-monsoon, it shows irregular pattern with relatively low content in the upstream region. Higher value is observed near the mouth i.e. station 18. High content of illite in the upper estuarine region can be attributed to its origin from metamorphosed argillites (phyllites). Since illite is one of the stable mineral, it can be transported further downstream due to low aggregation rates before deposition (Edzwald and O'Melia, 1975) and therefore must be maintaining higher concentration in the lower estuarine region (Grim,1968). Illite shows good correlation with Al ($r = 0.57$) and to some extent with silt ($r = 0.42$) whereas it shows negative or less significant correlation with other minerals during monsoon. During other two seasons, it shows insignificant correlation with metals, grain size component and other minerals.

Chlorite content during monsoon and post-monsoon is observed to be comparatively higher in the upper estuary than in the lower estuary. During pre-monsoon, values are almost constant with slightly lower values at stations 2, 4 and 14. During post-monsoon, chlorite shows good correlation with sand ($r = 0.56$) and insignificant correlation with other minerals. Presence of considerable percentage of illite and chlorite in the estuary indicates that the source areas are controlled by an intense mechanical alteration and a fast transport of the terrigenous supply to the sedimentary basin.

Smectite content shows a general increasing trend from head towards the downstream region. It is observed to be comparatively higher in the lower half of the estuary. It must be transporting towards the downstream region because of smallest grain size and low density. The fine particles such as fibrous clays and smectite (0.1 – 0.9 microns) are transported towards the

downstream region, compared to the coarser particles i.e. illite and chlorite (0.48 – 80 microns) and kaolinite with an average size of 1 – 2 microns (Bican-Brisan and Hosu, 2006). Thus the spatial variations in clay mineral content are determined by physical sorting (Chamley, 1989). During monsoon, smectite shows good correlation with silt (r = 0.72) and aluminium (r = 0.60). During post-monsoon, it shows good correlation with clay (r = 0.66), Cu (r = 0.50) and Al (r = 0.56) while during pre-monsoon it shows good correlation with Co (r = 0.75) and positive correlation with the fine grain size. Smectite did not show any significant correlation with other minerals in any of the three seasons. In the Zuari Estuary, grain size and also the hydrodynamic conditions prevailed in the region must have played a major role in transportation of smectite. In the lower half of the estuary especially during post-monsoon and pre-monsoon season, the quiet hydrodynamic conditions (Fig. 4.8) facilitated settling of the finer clay (smectite) resulting higher content in this region. Distributions of kaolinite and smectite are observed to be characteristics of the upper and lower estuary respectively in all the three seasons. Similar distribution pattern for these minerals were observed earlier for Mandovi Estuary by Bukhari and Nayak (1996). According to Rao and Rao (1993) Deccan basalts are the major source for smectite along western continental shelf of India. It is also reported that coastal laterites contain both smectite and kaolinite (Nair et al., 1982).

In the Zuari Estuary, major source of smectite may be either the catchment area of Zuari River or the offshore waters or both. Bukhari and Nayak (1996) have reported source for smectite as offshore in the adjacent Mandovi Estuary. Abundance of smectite in lower estuary also indicates its association with high salinity and finer sediments in Zuari Estuary. Smectite as an indicator of fine grained sediment source was observed earlier by Khim and Park (1992). Smectite owing to its small size forms aggregate and facilitates settling in high proportions in quiet hydrodynamic conditions. This explains its higher average concentration during pre-monsoon season. The gradual increase in rate of flocculation for smectite with increase in salinity has also been reported by Patchineelam and de Figueiredo (2000).

Clay mineralogical study has helped in understanding flocculation processes especially in lower estuary. Presence of kaolinite in higher percentage indicates intense chemical weathering process through hydrolysis under warm and humid climate. Also, mechanical alteration and transport of terrigenous supply to the estuarine sediments is revealed from the presence of higher chlorite and illite content. However, smectite is derived from either the catchment area or offshore or both and indicates deposition in quiet hydrodynamic conditions facilitating flocculation of suspended matter.

4.4 Geochemistry of Total Metals

4.4.1 Results

The abundance and distribution of the studied elements viz., Fe, Mn, Cr, Cu, Zn and Co, in the surface sediments of Zuari Estuary, for three seasons are presented in figures (Fig. 4.9 to 4.14).

a. Iron (Fe)

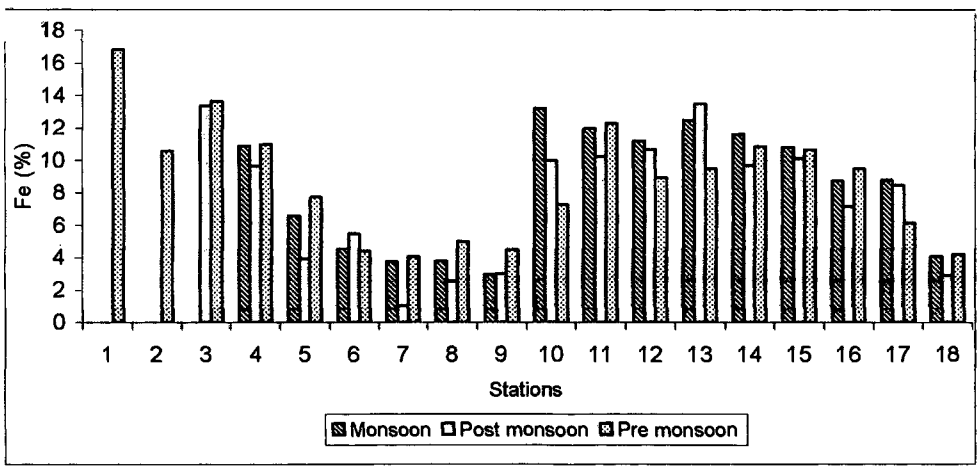


Fig. 4.9: Distribution and abundance of Fe in surface sediments of Zuari Estuary.

Concentration of Fe in surface sediments of Zuari Estuary during monsoon varies from 3.0 to 13.2 %. From the figure 4.9, it can be seen that Fe decreases from station 4 to 9. There is a sudden increase in the concentration

at station 10 and further downstream it decreases with some minor fluctuations in between. Fe content during post-monsoon varies from 1.1 to 13.5 %. It is seen from the figure that the value decreases from station 3 to 7, except at station 6 where slightly higher value is recorded. Again, there is a slight increase in concentration up to station 9 and further, considerable increase up to station 13. It then decreases towards mouth with some minor fluctuations. In case of pre-monsoon, concentration varies from 4.0 to 16.8 %. Fe content decreases from station 1 to 2, then increases at station 3 and again it shows a decreasing trend up to station 7. After fluctuations in values from 7 to 9 it shows an increasing trend from station 9 to 11 and also from station 12 to 14. Further it decreases gradually up to the mouth at station 18.

When the distribution of Fe concentration is considered for whole estuary from head to the mouth, the highest concentrations have been recorded between stations 10 to 14 and also at stations 3 and 4. When the average values of three seasons are compared pre-monsoon showed relatively higher concentration (8.7 %) followed by monsoon (8.4 %) and then by post-monsoon (7.6 %).

b. Manganese (Mn)

Mn content ranges from 612.5 to 5275.0 µg/g in monsoon season (Fig. 4.10). Mn shows a decreasing trend from station 4 to 6. Further downstream, it shows an increasing trend from station 8 up to station 11 and from station 12 to 14 and then it decreases towards the mouth of the estuary with minor fluctuations. During post-monsoon, Mn content ranges from 462.5 to 5362.5 µg/g. Mn decreases gradually from station 3 to 7 except at station 6. It shows an increasing trend from station 7 to 9 and also from station 10 to 12. Further downstream, Mn shows a decreasing trend with minor fluctuations. During pre-monsoon season, Mn concentration varies from 800.0 to 5937.5 µg/g. Mn concentration decreases from station 1 to 6 except at station 2.

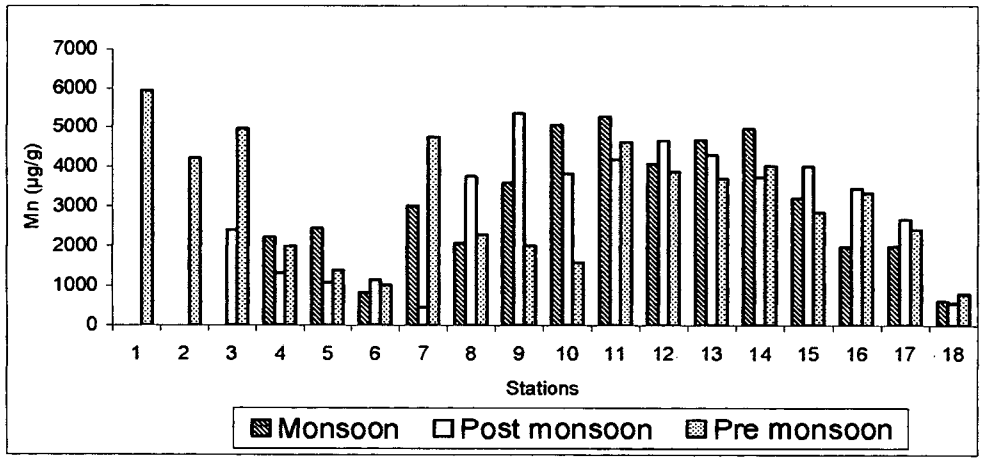


Fig. 4.10: Distribution and abundance of Mn in surface sediments of Zuari Estuary.

High concentration is recorded at station 7, which then decreases up to station 10. Again there is an increase at station 11, which further downstream decreases up to station 18 with minor fluctuations. When the whole estuary is considered the higher concentration of Mn is available in the surface sediments between stations 7 and 14. The distribution trend of the average Mn (µg/g) values is same as that of Fe, with high concentration during pre-monsoon (3099.3) followed by monsoon (3069.2) and post-monsoon (2936.7).

The higher concentration of Fe and Mn within the estuarine sediments can be directly related to mining activities carried out within the river basin of Zuari Estuary. As mentioned earlier, the catchment area of Zuari River is known for considerable anthropogenic activity especially, open cast mining of Mn and Fe ores. It is also important to understand the processes involved in the distribution and concentration of Fe and Mn within the estuarine system in addition to the source from where they have been received. The behavior of Mn with reference to salinity within the estuary (Kerdijk and Salomons, 1981) is quite different from that of Fe. It is well established that Mn remains in solution phase at lower salinity up to 10 psu. As the salinity increases towards the downstream region, Mn slowly flocculates and finally precipitates (Balachandran et al., 2005) around 18 psu salinity and gets incorporated in

the surface sediments. Fe, however, gets precipitated at low salinity. In Zuari Estuary, higher salinity is maintained from the mouth of Zuari Estuary up to slightly upstream end of the mouth of Cumbharjua Canal. Higher concentration of Mn obtained between stations 7 and 14 must be due to the availability of higher salinity in this part of the estuary. During pre monsoon, as the river input is considerably less and tidal influx controls the whole estuary, the salinity in the upstream region is also high which favours the precipitation of Mn. Therefore during pre-monsoon, higher values of Mn have been recorded in the sediments of upstream end. The distribution Fe and Mn can be better explained considering the additional input from Cumbharjua Canal in addition to the input of these elements from the catchment area of Zuari River. It is a known fact that the catchment area of Mandovi has large iron ore mines (27 major mines of Fe with lesser Mn ores). During monsoon, the fresh water flows from Mandovi to Zuari through Cumbharjua Canal, which is expected to carry considerable amount of Fe and once it reaches the Zuari Estuary due to the salinity it gets precipitated and possibly gets remobilized between 10 and 14. During monsoon, Fe shows significant correlation with Mn, Co, organic carbon, silt and clay. Mn also shows significant correlation with Cu, Zn, Co, organic carbon and clay. During post-monsoon, Fe and Mn exhibit good correlation with Cr, Cu, Zn, organic carbon and comparatively less correlation with silt and clay. During pre-monsoon, Fe exhibits significant correlation with Mn, Cr, Cu, Zn and organic carbon, while Mn shows significant correlation only with Cu. Fe and Mn do not show any significant correlation with clay and silt during this season. The decline of adsorption potential in finer sediments results from the tendency of these particles to flocculate in saline waters (Knox and Kilner, 1973; Knox, 1986), forming large particle-aggregates with a correspondingly low total surface-area-to-volume ratio. Due to this, Fe and Mn probably do not show significant correlation with silt and clay. The organic carbon present in the sediments acts as a trap for Fe and Mn in Zuari Estuary, which is supported by the significant correlation values obtained for Fe and Mn with organic carbon in all the three seasons (Table 4.1).

Table 4.1: Correlation matrix for metals, sand, silt, clay and organic carbon (OC) of surface sediments of Zuari Estuary for different seasons.

Monsoon

	Fe	Mn	Cr	Cu	Zn	Co	OC	Sand	Silt	Clay
Fe	1.000									
Mn	0.674**	1.000								
Cr	0.075	0.277	1.000							
Cu	0.181	0.464*	0.029	1.000						
Zn	0.384	0.562*	-0.412	0.476*	1.000					
Co	0.485*	0.708**	0.228	0.102	0.584*	1.000				
OC	0.667**	0.735**	-0.222	0.411	0.777**	0.674**	1.000			
Sand	-0.594**	-0.524*	0.183	-0.202	-0.552*	-0.561*	-0.835**	1.000		
Silt	0.469*	0.222	-0.083	-0.072	0.202	0.342	0.487*	-0.881**	1.000	
Clay	0.574*	0.704**	-0.240	0.436	0.775**	0.646**	0.985**	-0.870**	0.532*	1.000

Post-monsoon

	Fe	Mn	Cr	Cu	Zn	Co	OC	Sand	Silt	Clay
Fe	1.000									
Mn	0.416	1.000								
Cr	0.709**	0.499*	1.000							
Cu	0.839**	0.611**	0.803**	1.000						
Zn	0.900**	0.647**	0.801**	0.916**	1.000					
Co	-0.200	0.081	0.154	0.198	-0.086	1.000				
OC	0.677**	0.662**	0.634**	0.894**	0.806**	0.250	1.000			
Sand	-0.572*	-0.461*	-0.291	-0.775**	-0.619**	-0.230	-0.836**	1.000		
Silt	0.554*	0.539*	0.365	0.527*	0.677**	-0.324	0.684**	-0.504*	1.000	
Clay	0.481*	0.362	0.221	0.714**	0.499*	0.346	0.738**	-0.971**	0.281	1.000

Pre-monsoon

	Fe	Mn	Cr	Cu	Zn	Co	OC	Sand	Silt	Clay
Fe	1.000									
Mn	0.699**	1.000								
Cr	0.528*	0.243	1.000							
Cu	0.564**	0.538*	0.388	1.000						
Zn	0.623**	0.380	0.356	0.535*	1.000					
Co	0.053	0.182	0.125	0.573**	0.125	1.000				
OC	0.428*	0.363	0.113	0.861**	0.562**	0.415*	1.000			
Sand	0.232	0.226	-0.099	-0.830**	-0.524*	-0.419*	-0.867**	1.000		
Silt	0.150	0.180	-0.085	0.672**	0.316	0.337	0.706**	-0.891**	1.000	
Clay	0.255	0.230	0.196	0.840**	0.594**	0.427*	0.875**	-0.964**	0.739**	1.000

** - correlation is significant at 0.01 level, * - correlation is significant at 0.05 level

c. Chromium (Cr)

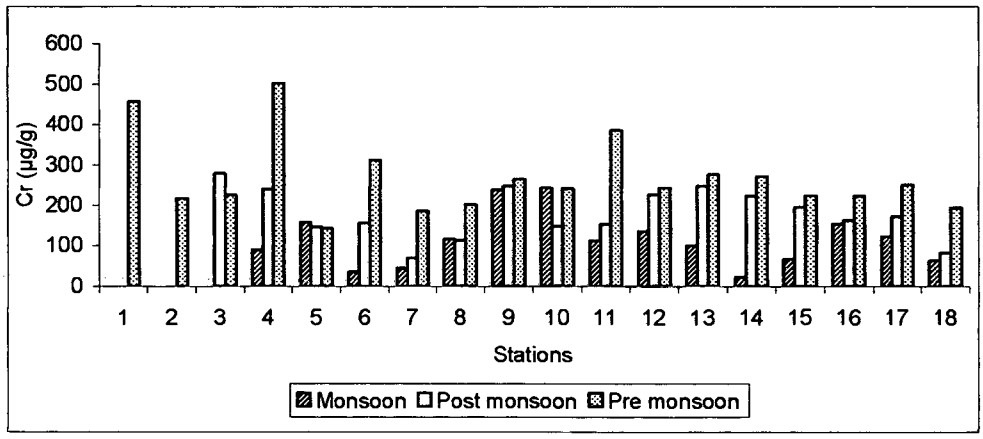


Fig. 4.11: Distribution and abundance of Cr in surface sediments of Zuari Estuary.

Concentration of Cr ranges from 22.8 to 242.0 µg/g (Avg. 113.5) during monsoon season (Fig. 4.11). Cr values show less variation during this season with slightly high concentrations recorded at stations 9 and 10. Cr concentration ranges from 70.3 to 279.5 µg/g (Avg. 178.9) during post-monsoon. Concentration of Cr decreases from station 3 to 7 with minor fluctuations. It shows an increase from station 8 to 9. Further downstream, lower values are recorded at stations 10 and 11 and slightly high values are recorded at stations 12 and 13. From here, Cr content decreases towards the mouth of the estuary i.e. up to station 18. During pre-monsoon, Cr concentration varies from 143.0 to 502.0 µg/g (267.4). Higher concentrations are noted at stations 1, 4 and 11 and low concentration at station 5. Cr maintained almost constant values at other stations. In general, Cr in the surface sediments of Zuari Estuary is high during pre-monsoon. Lesser values have been recorded specially during monsoon. The average Cr (µg/g) values in three seasons indicates relatively higher concentration during pre-monsoon (267.4) followed by post-monsoon (178.9) and then by monsoon (113.5). Except for the monsoon, the distribution of Cr in the surface sediments of Zuari Estuary largely follows the trend of Fe and Mn. This is also supported by the significant correlation obtained between these metals during post-monsoon and pre-monsoon. Association of Cr with Fe ores has been reported (Bukhari, 1994) within the catchment area of Mandovi Estuary. All along the

banks especially of Mandovi Estuary, ore processing units to enrich the percentage of iron ore are operating and it is expected that these industries are forced to release associated elements to the waters of the estuary. In addition, the loading jetties in the upstream region of Zuari Estuary are also expected to release considerable amount of Fe, Mn and Cr. As the river current is considerably low during pre-monsoon, Cr gets incorporated into the sediments to a large extent during this season.

d. Copper (Cu)

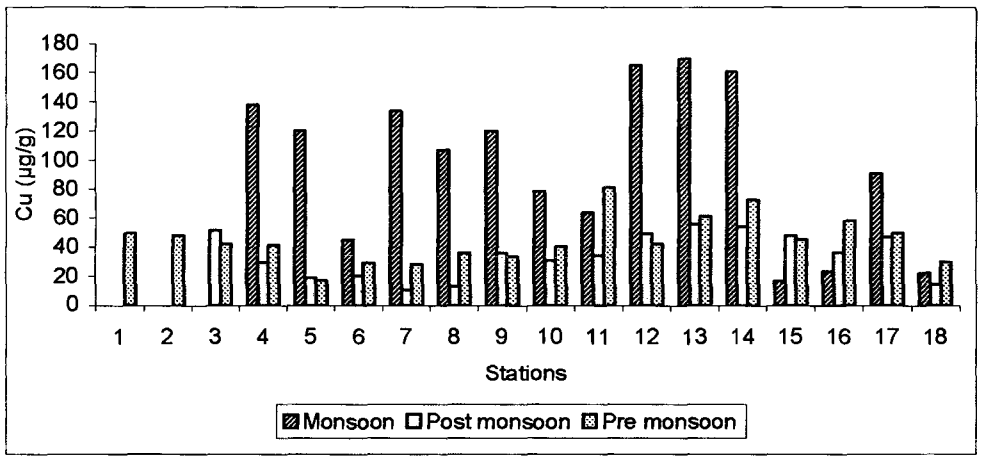


Fig. 4.12: Distribution and abundance of Cu in surface sediments of Zuari Estuary.

Cu content ranges from 16.5 to 169.5 µg/g (Avg. 96.9) during monsoon season (Fig. 4.12). During this season, Cu decreases from station 4 to 6 and it then increases at station 7. Further downstream, the values show a decreasing trend from station 7 to 11 with slightly higher value at station 9. Very high concentrations are observed at stations 12, 13 and 14 and very low values are recorded at stations 15, 16 and 18. There is a sharp decrease in concentration from station 14 to 15. During post-monsoon season, Cu value ranges from 10.5 to 56.0 µg/g (Avg. 34.3). Cu content decreases from station 3 to 7 with slightly higher value at station 6. From station 7 to 13, an increasing trend of Cu is noted. Further downstream Cu shows a decreasing trend towards the mouth of the estuary except at station 17 where it shows a

slight increase. During pre-monsoon, concentration of Cu varies from 17.3 to 80.8 µg/g (44.8). Concentration of Cu decreases from station 1 to 5 and further downstream, up to station 14, an increasing trend is seen with very high value noted at station 11. Further, it decreases from station 14 to 18 towards the mouth of the estuary with slightly lower value at station 15.

The concentration of Cu remains very low during pre-monsoon and post-monsoon compared to monsoon season, however, maintains similar distribution trend of Fe and other elements. No significant relation between Cu concentrations in waters with salinity has been reported earlier in Zuari Estuary (Sankaranarayanan and Reddy, 1973). The high concentration obtained during monsoon can be directly related to the material input from the catchment area brought by the tributaries and the river as well as input from Cumbharjua Canal. Foster and Morris (1971) have made similar observations elsewhere. During monsoon, Cu exhibits significant correlation with Zn and Mn. While during post-monsoon and pre-monsoon, it shows significant correlation with Fe, Mn, Zn, organic carbon, and clay and also with the silt, indicating its association and process of deposition.

e. *Zinc (Zn)*

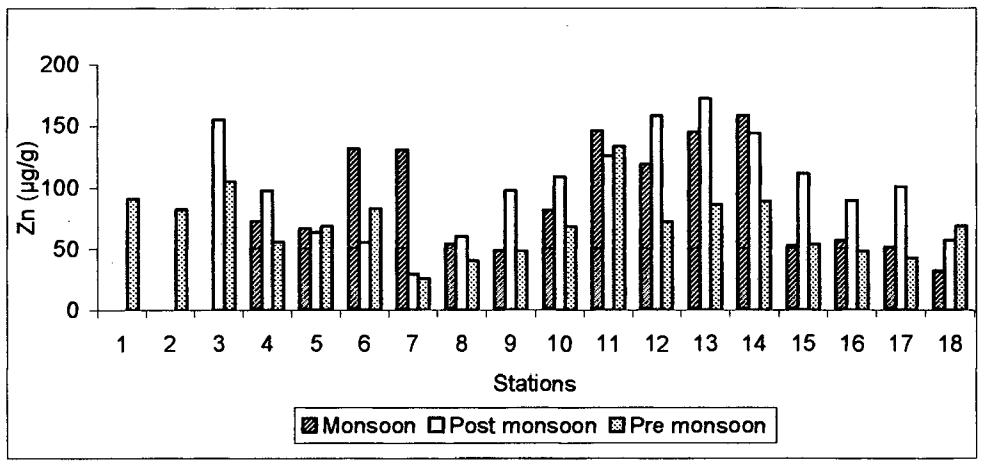


Fig. 4.13: Distribution and abundance of Zn in surface sediments of Zuari Estuary.

During monsoon, Zn concentration varies from 32.3 to 158.8 µg/g (Avg. 90.2). Zn is observed to be comparatively higher at stations 6, 7, 11, 12, 13 and 14 (Fig. 4.13). Increasing trend of Zn is seen from station 9 to 14 with slightly higher value at station 11. Relatively lower values are observed at stations 8 and 9 and also from station 15 to 18, lowest being at station 18. During post-monsoon, the values vary from 29.5 to 172.3 µg/g (Avg. 102.0). Zn concentration decreases from station 3 to 7 and then it shows an increasing trend from station 7 to 13. Further downstream, concentration decreases from station 13 to 18 with the exception of a high value at station 17. In general, concentrations are found to be comparatively higher at stations 3, 11, 12, 13 and 14 during this season. Zn values range from 26.3 to 133.5 µg/g (70.4) during pre-monsoon. Zn shows a general decreasing trend from station 1 to 7 with relatively higher values at stations 3 and 6. Further downstream, it shows an increasing trend from station 7 to 11 and then the values show a decreasing trend with lower value at station 12 and relatively higher value at station 18. In general, high concentration of Zn is seen in upper half of the lower estuary. The distribution of Zn also follows the trend of Fe with values decreasing from station 1 to 7 and maintaining higher values between stations 11 and 14. Exceptionally high values have also been recorded at station 6 and 7 during monsoon and at station 3 during post-monsoon.

The distribution of Zn within the estuary is controlled by variation in salinity. It is reported (Kerdijk and Salomons, 1981) that Zn gets incorporated in the surface sediments at zero salinity as well as at higher salinity of around 28 psu. Higher values obtained at the upstream and upper half of lower estuary between stations 11 and 14 can be very well explained with help of role of salinity in the deposition of Zn. The source for the Zn in the aquatic environment can be industrial as well as sewage effluents (Alagarsamy, 2006) in addition to land runoff. Role of Organic carbon holding Zn within the sediment is well known. The significant correlation obtained between Zn and organic carbon (Avg. 0.715) for the surface sediments of Zuari Estuary strongly supports the retention of Zn in the sediments by the organic carbon.

f. Cobalt (Co)

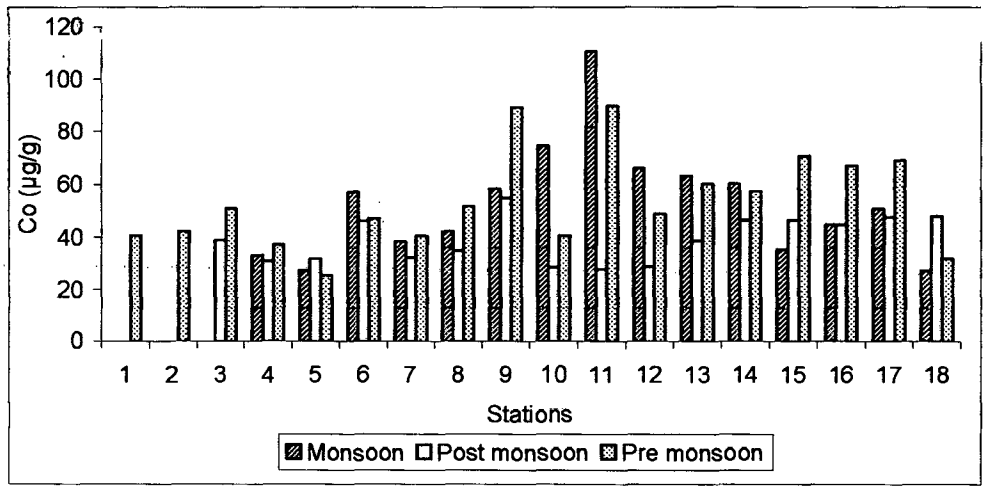


Fig. 4.14: Distribution and abundance of Co in surface sediments of Zuari Estuary.

Co concentration ranges from 27.0 to 110.8 µg/g (Avg. 52.6) during monsoon season (Fig. 4.14). It shows an increasing trend from station 4 to 11 with few high values in between. Further downstream, the values show a decreasing trend with slightly higher values observed at stations 16 and 17. During post-monsoon, the value varies from 27.8 to 55.0 µg/g (Avg. 39.1). The values show an increasing trend from station 4 to 9 with slightly higher value at station 6 as an exception. Further downstream, from station 10 to 18 Co values show an increasing trend. From station 9 to 10 there is sharp fall in concentration. During pre-monsoon, Co content ranges from 25.5 to 90.0 µg/g (Avg. 53.5). Concentrations are comparatively higher at stations 9 and 11. Excluding these two higher and some lower values observed at stations 5 and 18, the values in general show an increasing trend from upstream to downstream. Co concentrations are relatively high during pre-monsoon followed by monsoon and then by post-monsoon. During post-monsoon, the concentration of Co remains almost constant with minor fluctuations and without any particular trend. However, slightly higher values have been recorded between stations 13 and 18 and also at stations 3, 6 and 9. During

the other two seasons, the trend of distribution of Co can be compared with that of other elements described above.

Co is generally associated with Fe and the trend obtained for Co in the present study agrees with that of Fe during pre-monsoon. However during post-monsoon, values obtained at different stations remain almost constant with minor fluctuations. The concentrations are relatively higher during pre-monsoon and monsoon. The higher concentrations during pre-monsoon have also been reported in the adjacent Mandovi Estuary by Alagarsamy (2006).

4.4.2 Discussion

Except for few recorded variations, all the elements show decreasing trend from the upstream region to the middle of the Zuari Estuary, that is up to slightly upstream end of around the mouth of the Cumbharjua Canal and further downstream maintains higher concentration with gradual decrease towards the mouth. The distribution of various elements detailed above reveals that in the upstream end, mining and its associated activities are largely responsible for the concentration and distribution of Fe and to some extent for Cr. Kushawati tributary which joins the Zuari Estuary between stations 3 and 4, also contributes to increase in metal concentrations at these stations. In the lower half of the estuary, between stations 10 and 14 almost all the elements studied except for Cr during monsoon, maintain higher concentrations. Finer sediments (silt + clay) and organic carbon also maintain relatively higher concentration in this region, supporting the fact that the organic carbon acts as a trap for most of the metals within the estuarine region and finer sediments help in retaining the metals in sediments. It is a known fact that the organic matter decides the site of deposition of metals due to its ability of adsorption, which leads to strong correlation between organic matter and metals (Gonzalez et al., 1991; Ergin et al., 1996). As mentioned earlier the ratio C-org / surface is higher for finer sediments than for coarser sediments, such as sand particles (Hedges and Keil, 1995; Hedges, 2002; Wakeham, 2002). Also, the surface area of the sediment particles depends of

grain size and controls the metal adsorption processes (Summers et al., 1996; Zhang et al., 2002). It is appropriate to mention here that the concentration of organic carbon is relatively low in the upper part of the estuary except for few higher values during pre-monsoon.

The Zuari Estuary maintains strongly lower estuarine / marine conditions from mouth to the slightly upstream end of the mouth of the Cumbharjua Canal. Further upstream, it acts as a river (fresh water) during monsoon and also to lesser extent during early post-monsoon providing different environment compared to lower half of the estuary. Since the lower half of the estuary is wide and receives additional inputs of both water and sediment from the Cumbharjua Canal, it will be appropriate to look for various factors responsible for the higher concentration of the metals obtained in this part of the estuary. Factors like, TSM, tide and tidal currents, geomorphological set up, Cumbharjua Canal and lower estuarine / marine nature of the estuary may be responsible in enrichment of metals in this region. The studies carried out by Sankaranarayanan and Reddy (1973) and also by Zingde et al. (1976) indicated that the concentration of dissolved Mn and Cu are high at the upstream and gradually decreases towards downstream. In the present study, TSM concentration increases from head towards the mouth of the estuary in all the seasons with some fluctuations in between. Nayak and Bukhari (1992) reported increase in TSM concentration from the upstream end towards mouth especially during pre-monsoon and post-monsoon. The TSM concentration in bottom waters is higher than the surface waters during all the seasons. The zone of higher TSM was reported by (Nayak and Bukhari, 1992) near the Cumbharjua mouth and was related to resuspension by the tidal surge. TSM has been considered as one of the major carrier of trace metals into the estuary which finally transfers the metals into the sediments. It is important to note that the width of the river reduces to less than half of that at the mouth at this place and therefore causing tidal turbulence and resulting resuspension. Higher concentration of metals, observed in the present study, along this region can therefore be explained with reference to geomorphology as well as tidal surge. Metals brought by high velocity river currents, on

settling within the estuary, get incorporated into the sediments. Resuspension of bed load sediments due to tidal surge and geomorphological constriction involves drag and lift force resulting removal of less denser material from the surface sediments, which in turn helps in concentration of denser particles as well as the particles with adsorbed metals and therefore responsible for higher concentration of the studied metals along the region.

Further, it may be noted here that the Zuari Estuary maintains approximately same width from mouth up to the Cumbharjua Canal but further upstream it narrows slightly up to station 10 and then quickly narrows down to less than 0.5 km in the upstream region. It may be also necessary to mention here that the Cumbharjua Canal connect Mandovi and Zuari estuaries at about 14 and 11 km from their mouths respectively. As mentioned earlier, large mining activities are carried out in the basin area of Mandovi Estuary. During monsoon and during regular ebb tide, water flows from Mandovi to Zuari through Cumbharjua Canal and during high tide, tidal water flushes from Zuari to Mandovi. With this, it is expected that considerable quantity of metals are added to Zuari Estuary through Cumbharjua Canal.

From the results obtained, it is clear that most of the studied elements (Fe, Mn, Cr and Co) show higher concentration during pre-monsoon indicating favorable conditions for incorporation of the metals in the sediments during this season. During this season, estuary is largely controlled by saline water influx and therefore salinity largely controls the deposition of metals. The deposited metals get incorporated in sediments and remain in the sediments depending on the availability of organic matter as well as the sediment size. During monsoon, considerable quantity of fresh water is added to the estuary from the catchment area of Zuari, which is responsible for diluting the saline waters at the upstream end providing a different environment for deposition compared to pre-monsoon. Post-monsoon facilitates deposition for metals in a way largely similar to pre-monsoon.

a. Factor Analysis

R-mode factor analysis with Varimax-normalized rotation by means of the principal components extraction method was attempted in the present study to detect unrecognized multivariate structures in the data for all the three seasons. The multivariate statistical analysis was performed using the software STATISTICA (StatSoft, 1999). Factor analysis is a method of data reduction and is basically used to reduce the complexity of the data. Factor analysis helps in identifying common sedimentological and geochemical characteristic of the original data. Factor analysis has extracted three common factors viz. Factor 1 (F1), Factor 2 (F2) and Factor 3 (F3) with significant loadings within each factor for all the three seasons, that are presented in the figure (Fig. 15 a to c).

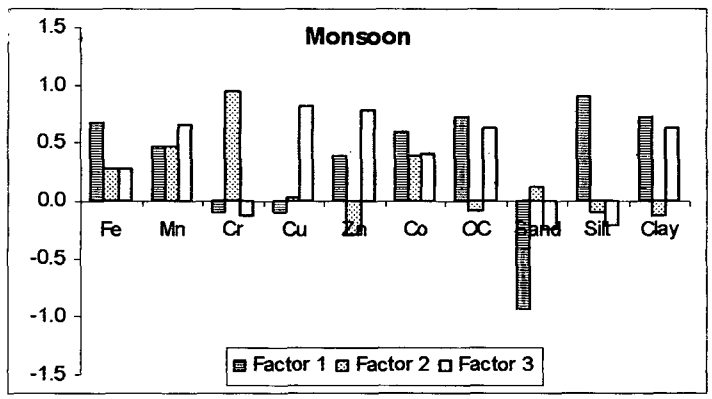


Fig. 4.15a: R-mode factors computed for surface sediments from Zuari Estuary during monsoon.

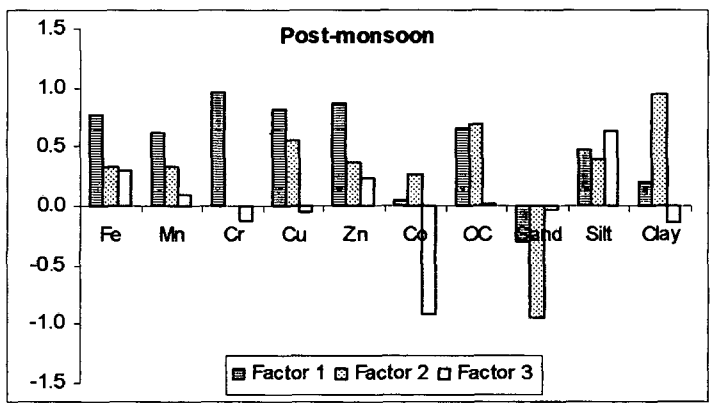


Fig. 4.15b: R-mode factors computed for surface sediments from Zuari Estuary during post- monsoon.

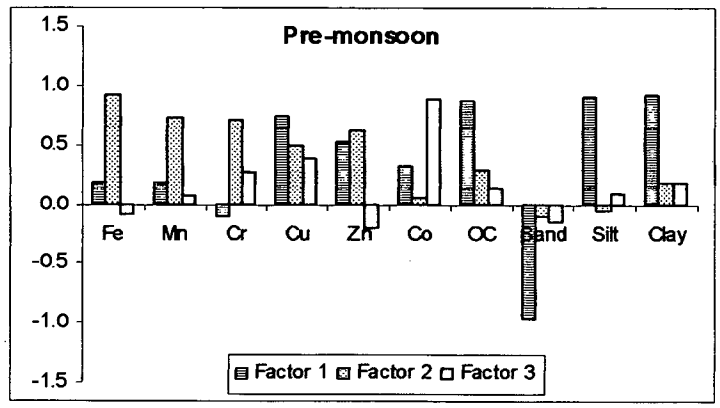


Fig. 4.15c: R-mode factors computed for surface sediments from Zuari Estuary during pre-monsoon.

During monsoon, first factor (F1) accounts for 55.0 % of total variance. High positive loading of elements such as Fe and Co with silt, clay and organic carbon indicates general association of these elements with finer fraction of the sediment and organic matter. Also strong negative effect of sand with the metals supports association of the metals with finer fractions. The second factor (F2) accounts for 14.9 % of total variance. The strong loading of Cr alone in this factor indicates that other metals are not associated with Cr in this season. The third factor (F3) accounts for 13.9 % of total variance. The strong association of Cu and Zn with Mn, clay and organic carbon in F3 is an indication of association of these metals with Mn oxides, finer size sediments and organic matter.

During post-monsoon, first factor (F1) accounts for 61.1 % of total variance. High positive loading of Fe, Mn, Cr, Cu, Zn and organic carbon and moderate loading of silt indicates role of Fe-Mn oxyhydroxides and organic matter in accumulation and incorporation of these metals into the sediments. Conversion of iron into complex hydroxy compounds which leads to precipitation (Riley and Chester, 1971) and helps in co-precipitation of other metals in the water is responsible for increase in concentration of these metals in the sediments. The second factor (F2) accounts for 16.2 % of total variance. Association of clay, organic carbon and Cu indicates adsorption of Cu to finer fraction and to humic substances. The third factor (F3) accounts

for 10.2 % of total variance. The high negative loading of Co alone in F3 indicates that other metals are not associated with Co.

During pre-monsoon, first factor (F1) accounts for 53.8 % of total variance. The high loading of Cu, Zn, organic carbon, clay and silt is observed in this factor. Cu can easily form complex with organic matter because of the high formation constants of organic-Cu compounds (Stumm and Morgan, 1981). The second factor (F2) accounts for 20.0 % of total variance. High loading of Fe, Mn, Cr, Zn and moderate association of Cu is observed in this factor. Fe-Mn oxyhydroxides may be the controlling factors here. The third factor (F3) accounts for 9.0 % of total variance. The high positive loading of Co alone, in F3 indicates that it is not associated with other metals in this season, as observed in post-monsoon season.

b. Cluster Analysis

Cluster analysis was also applied to the normalized data using complete linkage method, with Euclidean distances as the criterion for forming clusters (Fig. 4.16 a to c) to understand the source and association of metals.

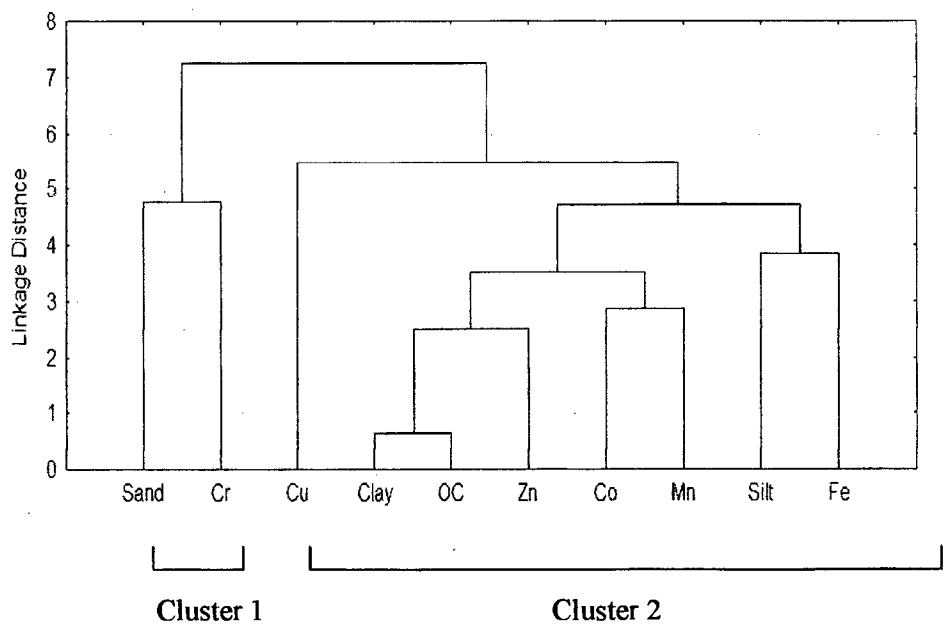


Fig. 4.16a: Dendogram based on complete linkage method for monsoon season.

During monsoon, two clusters are obtained (Fig. 4.16a). Cluster 1 includes the Cr and sand while cluster 2 includes other elements along with silt, clay and organic carbon. This indicates association of most of the elements with the finer size of the sediments and organic matter. Close association of most of the metals with Mn indicates role of Mn oxide in distribution and concentration of metals in this season.

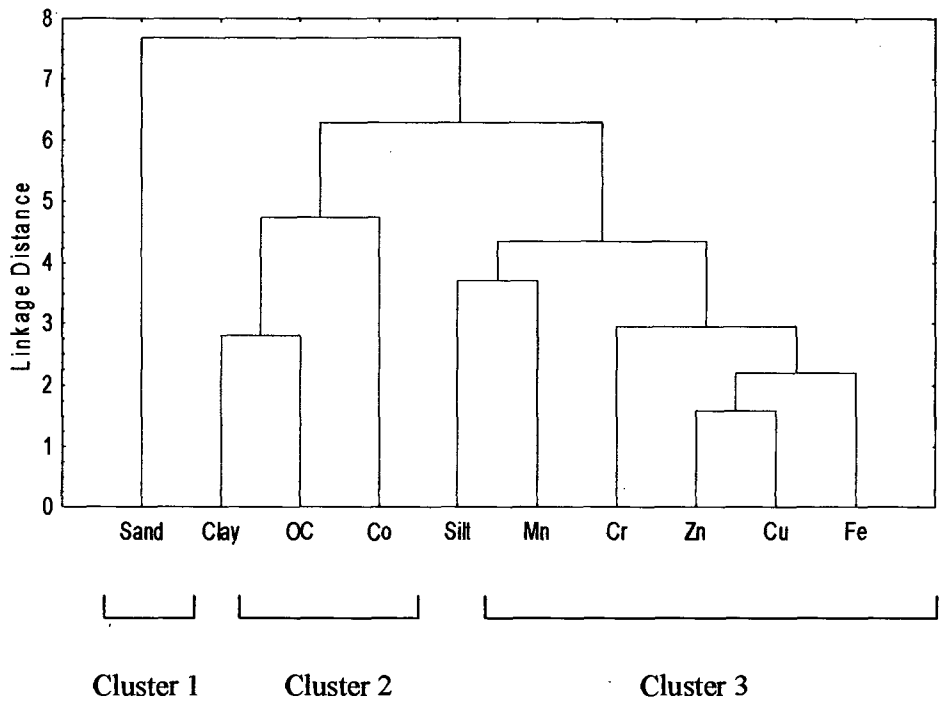


Fig. 4.16b: Dendogram based on complete linkage method for post-monsoon season.

In post-monsoon season, three clusters viz. cluster 1 (sand), cluster 2 (Co, clay, organic carbon) and cluster 3 (Fe, Cu, Zn, Cr, Mn, silt) are observed (Fig. 4.16b). Association of most of the elements along with Fe, Mn and silt indicates role of Fe-Mn oxide and finer fraction in distribution and abundance in this season whereas Co is mainly associated with the organic carbon and clay content.

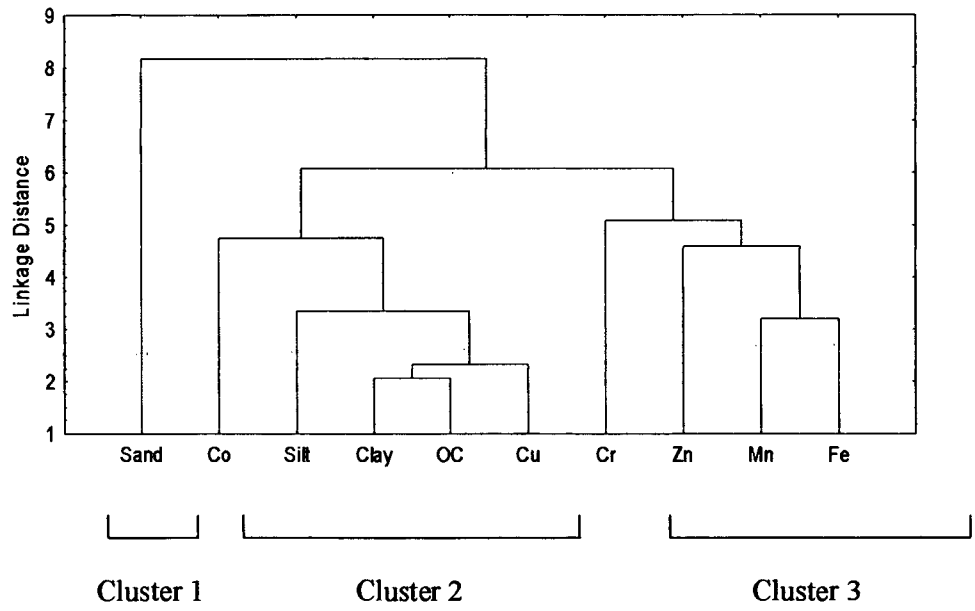


Fig. 4.16c: Dendogram based on complete linkage method for pre-monsoon season.

During pre-monsoon season, three clusters are formed. Cluster 1 contains sand alone indicating its insignificant role in retaining metals in sediments. Cluster 2 includes Cu, Co, silt, clay and organic carbon indicating their association. Cluster 3 consists of Fe, Mn, Cr and Zn indicating the major role of Fe-Mn oxide in distribution and abundance of metals(Fig. 4.16c).

Cluster analysis largely agrees with the results obtained from the factor analysis and the correlation analysis indicating major role of finer size sediments, organic matter, Fe-Mn oxide in distribution and concentration of metals in all three seasons.

Singh (2000) has studied the distribution of Fe, Mn, Cu, Zn, Cr and Co in the surface sediments of Zuari Estuary. The average concentrations of metals in the present study and those reported by Singh (2000) are presented in the table 4.2.

Table 4.2: Average metal concentrations in the sediments of Zuari Estuary in the three different seasons.

	Fe (%)		Mn (%)		Cu		Zn		Cr		Co	
	A	B	A	B	A	B	A	B	A	B	A	B
Monsoon	8.36	7.64	0.31	0.33	96.88	40.03	90.18	93.33	113.47	204.26	52.60	25.76
Postmonsoon	7.61	7.66	0.29	0.34	34.34	29.50	101.95	83.60	178.89	127.13	39.14	23.13
Pre-monsoon	8.72	4.27	0.31	0.30	44.78	36.41	70.39	87.25	267.43	148.67	53.46	17.49
Avg.	8.23	6.52	0.30	0.32	58.67	35.31	87.51	88.06	186.60	160.02	48.40	22.13

* A-present study, B-singh (2000), except for Fe and Mn all other values are in µg/g.

Most of the metals (Fe, Cu, Cr and Co) show higher concentration in the present study than in Singh (2000) indicating increase in anthropogenic input. However, Mn and Zn concentrations are slightly lower than those reported in the study carried out by Singh (2000). His studies also showed higher concentrations of metals in the upper as well as in the lower half of the Zuari Estuary, which is similar to the present study. Also, Mesquita and Kaisary (2007) reported higher concentrations of Fe and Mn in mid-estuarine region in addition to upper estuarine region during 2002.

c. Pollution Indices

With this background, to understand the level of concentration of metals, in the surface sediments of Zuari Estuary, an attempt has been made to compute index of geo-accumulation, contamination factor and pollution load index (PLI).

i. Geo-accumulation Index

The index of geo-accumulation has been computed using the formula given by Muller (1979) as,

$$I_{geo} = \log_2 C_n/1.5*B_n$$

Where, I_{geo} = Index of geo-accumulation, C_n = measured concentration of element "n" and B_n = element content in "average shale" (Turekian and Wedepohl, 1961) and the factor 1.5 is used because of possible variation of the background data due to lithogenic effects.

Muller (1979) suggested following grades to understand pollution level of individual elements, which have been followed for the sediments of Zuari Estuary.

Pollution Intensity class	Sediment accumulation (I_{geo})	I_{geo}
Very strongly polluted	> 5	6
Strong to very strongly polluted	> 4-5	5
Strongly polluted	> 3-4	4
Moderately to strongly polluted	> 2-3	3
Moderately polluted	> 1-2	2
Unpolluted to moderately polluted	> 0-1	1
Practically unpolluted	< 0	0

It is interesting to note that the geo-accumulation index calculated for Fe indicates that the sediments of Zuari Estuary fall under the grade of unpolluted to moderately polluted (Table 4.3) during all the three seasons except for station 9 during monsoon, stations 7, 8, 9 and 18 during post monsoon and station 9 during pre monsoon. Among these, only at station 7 during post monsoon the value of I_{geo} for Fe was above 2.00 and was the highest (2.75). In the adjacent Mondovi Estuary, I_{geo} values for Fe reported for different seasons (Alagarsamy, 2006), maintain values higher than 2.5, at the upstream end during pre monsoon. In the Zuari Estuary, however, higher values are specially noted in mid estuarine region, between station 7 and 9.

Geo-accumulation index calculated for Mn for the three seasons indicates that the sediments of Zuari Estuary fall under the grade of moderately to strongly polluted (Table 4.3) during monsoon between stations 9 and 14 during monsoon, between stations 8 and 15 during post-monsoon and between stations 11 and 14 and also at stations 1, 2, 3 and 7 during pre-monsoon. It is clear from the computed index that the sediments of Zuari Estuary fall under higher grade of geo-accumulation index for Mn than that of Fe. It is necessary to mention here that the catchment area of Zuari River is known for the presence of large mines of Mn ore associated with lesser Fe ore deposits.

Table 4.3: Geoaccumulation index computed for surface sediments of Zuari Estuary.

Stn	Monsoon						Post-monsoon						Pre-monsoon					
	Fe	Mn	Cr	Cu	Zn	Co	Fe	Mn	Cr	Cu	Zn	Co	Fe	Mn	Cr	Cu	Zn	Co
1	-	-	-	-	-	-	-	-	-	-	-	-	1.25	2.72	1.87	-0.44	-0.64	0.52
2	-	-	-	-	-	-	-	-	-	-	-	-	0.58	2.23	0.79	-0.48	-0.78	0.58
3	-	-	-	-	-	-	0.92	1.42	1.17	-0.38	0.13	0.45	0.95	2.46	0.85	-0.68	-0.43	0.84
4	0.62	1.31	-0.46	1.03	-0.96	0.21	0.45	0.56	0.94	-1.21	-0.54	0.11	0.63	1.15	2.01	-0.70	-1.33	0.39
5	-0.10	1.44	0.34	0.83	-1.08	-0.06	-0.84	0.27	0.23	-1.83	-1.15	0.16	0.12	0.62	0.20	-1.97	-1.05	-0.16
6	-0.63	-0.13	-1.84	-0.58	-0.11	1.00	-0.37	0.35	0.33	-1.75	-1.35	0.70	-0.69	0.17	1.32	-1.22	-0.78	0.73
7	-0.93	1.74	-1.46	0.98	-0.12	0.43	-2.75	-0.96	-0.83	-2.68	-2.27	0.18	-0.81	2.40	0.58	-1.26	-2.44	0.52
8	-0.90	1.21	-0.10	0.66	-1.39	0.58	-1.48	2.06	-0.13	-2.38	-1.24	0.28	-0.50	1.35	0.70	-0.91	-1.81	0.86
9	-1.25	2.00	0.93	0.83	-1.55	1.03	-1.24	2.57	1.00	-0.92	-0.55	0.95	-0.66	1.16	1.09	-1.03	-1.57	1.65
10	0.90	2.50	0.96	0.21	-0.80	1.39	0.50	2.09	0.25	-1.15	-0.39	-0.01	0.04	0.82	0.95	-0.74	-1.05	0.52
11	0.76	2.55	-0.16	-0.08	0.04	1.96	0.53	2.22	0.30	-0.99	-0.17	-0.04	0.80	2.36	1.63	0.26	-0.09	1.66
12	0.66	2.18	0.12	1.29	-0.26	1.21	0.59	2.37	0.86	-0.45	0.15	0.00	0.34	2.11	0.96	-0.68	-0.98	0.78
13	0.82	2.38	-0.30	1.33	0.03	1.15	0.93	2.26	1.00	-0.27	0.27	0.44	0.42	2.04	1.15	-0.15	-0.72	1.08
14	0.71	2.46	-2.45	1.25	0.16	1.08	0.45	2.05	0.83	-0.32	0.02	0.71	0.62	2.16	1.13	0.11	-0.68	1.01
15	0.61	1.83	-0.89	-2.03	-1.41	0.31	0.52	2.15	0.65	-0.48	-0.35	0.71	0.59	1.66	0.85	-0.57	-1.39	1.31
16	0.30	1.14	0.31	-1.55	-1.32	0.65	0.01	1.94	0.39	-0.90	-0.67	0.65	0.42	1.89	0.84	-0.21	-1.56	1.23
17	0.31	1.15	-0.02	0.43	-1.45	0.83	0.26	1.57	0.46	-0.52	-0.50	0.74	-0.20	1.43	1.01	-0.43	-1.74	1.28
18	-0.80	-0.56	-0.98	-1.62	-2.14	-0.08	-1.30	-0.65	-0.60	-2.22	-1.31	0.75	-0.76	-0.17	0.64	-1.18	-1.05	0.16

Therefore the release of mining materials from these mines to the Zuari Estuary is expected to carry large quantity of Mn than Fe. Further, Mn is remobilized within the estuary with response to oxidation redox potential.

Geo-accumulation index computed for the other metals, viz. Cr, Cu, Zn and Co, indicate that the values are less than 2 (Table 4.3) at most of the stations except for two values, one each for monsoon and pre-monsoon for Cr. Also, four values, one in monsoon and three in post-monsoon, for Cu and three values, one each in monsoon, post-monsoon and pre-monsoon, for Zn. Among these, two values of Zn and one value of Cu are obtained for station 7. From the I_{geo} indices computed for these metals for the surface sediments of Zuari Estuary, it can be stated that the sediments are in the range of practically unpolluted to moderately polluted as per Muller (1979).

ii. Contamination Factor (Cf), Pollution Load Index (PLI) and Degree of Contamination (C_d)

The formula used to compute Cf is given below:

Cf. = Metal concentration of polluted sediment / Background value of that metal.

Background value used here is same as that used for calculating the Geo-accumulation index.

The contamination factor was classified by Pekey et al. (2004) and is as follows.

$Cf \leq 1$ – low contamination factor

$1 \leq Cf < 3$ – moderate contamination factor

$3 \leq Cf < 6$ – Considerable contamination factor

$Cf > 6$ – Very high contamination factor

Contamination factors (Cf) for each of the studied metals, for three seasons, at all 18 stations were computed (Table 4.4) for surface sediments of Zuari Estuary.

During monsoon, low Cf value is obtained between stations 6 and 9 and also at station 18 while moderate Cf value is obtained at rest of the stations for Fe. During post-monsoon, low Cf value is observed at station 5, between stations 7 and 9 and at station 18, while other stations fall under moderate Cf class. It is noted that Fe does not show high contamination during monsoon and post-monsoon. Considerable Cf value is observed at station 1 during pre-monsoon season. Stations 6, 7, 9 and 18 fall under low Cf class while other stations fall under moderate Cf class.

In case of Mn, during monsoon, station 6 and 18 fall within moderate Cf class. Considerable Cf value is observed at stations 4, 5, 7, 8, 15, 16 and 17 and very high Cf is seen between stations 9 and 14. During post-monsoon, stations 7 and 18 shows low Cf values while stations 4, 5, and 6 fall under moderate Cf class. Considerable Cf value of Mn is observed at stations 3, 16 and 17 and very high Cf is seen between stations 8 and 15. Moderate Cf values are observed at stations 5, 6, 10 and 18 during pre-monsoon. Considerable Cf value is observed at stations 4, 8, 9, 15, 16 and 17 and very high Cf value is obtained for stations 1, 2, 3, 7 and between stations 11 and 14, during this season.

Low Cf value for Cr is observed at stations 6, 7, 14, 15 and 18 while rest of the stations fall under moderately contaminated class during monsoon. During post-monsoon, low Cf values are observed at stations 7 and 18. Stations 3 and 13 fall into considerable Cf class while rest of the stations fall under moderate Cf class. Very high Cf is observed at station 4 and considerable Cf value is observed at stations 1, 6, 9, 11, 13, 14 and 17 while rest of the stations fall under moderate Cf class during pre-monsoon.

Table 4.4: Contamination factor and pollution load index (PLI) of surface sediments from Zuari Estuary.

Stn	Monsoon							Post-monsoon							Pre-monsoon						
	Fe	Mn	Cr	Cu	Zn	Co		Fe	Mn	Cr	Cu	Zn	Co		Fe	Mn	Cr	Cu	Zn	Co	
	Contamination Factor						PLI	Contamination Factor						PLI	Contamination Factor						PLI
1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3.56	9.90	5.50	1.11	0.96	2.14	2.76
2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.24	7.02	2.60	1.07	0.87	2.24	2.10
3	-	-	-	-	-	-	-	2.83	4.02	3.37	1.15	1.64	2.05	2.30	2.89	8.27	2.70	0.94	1.11	2.68	2.38
4	2.31	3.71	1.09	3.07	0.77	1.74	1.84	2.04	2.21	2.88	0.65	1.03	1.62	1.55	2.33	3.33	6.05	0.92	0.59	1.96	1.92
5	1.40	4.08	1.90	2.66	0.71	1.43	1.76	0.84	1.81	1.76	0.42	0.68	1.67	1.04	1.63	2.31	1.72	0.38	0.73	1.34	1.16
6	0.97	1.38	0.42	1.01	1.39	3.00	1.15	1.16	1.92	1.88	0.44	0.59	2.43	1.18	0.93	1.69	3.75	0.64	0.88	2.49	1.42
7	0.79	5.02	0.55	2.97	1.38	2.03	1.62	0.22	0.77	0.85	0.23	0.31	1.70	0.51	0.85	7.92	2.24	0.63	0.28	2.14	1.33
8	0.80	3.46	1.40	2.37	0.57	2.24	1.51	0.54	6.27	1.37	0.29	0.64	1.82	1.07	1.06	3.81	2.43	0.80	0.43	2.72	1.45
9	0.63	6.00	2.86	2.67	0.51	3.07	1.89	0.64	8.94	2.99	0.79	1.03	2.89	1.85	0.95	3.35	3.20	0.73	0.51	4.71	1.62
10	2.80	8.46	2.92	1.74	0.86	3.92	2.72	2.12	6.40	1.78	0.68	1.15	1.49	1.74	1.54	2.65	2.89	0.90	0.72	2.14	1.60
11	2.54	8.79	1.35	1.42	1.54	5.83	2.70	2.17	6.98	1.85	0.76	1.33	1.46	1.86	2.60	7.71	4.64	1.79	1.41	4.74	3.22
12	2.37	6.79	1.63	3.68	1.26	3.47	2.74	2.26	7.77	2.72	1.10	1.67	1.50	2.25	1.90	6.46	2.91	0.94	0.76	2.58	2.01
13	2.64	7.79	1.22	3.77	1.53	3.33	2.80	2.85	7.17	3.00	1.24	1.81	2.04	2.56	2.01	6.17	3.33	1.36	0.91	3.17	2.33
14	2.46	8.25	0.27	3.57	1.67	3.17	2.17	2.05	6.23	2.67	1.21	1.52	2.45	2.31	2.30	6.71	3.28	1.62	0.94	3.03	2.48
15	2.30	5.33	0.81	0.37	0.56	1.86	1.25	2.14	6.67	2.35	1.07	1.18	2.45	2.17	2.26	4.75	2.70	1.01	0.57	3.72	1.99
16	1.85	3.31	1.86	0.51	0.60	2.36	1.42	1.52	5.75	1.97	0.81	0.94	2.36	1.77	2.01	5.56	2.68	1.29	0.51	3.53	2.03
17	1.86	3.33	1.48	2.02	0.55	2.67	1.73	1.80	4.46	2.06	1.04	1.06	2.51	1.89	1.30	4.04	3.03	1.11	0.45	3.63	1.75
18	0.86	1.02	0.76	0.49	0.34	1.42	0.73	0.61	0.96	0.99	0.32	0.61	2.53	0.81	0.89	1.33	2.33	0.66	0.72	1.67	1.14

Cu shows considerable Cf at stations 4, 12, 13 and 14 during monsoon. Low Cf value of Cu is observed at stations 15, 16 and 18 while rest of the stations fall under moderate Cf class in this season. During post-monsoon, stations 3, 17 and stations between 12 and 15 falls under moderate Cf class and others fall under low Cf class. In case of pre-monsoon, stations 1, 2, 11 and stations between 13 and 17 falls under moderate Cf class and rest of the stations fall under low Cf class.

In case of Zn, the sediment collected at stations 6, 7 and stations between 11 and 14 falls into moderate Cf class and rest of the stations fall into low Cf class during monsoon. During post-monsoon, stations 3, 4, 17 and stations between 9 and 15 fall into moderate Cf class and rest of the stations fall into low Cf class. During pre-monsoon, except stations 3 and 11 (moderate Cf) all the stations fall under low Cf class.

Stations 4, 5, 7, 8 and stations from 15 to 18 falls under moderate Cf class for Co, while rest of the stations fall under considerable Cf class during monsoon. During post-monsoon, all the sediment samples fall under moderate contamination while during pre-monsoon, stations 9, 11 and stations between 13 and 17 fall under considerable Cf and rest of the values fall under moderate Cf class.

From the distribution of contamination factors computed for elements studied for surface sediments of Zuari Estuary during three seasons, it is clear that the surface sediments are highly contaminated by Mn at most of the stations in all the three seasons. In general, Cf values of Fe fall under moderate contamination at most of the station in all the three seasons. Higher values of contamination factor for Cr are obtained during pre-monsoon season and for Cu during monsoon season. Cf values of Co fall under moderately to considerable contamination class at most of the stations and Zn values mainly fall under low to moderate contamination class at most of the stations.

Further, Pollution Load Index (PLI) (Tomlinson et al., 1980) and Degree of contamination (Hakanson and Jasson, 1983) were also computed to assess the extent of pollution by metals in the surface sediments of Zuari Estuary. The PLI helps in understanding the overall level of metal content in a particular sample. The equation used for computing PLI is the following:

$$PLI = \sqrt[n]{\text{Product of n number of Cf Values}}$$

Where, Cf. = Contamination factor, n = Number of metals

The PLI values computed for all the 18 stations separately for the three seasons taking all the six elements together are presented in the Table 4.4. The values obtained during the monsoon vary between 1 and 2 at all the stations except at 18 (<1). The values for station 3 and stations between 12 and 15 are above 2 during post-monsoon. In the same season the values are between 1 and 2 for stations between 4 and 6, 8 and 12, 16 and 17. However, PLI values of < 1 have been observed at station 7 and 18. Similarly, PLI values of > 2 have been recorded between stations 1 and 3, 11 and 14 and at station 16 during pre-monsoon. At all the remaining stations, PLI values fall within the range of 1 and 2.

It may be noted from the distribution of PLI that 8 values out of 18 during pre-monsoon are more than 2 with the highest value as 3.22 at station 11. However, during post-monsoon PLI values > 2 have been recorded at 5 stations with highest value of 2.56 at station 13. It is interesting to note that the higher values obtained during both pre-monsoon and post-monsoon are recorded between the stations 11 and 14 and also at the upstream end.

Generally, degree of contamination (C_d) is computed considering sum of all contamination factors larger than one. However in the present work, all the values of Cf are considered.

Grade of sediment contamination is given below, wherein C_d is degree of contamination and n is number of elements considered to calculate the factor.

$C_d < n$ = Low degree of contamination

$n < C_d < 2n$ = Moderate degree of contamination

$2n < C_d < 4n$ = Considerable degree of contamination

$C_d > 4n$ = Very high degree of contamination.

Table 4.5: Degree of contamination for surface sediments of Zuari Estuary.

Stations	Degree of Contamination (C_d)		
	Monsoon	Post-monsoon	Pre-monsoon
1	-	-	23.17
2	-	-	16.05
3	-	15.06	18.60
4	12.68	10.44	15.19
5	12.18	7.18	8.12
6	8.16	8.43	10.38
7	12.72	4.08	14.06
8	10.84	10.92	11.26
9	15.73	17.28	13.45
10	20.69	13.61	10.85
11	21.47	14.54	22.88
12	19.20	17.01	15.55
13	20.28	18.12	16.95
14	19.39	16.13	17.86
15	11.22	15.85	15.01
16	10.49	13.34	15.58
17	11.91	12.93	13.57
18	4.89	6.01	7.61

During monsoon, station 18 falls under low degree of contamination, stations 6, 8, 15, 16 and 17 fall under moderate degree of contamination, while, rest of the stations namely 4, 5, 7, 9, 10, 11, 12, 13 and 14 fall under considerable degree of contamination. During post-monsoon, station 7 falls under low degree of contamination and stations 4, 5, 6, 8 and 18 fall under moderate degree of contamination, while stations 3, 9, 10, 11, 12, 13, 14, 15, 16 and 17

fall under considerable degree of contamination. In case of pre-monsoon, stations 5, 6, 8, 10 and 18 fall under moderate degree of contamination while all others fall under considerable degree of contamination (Table. 4.5).

Degree of contamination computed (Table 4.5) for whole Zuari Estuary taking sum of the averages of selected elements (Fe, Mn, Cr, Cu, Zn, and Co) is 14.13 (n = 6) for monsoon, 12.55 (n = 6) for post-monsoon and 14.79 (n=6) for pre-monsoon. As the values lie between 2n and 4n, surface sediments of Zuari Estuary can be classified under the class of considerable degree of contamination.

4.5 Magnetic Susceptibility

Sediments are the natural sink for magnetic minerals of different origin viz. lithogenic, pedogenic and anthropogenic sources (Desenfant et al., 2004). Magnetic properties of sediments are largely acquired as a consequence of the presence of different forms of iron. Magnetic measurement in sediments is used in a variety of studies covering palaeoclimatology, provenance, sediment transport pathways and recently has become an important tool in assessing environmental quality and discriminating pollution sources, either independently or in combination with geochemical analysis (Oldfield et al., 1978; Scoullos et al., 1979; Lepland and Stevens, 1996; Hoffmann et al., 1999; Shu et al., 2000; Booth, 2002; Lecoanet et al., 2003; Urbat et al., 2004; Shilton et al., 2005). It is widely known that sediment related parameters can be strongly affected by the particle size. Finer sediments contain higher concentration of both natural as well as anthropogenic pollutants (Forstner and Salomons, 1980; Thorne and Nickless, 1981; Loring, 1990; Clifton et al., 1999; McCubbin et al., 2000). Magnetic susceptibility can be used to characterize granulometry and mineralogy in combination with other magnetic parameters (Peters and Dekkers, 2003).

In the present study, different magnetic parameters like concentration, mineralogy and grain size dependent parameters are used in order to study their distribution, abundance and their relation with metals in the sediments.

The magnetic parameters which depend on the concentration of magnetic minerals are magnetic susceptibility (χ), saturation isothermal remnant magnetisation (SIRM) and susceptibility of anhysteretic remnant magnetization (χ_{ARM}). These parameters increase in value as the concentration of magnetic material in sediment increases. Although these parameters are concentration based, they also depend on the grain size. SIRM is also dependent on the magnetic mineralogy, for example the minerals having larger magnetisation contribute to larger SIRM values.

Mineral dependent parameters are hard isothermal remnant magnetisation (HIRM), soft isothermal remnant magnetisation (IRM_S) and S-ratio. The HIRM parameter is a measure of concentration of high coercivity magnetic minerals (e.g. haematite and goethite) and it varies directly with the concentration of high coercivity minerals while IRM_S reflects low coercivity magnetic minerals (e.g magnetite). The S-ratio is the ratio of higher coercivity to lower coercivity magnetic minerals. The values of S-ratio about 100 %, indicate a high proportion of magnetite, whereas lower values indicate an increasing proportion of haematite and goethite (Thompson and Oldfield, 1986; Robinson, 1986; King and Channell, 1991). Magnetic grain size is indicated by frequency dependent susceptibility (χ_{fd}), χ_{ARM} / χ and χ_{ARM} / SIRM. Increase in values of these parameters indicates the increase in fine grained magnetic minerals (single domain).

4.5.1 Results

The distribution of the various magnetic parameters in terms of concentration, mineralogy and grain size in surface sediments of the Zuari Estuary in the three different seasons is presented in the figures (Fig. 4.17 to 4.19).

During monsoon, magnetic susceptibility (χ) shows a decreasing trend from station 4 up to station 9 with a slightly higher value at station 7. A sudden

a. Monsoon

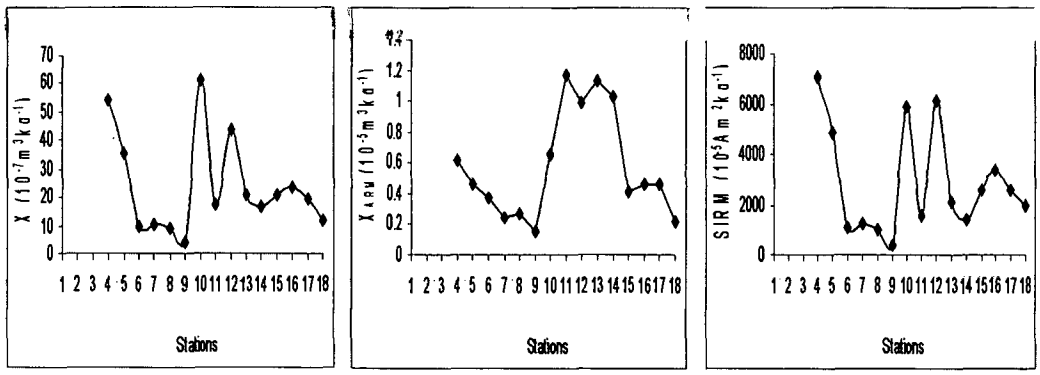


Fig. 4.17a: Variation of magnetic concentration in surface sediments of Zuari Estuary during monsoon.

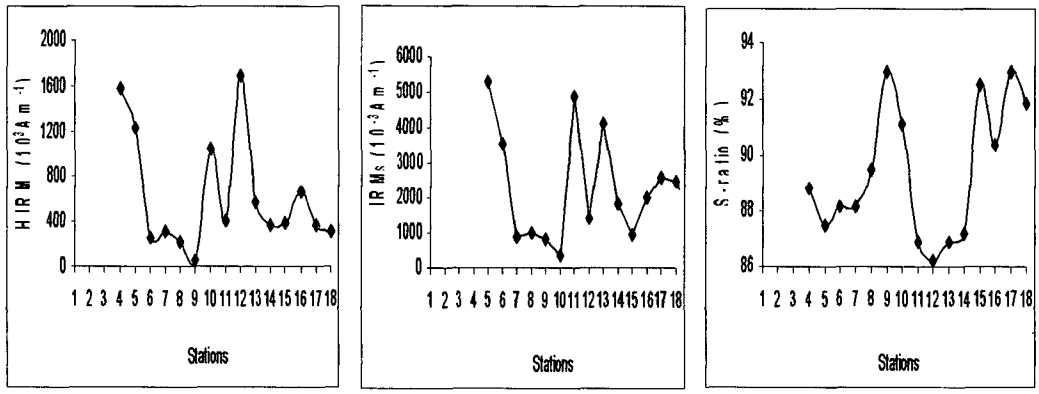


Fig. 4.17b: Variation of magnetic minerals in surface sediments of Zuari Estuary during monsoon.

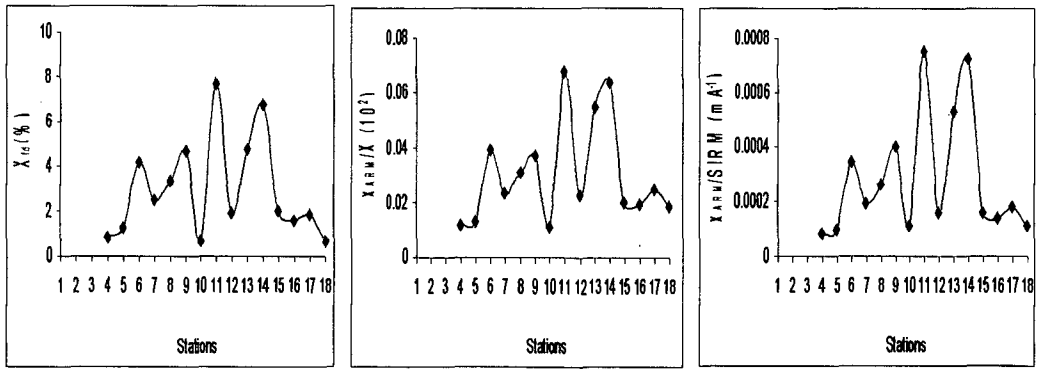


Fig. 4.17c: Variation of magnetic grain size in surface sediments of Zuari Estuary during monsoon.

increase is observed at station 10 and then the value decreases at station 11. An increase is observed at station 12 which then shows a decreasing trend up to station 14. Further downstream the values increase up to station 16 and then show a decreasing trend towards the mouth.

χ_{ARM} shows a decreasing trend from station 4 to station 9 with a slightly higher value at station 8. Further downstream, it shows an increasing trend up to station 11 and then the value decreases at station 12. An increase is observed at station 13, which then shows a decreasing trend up to station 15. A slight increase in value is again observed at station 16 and then a decreasing trend is observed towards the mouth. SIRM shows a distribution pattern similar to that of χ. In general, all the three parameters show a similar distribution pattern. Relatively higher values are observed at stations 4, 10 and 12 for both χ and SIRM and at stations 4, 11, 12, 13 and 14 for χ_{ARM} indicating higher magnetic concentrations at these stations.

HIRM and IRM_S show similar distribution trend throughout the estuary and it largely agrees with the distribution pattern of χ. This indicates the presence of both higher coercivity (haematite) and lower coercivity (magnetite) minerals at a particular station. Further, the S-ratio which reflects both minerals, shows decrease from station 4 to 5 and then shows general increasing trend from station 5 up to station 9 and then shows a decreasing trend up to station 12. Increasing trend is observed from station 12 up to station 15 and then a decrease in value is observed at station 16. The value increases at station 17 and then decreases at station 18. Comparatively lower values are observed in the upper estuary between stations 4 and 8 and also between stations 11 and 14 indicating the presence of haematite like minerals in this region. Relatively higher values are observed at station 9, and also in the lower estuary at stations 15, 16, 17 and 18 indicating the presence of less haematite like minerals.

χ_{fd} shows an increasing trend from station 4 up to station 6. Further, it shows decrease at station 7. An increasing trend is observed from station 7 up to

b. Post-monsoon

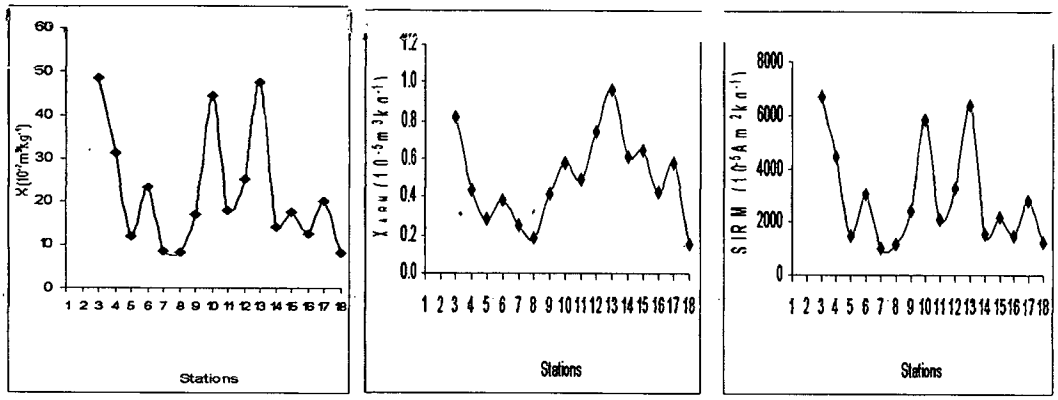


Fig. 4.18a: Variation of magnetic concentration in surface sediments of Zuari Estuary during post-monsoon.

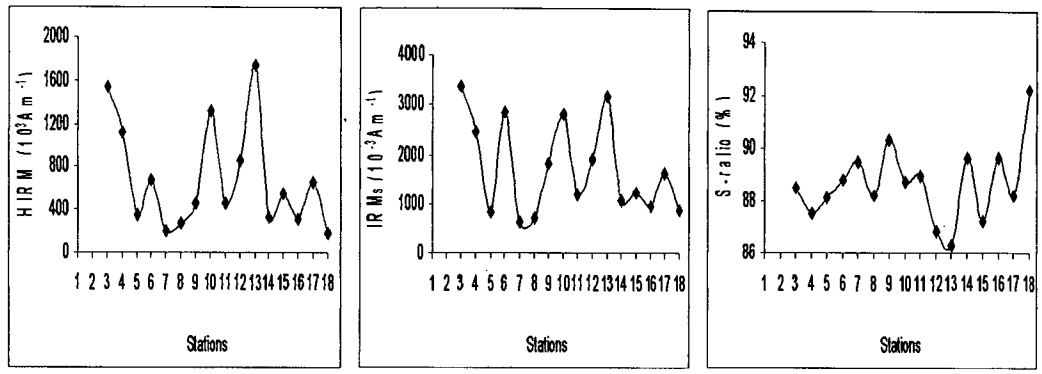


Fig. 4.18b: Variation of magnetic minerals in surface sediments of Zuari Estuary during post-monsoon.

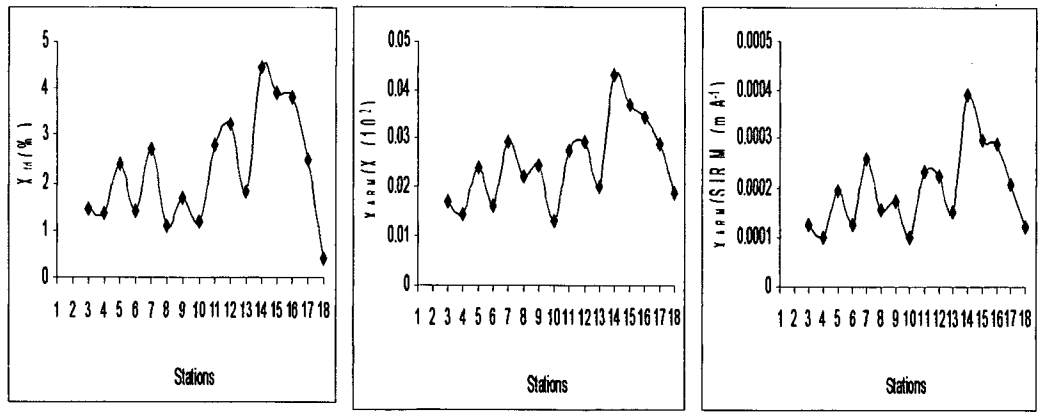


Fig. 4.18c: Variation of magnetic grain size in surface sediments of Zuari Estuary during post-monsoon.

station 9. Decrease in value is observed at station 10 which then increases at station 11 and subsequently decreases at station 12. Further downstream, an

increasing trend is observed from station 12 up to station 14 which then shows decreasing trend towards the mouth of the estuary with minor variations. The χ_{ARM} / χ and χ_{ARM} / SIRM also follow the distribution trend of χ_{fd}. Relatively higher values are observed at stations 12 and 14. During post-monsoon, χ shows a decreasing trend from station 3 up to station 7 with slightly higher value at station 6. It then shows an increasing trend up to station 10. The value decreases at station 11, then increases up to station 13 and then shows a general decreasing trend with slightly higher values at stations 15 and 17. χ_{ARM} shows a decreasing trend from station 3 up to station 8 with slightly higher value at station 6. Further downstream it shows an increasing trend up to station 13 with slightly lower value at station 11. Decreasing trend is observed towards the mouth region with minor fluctuations in between. In general, it follows trend similar to that of χ. Also, distribution pattern of SIRM is similar to that of χ, maintaining higher concentrations in the upstream end i.e. at stations 3 and 4 and also at stations 10 and 13.

Mineral dependent parameters viz. HIRM and IRM_S show distribution pattern similar to that of χ. S-ratio decreases from station 3 to 4. Further downstream, it shows an increasing trend up to station 9 with a slightly lower value at station 8. Further downstream, a decreasing trend is observed up to station 13 and then shows an alternate increasing and decreasing trend towards the mouth of the estuary.

χ_{fd}, χ_{ARM} / χ and χ_{ARM} / SIRM show similar distribution patterns maintaining relatively higher values in the lower half of the estuary that indicates finer magnetic grain size. In general, it shows an increasing trend from head up to station 14 and further downstream shows a decreasing trend with fluctuations in between.

c. Pre-monsoon

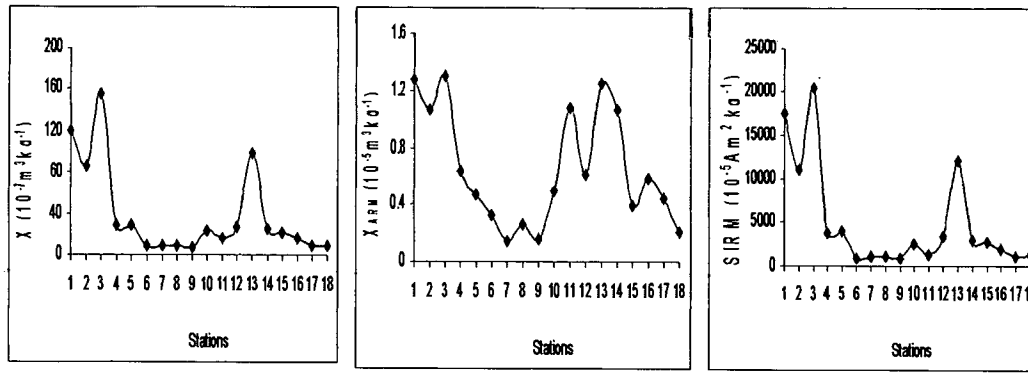


Fig. 4.19a: Variation of magnetic concentration in surface sediments of Zuari Estuary during pre-monsoon.

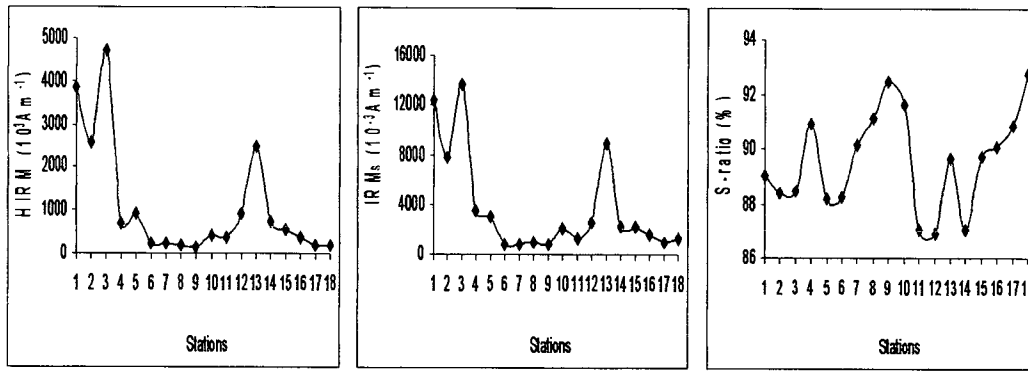


Fig. 4.19b: Variation of magnetic minerals in surface sediments of Zuari Estuary during pre-monsoon.

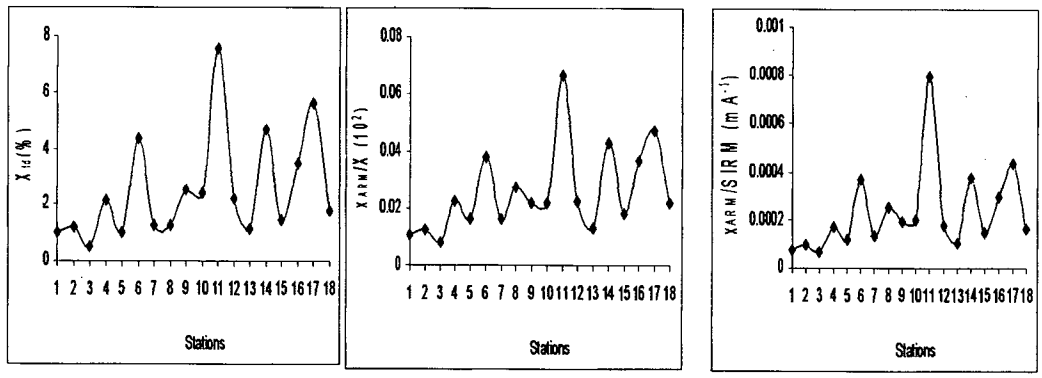


Fig. 4.19c: Variation of magnetic grain size in surface sediments of Zuari Estuary during pre-monsoon.

During pre-monsoon, χ decreases from station 1 to 2 and then increases at station 3. Further downstream, it shows a general decreasing trend up to

station 9 and then shows an increasing trend up to station 13. From here it again shows a decreasing trend towards the mouth. SIRM also shows a distribution pattern similar to that of χ. χ_{ARM} shows a decrease from station 1 to 2. An increase is observed at station 3 which further downstream shows a decreasing trend up to station 7. An increasing trend is observed from station 7 up to station 13 with low values at stations 9 and 12 and then a decreasing trend towards the downstream region with some fluctuations in between. Relatively higher concentration is observed at station 3.

Like in monsoon and post-monsoon, in pre-monsoon also HIRM and IRM_S show distribution patterns similar to that of χ. S-ratio shows a slight decrease from station 1 to 2. Further downstream the value increases up to station 4. A decrease is observed at station 5 and then an increasing trend is seen up to station 9. From here the value decreases up to station 11, which further downstream shows an increasing trend towards the mouth of the estuary with some variations. Lower value is observed at station 14.

χ_{fd}, χ_{ARM} / χ and χ_{ARM} / SIRM shows similar distribution pattern through out the estuary. In general, it shows an increasing trend from the head to the mouth of the estuary with fluctuations in between. Relatively higher peaks are observed at stations 4, 6, 12, 14 and 17 indicating presence of finer magnetic grain size at these stations.

4.5.2 Discussion

The release of material from industries and urban sources include high concentrations of magnetic particles, rich in both magnetite and haematite in varying proportions (Hunt, 1988). Once they are deposited in the estuarine environment they display distinctive magnetic properties such as magnetic enhancement (Thompson and Oldfield, 1986). Magnetic susceptibility is a measure of magnetic concentration which in combination with magnetic grain size and magnetic mineralogy parameters helps in understanding the environmental aspects. Some researchers have found good relationship between metals and certain magnetic properties such as magnetic

susceptibility (eg. Williams, 1991; Clifton et al., 1999; Chan et al., 2001; Urbat et al., 2004; Shilton et al., 2005; Zhang et al., 2007). In the present study, during monsoon, relatively higher concentrations are observed in the upper estuarine region in Zuari Estuary i.e. at stations 4 and 5 and also in the lower half of the estuary which includes stations 10 and 12. Also, grain size parameters show lower values at these stations indicating association of higher concentrations of mineral with the coarser grains, suggesting that the control is detrital as well as authigenic components (Sangode et al., 2001). Concentration dependent parameters such as χ, SIRM and χ_{ARM} are significantly correlated with Fe indicating anthropogenic origin and its association with coarser magnetic grains (Table 4.6). χ_{fd}, χ_{ARM} / χ and χ_{ARM} / SIRM along with χ_{ARM} show significant correlations with Mn, Zn, Co, Al and clay content indicating the role of both magnetic concentration and grain size in their association. HIRM and IRM_s show similar distribution pattern and follows the trend of χ indicating that both soft (magnetite like phase) and hard (haematite like phase) minerals are contributing to the sediment. From changes in S-ratio it is observed that high coercivity minerals such as haematite like minerals phases are dominating in the upper estuarine region i.e. between stations 1 to 8 and also between stations 11 and 14. Less haematite like minerals are dominating in other stations of lower estuarine region and also at station 9.

Table 4.6: Correlation between elements and the different magnetic parameters studied during monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al	Sand	Silt	Clay	OC
χ_{ARM}	0.82**	0.73**	-0.09	0.43	0.72**	0.68**	0.65**	-0.77**	0.49*	0.87**	0.91**
χ_{ARM}/SIRM	0.24	0.58*	-0.24	0.26	0.69**	0.69**	0.61**	-0.70**	0.37	0.87**	0.82**
χ_{Arm}/χ	0.20	0.50*	-0.30	0.24	0.70**	0.66**	0.62**	-0.72**	0.40	0.86**	0.81**
χ_{fd}	0.12	0.51*	-0.23	0.23	0.67**	0.67**	0.61**	-0.61**	0.31	0.77**	0.72**
χ	0.64**	0.28	0.38	0.20	-0.03	0.06	-0.10	0.12	-0.10	-0.10	0.01

** - correlation is significant at 0.01 level, * - correlation is significant at 0.05 level

During post-monsoon, magnetic susceptibility is observed to be lower wherever granulometric parameters are higher indicating its association with

coarser magnetic grains. The values of S-ratios are between 86 and 92 % indicating the presence of both haematite and magnetite like minerals. Concentration dependent parameters show significant correlation with Fe, Cr, Cu, and Zn. χ_{ARM} shows significant correlation with Mn and Al and also with silt and clay. Grain size parameters such as χ_{fd}, χ_{ARM} / χ and χ_{ARM} / SIRM do not show significant correlation with the metal concentrations indicating association of metals towards the coarser magnetic grains.

Table 4.7: Correlation between elements and the different magnetic parameters studied during post-monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al	Sand	Silt	Clay	OC
χ_{ARM}	0.91**	0.52*	0.78**	0.92**	0.92**	-0.04	0.74**	-0.66**	0.72**	0.53*	0.84**
χ_{ARM}/SIRM	0.02	0.27	-0.02	0.34	0.14	0.21	0.28	-0.57*	0.07	0.62**	0.48*
χ_{Arm}/χ	0.00	0.31	0.00	0.37	0.15	0.28	0.34	-0.61**	0.05	0.66**	0.50*
χ_{fd}	0.24	0.33	0.16	0.49	0.29	0.08	0.42	-0.63**	0.18	0.65**	0.58*
χ	0.77**	0.22	0.63**	0.53*	0.66**	-0.25	0.36	-0.15	0.53*	0.02	0.38

** - correlation is significant at 0.01 level, * - correlation is significant at 0.05 level

In case of pre-monsoon, relatively higher magnetic concentration is observed in the upper end of the estuary at stations 1, 2 and 3 and it seems to be due to anthropogenic input. But excluding the first three stations, when the upper estuary is compared with lower estuary, higher concentrations are observed in the lower half of the estuary especially between stations 10 and 14. The distribution of HIRM and IRM_S shows similar distribution pattern indicating presence of both haematite like and magnetite like minerals which are contributing to the sediment. S-ratio indicates relatively higher concentrations of haematite like minerals in the upstream end of the estuary and also between station 11 and 14. The distribution of granulometric parameters shows that they are dominating in the lower half of the estuary with fluctuating trend. Fe, Mn and Zn show significant correlation withχ, SIRM and χ_{ARM}. χ_{ARM} also shows significant correlation with Cu and clay. Granulometric parameters show significant correlation with clay and silt and also with Cu and Co.

Table 4.8: Correlation between elements and the different magnetic parameters studied during pre-monsoon.

	Fe	Mn	Cr	Cu	Zn	Co	Al	Sand	Silt	Clay	OC
χ_{ARM}	0.86**	0.70**	0.39	0.66**	0.76**	0.06	-0.27	-0.49*	0.36	0.51*	0.63**
χ_{ARM}/SIRM	-0.05	-0.02	0.23	0.57*	0.34	0.58*	0.15	-0.63	0.43	0.69**	0.48*
χ_{Arm}/χ	-0.11	-0.09	0.21	0.55*	0.23	0.55*	0.11	-0.63	0.47*	0.67**	0.48*
χ_{fd}	-0.05	-0.05	0.28	0.58*	0.30	0.58*	0.05	-0.65	0.48*	0.69**	0.49*
χ	0.71**	0.61**	0.18	0.17	0.50*	-0.19	-0.18	0.01	0.01	-0.02	0.18

** - correlation is significant at 0.01 level, * - correlation is significant at 0.05 level

Correlation analysis revealed that most of the studied metals display significant positive correlation with the χ_{ARM} in all the three seasons. χ_{ARM} in turn shows significant correlation with χ during post-monsoon and pre-monsoon seasons and to some extent during monsoon season. χ_{fd}, which is a measure of ultra-fined superparamagnetic grains, does not show significant correlation with metals in most of the cases indicating shift of metals towards the coarser grains. It is well established that the metals are in association with the iron oxides in the environment and the reduction of iron oxides have direct influence on the recycling of metals (Burdige, 1993). The strong correlation between χ_{ARM} and metals in most of the cases indicates the role of particle size and iron oxide played in the distribution of metals. Fine grains due to their high surface to volume ratio are more sensitive to the active portion of iron oxides. The grain size and hence the surface area, rather than degree of iron oxide crystallinity or structural form, impose a great influence on the kinetics and extent of iron oxide dissolution (Roden and Zachara, 1996; Haese et al., 1997). The finer grain is dissolved first due to high surface to volume ratio, which results in reduction of magnetic intensity as well as a shift in grain size towards the coarser end (Karlin and Levi, 1983). This can be seen from magnetic susceptibility plots where lower values of susceptibility coincides with increase in grain size (i.e χ_{fd}). The iron oxide dissolution in the present study is indicated by variation in concentration, grain size and mineralogy of magnetic minerals. The strong magnetic layer observed in all three seasons in the upper estuarine region could be due to moderate iron reduction with the

generation of fine-grained magnetite (Karlin et al., 1987). The distribution of most of the metals in the present study follows largely the pattern of Fe in the sediments, thus reduction of Fe oxides can be one of the factors in the distribution of metals in the sediment.

Although granulometric parameters such as χ_{fd}, χ_{ARM} / χ and χ_{ARM} / SIRM show significant correlation with fine size sediments i.e. clay, in most of the cases, these parameters did not show significant correlation with the metals. The significant correlation obtained between metals and magnetic parameters especially χ_{ARM} suggest that it can be used to evaluate the environmental significance. Significant correlation of χ_{ARM} with fine sediments (clay) and magnetic granulometric parameters suggest that χ_{ARM} can be used as grain size proxy for clay content in Zuari Estuary. χ_{ARM} is sensitive to single domain (SD, ~0.03 – 0.07 μm) ferromagnetic minerals (Maher, 1988). More recently Zhang et al. (2001) and Booth et al. (2005) suggested that χ_{ARM} can be a proxy for clay content. Zhang et al. (2007) used χ_{ARM} for normalizing heavy metal concentrations for particle size effects. The association of metals with fine-grained sediments is generally related to mineralogy, since clay minerals and iron oxides are the most important phases of sediments in which the metals are dominantly associated (Rae, 1997). The strong correlation of Fe with the magnetic susceptibility also indicates major role of iron oxides in controlling the distribution of other metals.

The increase in χ and SIRM and decrease in grain size parameters such as χ_{fd}, χ_{ARM}/χ and χ_{ARM}/SIRM reflects an increase in both total magnetic mineral concentrations and the relative importance of coarser magnetic grain size, i.e. pseudo-single domain (0.1μm) and multidomain (> 1.0 μm) especially during post-monsoon and pre-monsoon seasons as compared to monsoon season. In general, during monsoon season, most of the studied metals show significant and/or positive correlation with the grain size parameters and these in turn show significant correlation with the clay content, indicating the role of finer sediments in the distribution of metals in this season. In case of post-monsoon season, although the metals exhibit significant correlation with the

clay content, they did not show significant correlation with magnetic grain size. Also during pre-monsoon season, most of the metals did not show significant correlation with the finer size of the sediment indicating shift of minerals towards the coarser grains in these two seasons. This indicates that hydrodynamic conditions prevailing during these two seasons facilitates shift of minerals towards coarser size due to dissolution of finer size minerals. It is important to note here that during these seasons geochemical changes leading to remobilization and concentration of metals has taken place. Similar distribution pattern of magnetic minerals such as magnetite and haematite in all the three seasons suggest that they are from the same source, probably of anthropogenic origin. Combined with the higher SIRM, the increased importance of the hardest remanence component (HIRM) points to an increase in 'haematite' in both relative and absolute terms.

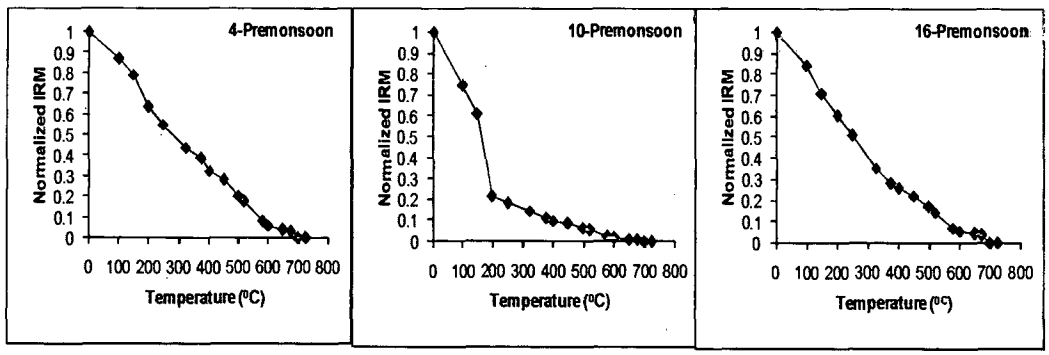


Fig. 4.20: Thermal demagnetization curves for pre-monsoon season.

Changes in magnetic properties under conditions of varying temperatures or magnetic fields provide information on type of minerals present and on their particle size (Laj et al., 2000; Deng et al., 2000). The thermal demagnetization curves for three selected sediment samples for pre-monsoon season show similar curves, wherein the IRM undergoes a monotonic decay until their unblocking at ~ 680 ^{0}C, that is indicative of the presence of haematite (Fig. 4.20). Also, curve of temperature dependence of magnetic susceptibility confirmed that haematite like minerals are dominating in the estuary (Fig. 4.21).

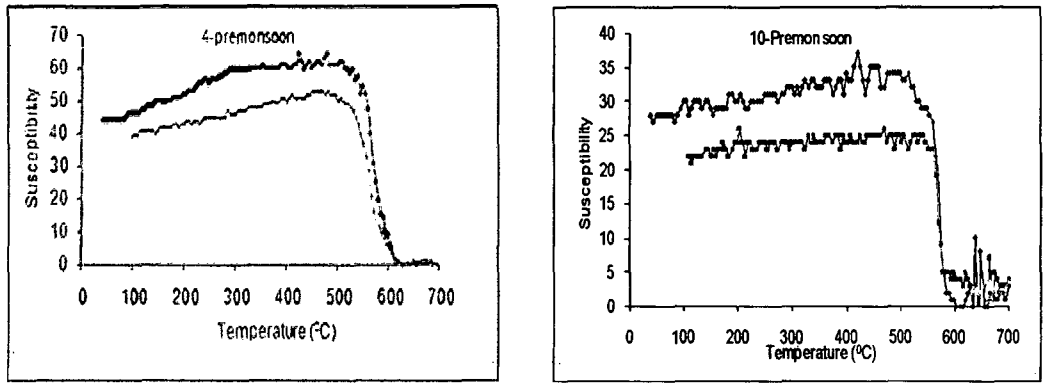


Fig. 4.21: Curve of temperature dependence of magnetic susceptibility.

The dominance of haematite in the Zuari estuarine sediments suggest that it is of anthropogenic source, possibly from iron ore which mainly consists of haematite along with minor quantity of magnetite.

4.6 Relation Between Suspended Sediments and Bed-Load Sediments

The processes that control the metal distribution in estuaries depend on their physical and geochemical characteristics. Significant seasonal and spatial variations of metals in TSM (surface and bottom) and bed load (surface sediments) were observed in the Zuari Estuary. The seasonal distribution indicates a relatively higher concentration of most of the metals in suspended sediments during post-monsoon season and in bed load sediments during pre-monsoon season. The sediments brought during monsoon season from catchment area were possibly retained in suspension during post-monsoon and slowly settled through the water column during post-monsoon and pre-monsoon seasons.

In order to understand the probable source and processes involved in the distribution of various studied parameters and to understand factors controlling the distribution of metals in the Zuari Estuary, with respect to land and marine sources, estuary was divided into two halves i.e. upper estuary

(head to station 10) and lower estuary (11 to 18). Data from the two regions were subjected for correlation analysis separately during the three seasons.

Monsoon: In upper estuarine region, both surface and bottom TSM are not significantly correlated with sand, silt, clay and organic carbon. Although, clay shows weak positive correlation with the metal concentrations in TSM, χ_{fd}, indicative of magnetic grain size, shows significant or relatively good correlation with most of the metals in both surface and bottom TSM. In general significant correlation ($p < 0.05$) is obtained between few metals in TSM (Fe, Mn, Al, Co) and TSM indicating metal content is dependent on the TSM concentration in this season. The metals in surface and bottom TSM are poorly correlated with the metal in the surface sediments (bed load). No significant correlation is observed for metals in both surface sediments and TSM with sand, silt, clay and organic carbon, except for Co (surface sediments and bottom TSM) which displays significant correlation with clay content. Fe in surface sediments exhibits significant correlation with χ ($r = 0.98$, $p < 0.05$) while other elements are positively correlated with χ except for Zn which displays negative correlation.

Similar to upper estuary, surface and bottom TSM concentration did not show significant correlation with sand, silt, clay and organic carbon in lower estuarine region during monsoon season. Among these, TSM concentration exhibits comparatively good correlation with silt content. Metals in both surface and bottom TSM exhibit weak correlation with their respective concentrations. While most of the metals in surface TSM exhibit significant positive correlation with clay, organic carbon and χ_{fd}, metals in bottom TSM display negative or weak positive correlation. Also, metals in surface sediments are significantly ($p < 0.05$; $p < 0.1$) correlated with each other and in turn show significant correlation with clay and organic carbon except for Cr which is negatively correlated. Metals in surface sediments do not exhibit significant correlation with χ but are positively correlated. Cr in surface TSM exhibits significant correlation with Fe ($r = 0.75$), Mn ($r = 0.90$), Zn ($r = 0.90$), Co ($r = 0.85$), clay ($r = 0.86$), organic carbon ($r = 0.85$), χ_{fd} ($r = 0.95$) and also

to some extent with Cu (r = 0.50) in surface sediments. Significant or weak positive correlation is also observed for Zn in surface TSM with most of the metals in the surface sediments.

Post-monsoon: In the upper estuary, surface TSM exhibits significant correlation (r = 0.60, p < 0.1) with clay and silt. Similar pattern is also seen for bottom TSM wherein it exhibits significant correlation with clay (r = 0.71; p < 0.05) and silt (r = 0.65, p < 0.1). Most of the metals in both surface and bottom TSM are significantly correlated with their respective TSM concentration, except for Co in bottom TSM which is negatively correlated with the TSM concentration. Significant correlation is also observed for most of the metals in TSM with clay content. Most of the metals in TSM and surface sediments did not show significant correlation with each other. But it is noted that most of the metals in surface sediments viz. Fe (r = 0.83), Cr (r = 0.84), Cu (r = 0.80) and Zn (r = 0.80) exhibits significant correlation (p < 0.05) with Co in bottom TSM. Metals in surface sediments do not exhibit significant correlation with either silt or clay content although they exhibit positive correlations, while organic carbon exhibits comparatively good correlations with the metals. Most of the metals except for Mn and Co in surface sediments are significantly correlated with Fe. χ displays significant correlation with most of the metals in this region, Fe (r = 0.96), Cu (r = 0.81), Zn (r = 0.86) and also to some extent with Cr (r = 0.61).

In the lower estuary, both surface and bottom TSM concentration display significant correlation (p < 0.05) with organic carbon (r = 0.72; 0.70) and χ_{fd} (r = 0.83; 0.74) respectively and weak positive correlation with silt and clay. Metals in surface TSM exhibit significant correlation (p < 0.05) with TSM concentration. This relationship also agrees with some metals in bottom TSM with its concentration. In general, metals in TSM display weak correlation with the clay content, while they exhibit good correlation with silt and χ_{fd}. Most of the metals in both surface and bottom TSM exhibit significant correlation with metals in surface sediments. Metals in surface sediments are significantly correlated with each other except for Co and these metals also exhibit

significant correlation with silt and organic carbon and weak positive correlation with clay and χ_{fd}. Significant and / or weak positive correlation is also observed between metals in surface sediments and TSM concentration. χ shows significant correlation with most of the metals in sediments in this region but the relationship is relatively weak.

Pre-monsoon: In upper estuarine region, both surface and bottom TSM concentration do not show significant correlation with silt and clay. Fe, Co and Al in bottom TSM, exhibit significant correlation with bottom TSM concentration. Most of the metals in surface sediments are not significantly correlated with silt and clay. But they show significant correlation with theχ.

Even in the lower estuary surface and bottom TSM concentration did not show significant correlation with silt and clay. Most of the metals in bottom TSM show significant and / or positive correlation with bottom TSM concentration viz. Fe (r = 0.96), Mn (r = 0.75), Cr (r = 0.52), Cu (r = 0.91), Zn (r = 0.91), Co (r = 0.56) and Al (r = 0.97). Most of the metals in surface sediments are significantly correlated with each other which in turn are significantly and / or positively correlated with clay and organic carbon. In this season, although most of the metals in surface sediments did not show significant correlation with metals in both surface and bottom TSM, these metals showed comparatively good correlation with the metals in the surface TSM than in bottom TSM. Metals in surface sediments did not display significant correlation with χ in this region.

From the correlation analysis it can be concluded that the distribution pattern of metals in the TSM can be compared with some of the sediment component of the surface sediments although it doesn't fully agree with the obtained data. Since the estuary is dynamic, several other factors like resuspension, mobilization, flocculation, adsorption, desorption, industrial discharges etc. count in distribution pattern of TSM and its associated metals. The combinations of these factors make the elemental chemistry very complex in the estuarine environment.

During monsoon season, metals in surface and bottom TSM show significant and / or weak positive correlation with their respective TSM concentrations in the upper estuary, while in lower estuary they exhibit poor correlation. This indicates that salinity must have played role in desorbing the metals from suspended matter in the lower estuarine region. Desorption of metals from suspended matter in the higher salinity region has also been observed by many researchers (Jouanneau et al., 1983; Zwolsman et al., 1997). During monsoon estuary behaves like a salt-wedge and therefore stratification occurs maintaining low salinity in surface waters and comparatively very high salinity in bottom waters especially in lower estuarine region which facilitates desorption of metals from suspended matter. It is interesting to note that the metals in surface and bottom TSM are poorly correlated with metals in surface sediments especially in upper estuarine region during monsoon season. This can be attributable to the high river discharge due to which materials are transported further into the lower estuary rather than settling in the bed load sediments. This must have led to differences in the distribution pattern of metals in TSM and surface sediments. Comparatively better correlation is obtained between metals in surface sediments and metals in surface TSM in the lower estuarine region. The relative difference in distribution of metals essentially depends on the variation in the river flow which brings the material into the estuary. Similar observations are also made by Helz and Sinex (1986) and Balls (1990).

In post-monsoon, metals in surface and bottom TSM are significantly and / or positively correlated with TSM concentration in upper estuarine region while in lower estuary metals in both surface and bottom TSM are not significantly correlated with the respective concentration. Salinity can be a factor in desorption of metals in lower estuarine region as discussed for the monsoon season. Correlation analysis indicated partial role of grain size in distribution of metals in the upper and lower part of the estuary. In lower estuary, both finer sediments and organic carbon played a major role in retaining metals in surface sediments while in upper estuary, organic carbon must have played role in distribution of metals rather than particle size. Most of the metals display comparatively good correlation with χ in upper estuary as well as in

lower estuary indicating their anthropogenic input. This relationship is more significant in upper estuarine region than in lower part of the estuary. The relationship between metals in both surface and bottom TSM is comparatively good in this season and is much better in the lower estuarine region. During this season hydrodynamic conditions are relatively less violent due to reduced rate of flow and the lower estuarine region becomes relatively calm. Thus the materials try to settle down and get deposited in the bed sediments. A distinct pattern of distribution of metals is observed during this season in case of both surface and bottom TSM wherein higher concentrations are observed in the lower half of the estuary, roughly between stations 10 and 16. Interestingly, higher concentrations of metals are also seen in the surface sediments in this zone. This region is also enriched with the clay, silt and organic carbon. The flocculation process which generally leads to settling of finer particles must have facilitated sedimentation at this region. This can be seen from relatively higher concentration of metals in the bottom TSM than in surface TSM. Flocculation process in this region is seen from the SEM photographs.

During pre-monsoon, most of the metals in surface sediments as well as in TSM do not show significant correlation with the clay and silt in the upper estuary, whereas in the lower estuary, most of the metals in surface sediments exhibit significant correlation with clay and organic carbon indicating that the concentration of metals in lower estuarine region is largely controlled by amount of finer sediments and organic matter present in the region. Significant correlation obtained between most of the metals and χ indicates their anthropogenic origin. Large variation in metal concentrations in both surface and bottom TSM are observed throughout the estuary during this season. Several peaks obtained for TSM in the estuarine region reflect repeated resuspension of the sediments. Three major peaks were observed wherein metal concentrations were also found to be higher, especially in case of bottom TSM. Sediment resuspension mainly depends on the hydrodynamic conditions and is dominated in shallow waters due to waves, tides and wind induced currents which are more prominent in this season due to high tidal activity or by local anthropogenic activities such as barge traffic. In surface

sediments metal concentration are observed to be higher in upper estuary and also in the upper half of the lower estuary with decreasing trend towards the mouth. Changes in sediment chemistry (TSM and surface sediments) can be induced by the seabed disturbance and particle in the surrounding water which result in remobilization of metals via desorption or transformation (Eggleton and Thomas, 2004).

Chapter V

SPECIATION OF METALS

5.1 Introduction

Sediments being important reservoirs of metals, accumulation of metal contaminants over the time, in sediments can pose serious environmental problems. Although, total metal concentration in surface sediment is a valuable index of environmental contamination, it is less useful in assessing the sources and pathways. Distribution of species may provide better information on pathways. Metals exist in different forms and selected species of metals get accumulated in the food chain affecting the life cycle of various aquatic organisms and become hazardous. Thus, knowledge on metal speciation in the sedimentary environment is important for hazard assessment studies (Barona et al., 1999; Filgueiras et al., 2004).

Chemical speciation is defined as the identification and quantification of the different species, forms or phases present in a material. The speciation aims at understanding the distribution of a metal over the various sedimentary substrates / phases such as carbonates, iron and manganese oxyhydroxides, organic matter, sulfides, silicates, etc. The principle of this procedure is based on the selective extraction of heavy metals in different physico-chemical fractions of a material using specific solvents. Considerable interest exists in determining the chemical speciation of metals in sediments, since the mobility of trace metals, along with their bioavailability and related ecotoxicity to plants, critically depends upon the chemical form in which a metal is present in the sediment (Davidson et al., 1994). Changing environmental conditions, either natural or anthropogenically induced can strongly influence the behaviour of both essential and toxic elements by altering the forms in which they occur. Some of the important factors which influence chemical speciation include sediment particle-size distribution, organic matter content, salinity, pH and redox potential (Song et al., 1999; Dollar et al., 2001). Since the bioavailability is related to solubility, metal bioavailability decreases in the order: exchangeable > carbonate > Fe–Mn oxide > organic > residual (Tessier et al., 1979; Ma and Rao, 1997). Therefore, residual fraction could be considered as an inert phase corresponding to the part

of metal that cannot be mobilised or not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature (Tessier et al., 1979). A large number of sequential extraction schemes have been designed for the determination of chemical forms of metals in sediments and increasingly used over the last 10 years (Quevauviller et al., 1994; Lima et al., 2001). As mentioned earlier sequential extraction scheme proposed by Tessier et al. (1979) has been applied to evaluate the metal bound to different phases of sediment in the present study. This is one of the widely accepted and thoroughly researched procedures that involves following five-stage extraction steps viz. i) exchangeable, ii) carbonate bound, iii) Fe-Mn oxide, iv) organic bound and v) residual. The procedure involved and the importance of each phase / fraction is provided in detail in chapter 2.

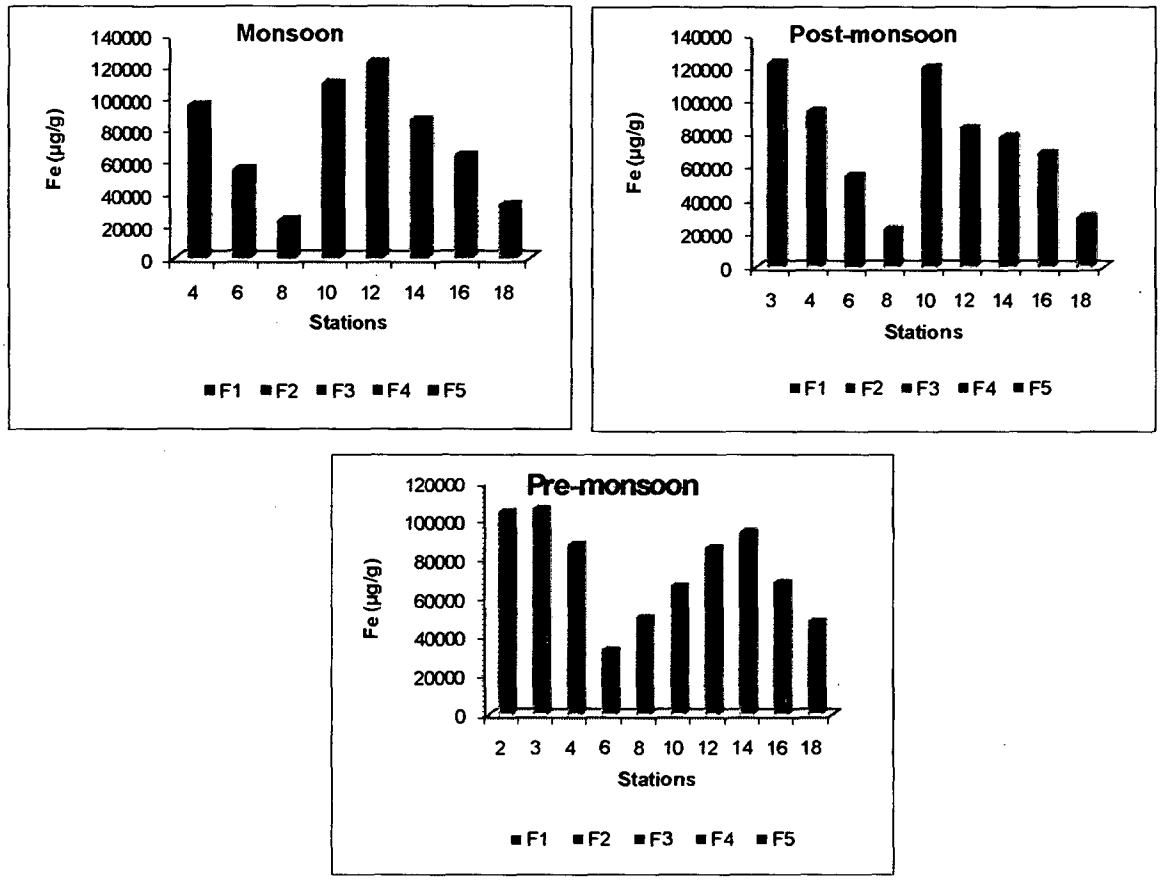
5.2 Results

5.2.1 Metal Speciation

The distribution of six metals viz. Fe, Mn, Cu, Zn, Cr and Co in different fractions of surface sediments of Zuari Estuary is diagrammatically represented in the figures (Fig. 5.1 to 5.6) and is discussed in this chapter.

a. Iron (Fe)

Major quantity of Fe is found to be associated with residual fraction and the least with the exchangeable fraction in all the three seasons (Fig. 5.1). The residual Fe ranges from 21888 to 110500 µg/g (Avg. 68442), 15900 to 120225 µg/g (Avg. 68368) and 27775 to 98513 µg/g (Avg. 67478) during monsoon, post-monsoon and pre-monsoon seasons respectively. Large amount of Fe is available in the residual fraction, probably because it is one of the most common elements in the earth's crust. The present results are in good agreement with the data reported by Usero et al. (1998) and Yuan et al. (2004). They have reported more than 89 % of the total Fe in the residual fraction.



F1: Exchangeable, F2: Carbonate, F3: Fe-Mn oxide, F4: Organic bound, F5: Residual

Fig. 5.1: Extractable contents of Fe in surface sediments of Zuari Estuary using Tessier sequential extraction protocol.

Next to residual fraction, Fe is mainly bound to Fe-Mn oxides fraction in the present study, which ranges from 1821 to 10704 µg/g (Avg. 4936), 2733 to 11501 µg/g (Avg. 5927) and 3860 to 9660 µg/g (Avg. 6003) during respective seasons. On an average, Fe accounts for 8 % in this fraction. Fe concentration in exchangeable fraction ranges from 1 to 10 µg/g (Avg. 3), 1 to 4 µg/g (Avg. 3) and 2 to 18 µg/g (Avg. 8) during respective seasons. Organic bound Fe (µg/g) is found to be comparatively higher during post-monsoon season (Avg. 1077) followed by pre-monsoon (Avg. 1047) and monsoon season (Avg. 984). On the other hand, Fe (µg/g) in carbonate fraction is observed to be higher during post-monsoon season (Avg. 53) followed by monsoon (Avg. 41) and pre-monsoon (Avg. 28). In general, the distribution of exchangeable, carbonate bound and

organic bound Fe is less throughout the estuary in all the three seasons. However, organic bound Fe is relatively higher in the lower half of the estuary and also at two stations in the upper estuary during pre-monsoon season.

Residual Fe is observed to be higher at the extreme end of the upper estuary, from there it decreases up to station 8, and then it increases in the lower estuary, and subsequently decreases towards the mouth of the estuary in all the three seasons. Correlation between metals, sand, silt, clay and organic carbon with five different fractions of surface sediments for three different seasons is presented in the tables (Table 5.1 to 5.3).

Table 5.1: Correlation between metals, sand, silt, clay and organic carbon (OC) in different fractions of the surface sediments of Zuari Estuary for monsoon season.

Exchangeable

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	0.655	1.000								
Cu	0.675	**0.831**	1.000							
Zn	0.122	0.362	0.056	1.000						
Cr	0.037	0.547	0.359	-0.240	1.000					
Co	0.567	0.439	0.326	0.147	0.342	1.000				
Sand	-0.681	-0.696	-0.408	-0.189	-0.476	-0.557	1.000			
Silt	0.340	0.286	0.008	0.040	0.382	0.530	**-0.853**	1.000		
Clay	**0.820**	**0.898**	0.679	0.279	0.435	0.463	**-0.866**	0.477	1.000	
OC	**0.829**	**0.858**	0.656	0.286	0.334	0.356	**-0.827**	0.420	**0.989**	1.000

Carbonate

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	-0.130	1.000								
Cu	0.279	0.559	1.000							
Zn	-0.163	**0.910**	0.495	1.000						
Cr	-0.220	-0.516	-0.178	**-0.761**	1.000					
Co	0.310	0.621	**0.743**	**0.740**	-0.659	1.000				
Sand	0.364	**-0.782**	-0.182	**-0.893**	0.668	-0.611	1.000			
Silt	-0.242	0.493	0.068	0.607	-0.453	0.580	**-0.853**	1.000		
Clay	-0.381	**0.844**	0.241	**0.921**	-0.689	0.473	**-0.866**	0.477	1.000	
OC	-0.367	**0.841**	0.237	**0.886**	-0.638	0.436	**-0.827**	0.420	**0.989**	1.000

Table. 5.1 (continued).

Fe-Mn oxide

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	0.153	1.000								
Cu	0.219	0.436	1.000							
Zn	0.681	0.326	**0.840**	1.000						
Cr	0.200	0.652	0.509	0.502	1.000					
Co	0.525	**0.748**	0.629	**0.745**	**0.816**	1.000				
Sand	-0.390	-0.317	**-0.969**	**-0.926**	-0.496	-0.646	1.000			
Silt	0.427	0.041	**0.796**	**0.789**	0.305	0.339	**-0.853**	1.000		
Clay	0.248	0.493	**0.869**	**0.802**	0.543	**0.762**	**-0.866**	0.477	1.000	
OC	0.270	0.609	**0.841**	**0.780**	0.606	**0.832**	**-0.827**	0.420	**0.989**	1.000

Organic bound

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	**0.967**	1.000								
Cu	0.660	**0.744**	1.000							
Zn	0.439	0.508	**0.851**	1.000						
Cr	**0.909**	**0.946**	0.697	0.562	1.000					
Co	**0.807**	**0.730**	0.531	0.263	0.558	1.000				
Sand	**-0.833**	**-0.783**	-0.494	-0.315	-0.645	**-0.941**	1.000			
Silt	0.436	0.400	0.198	0.032	0.199	**0.808**	**-0.853**	1.000		
Clay	**0.984**	**0.935**	0.641	0.498	**0.894**	**0.809**	**-0.866**	0.477	1.000	
OC	**0.973**	**0.955**	**0.725**	0.602	**0.933**	**0.759**	**-0.827**	0.420	**0.989**	1.000

Residual

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	-0.409	1.000								
Cu	0.615	-0.312	1.000							
Zn	0.446	-0.176	0.497	1.000						
Cr	0.310	0.622	-0.112	-0.230	1.000					
Co	0.688	0.056	0.012	0.262	0.621	1.000				
Sand	-0.257	-0.357	-0.192	**-0.723**	-0.237	-0.551	1.000			
Silt	0.106	0.661	-0.149	0.399	0.552	0.636	**-0.853**	1.000		
Clay	0.330	-0.031	0.465	**0.834**	-0.129	0.318	**-0.866**	0.477	1.000	
OC	0.442	-0.107	0.546	**0.821**	-0.095	0.364	**-0.827**	0.420	**0.989**	1.000

Bold figures are statistically significant at $p < 0.05$, $n = 8$.

Table 5.2: Correlation between metals, sand, silt, clay and organic carbon (OC) in different fractions of the surface sediments of Zuari Estuary for post-monsoon season.

Exchangeable

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	-0.363	1.000								
Cu	0.018	0.156	1.000							
Zn	-0.316	**0.899**	-0.216	1.000						
Cr	0.477	0.268	-0.240	0.418	1.000					
Co	0.357	-0.527	0.230	**-0.685**	-0.459	1.000				
Sand	-0.044	0.135	**-0.809**	0.480	0.380	-0.560	1.000			
Silt	-0.016	0.353	0.323	0.071	0.055	0.356	-0.536	1.000		
Clay	0.053	-0.248	**0.817**	-0.557	-0.441	0.529	**-0.973**	0.326	1.000	
OC	-0.169	0.250	**0.805**	-0.095	-0.179	0.217	**-0.900**	0.642	**0.832**	1.000

Carbonate

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	0.511	1.000								
Cu	-0.198	-0.232	1.000							
Zn	-0.315	-0.438	0.041	1.000						
Cr	0.437	-0.068	0.085	-0.254	1.000					
Co	0.371	**0.781**	-0.277	-0.221	0.230	1.000				
Sand	-0.353	**-0.856**	0.016	0.576	-0.195	**-0.826**	1.000			
Silt	0.401	**0.821**	-0.404	-0.429	-0.156	0.549	-0.536	1.000		
Clay	0.285	**0.733**	0.092	-0.527	-0.261	**0.774**	**-0.973**	0.326	1.000	
OC	0.361	**0.864**	-0.019	-0.415	-0.019	**0.741**	**-0.900**	0.642	**0.832**	1.000

Fe-Mn oxide

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	**0.690**	1.000								
Cu	0.329	0.399	1.000							
Zn	**0.703**	0.439	**0.789**	1.000						
Cr	-0.202	-0.088	**0.732**	0.534	1.000					
Co	**0.770**	**0.762**	0.409	0.585	-0.092	1.000				
Sand	-0.362	0.047	0.125	-0.191	0.285	-0.577	1.000			
Silt	0.575	0.435	0.368	**0.677**	0.248	**0.744**	-0.536	1.000		
Clay	0.248	-0.172	-0.241	0.029	-0.387	0.442	**-0.973**	0.326	1.000	
OC	0.248	-0.069	0.135	0.383	0.128	0.556	**-0.900**	0.642	**0.832**	1.000

Table 5.2 (continued).

Organic bound

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	**0.847**	1.000								
Cu	**0.682**	0.544	1.000							
Zn	**0.717**	0.555	**0.948**	1.000						
Cr	**0.713**	**0.672**	0.276	0.199	1.000					
Co	**0.846**	**0.820**	0.532	0.568	0.502	1.000				
Sand	**-0.691**	-0.578	**-0.809**	**-0.846**	-0.153	**-0.806**	1.000			
Silt	0.395	0.358	**0.875**	**0.817**	0.103	0.191	-0.536	1.000		
Clay	**0.665**	0.550	**0.666**	**0.724**	0.143	**0.850**	**-0.973**	0.326	1.000	
OC	**0.684**	0.624	**0.824**	**0.809**	0.369	**0.764**	**-0.900**	0.642	**0.832**	1.000

Residual

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	-0.078	1.000								
Cu	**0.713**	0.282	1.000							
Zn	**0.775**	0.249	**0.688**	1.000						
Cr	**0.834**	0.236	**0.739**	0.534	1.000					
Co	0.022	0.234	0.615	0.037	0.293	1.000				
Sand	-0.105	-0.019	-0.475	-0.311	0.156	-0.325	1.000			
Silt	0.372	0.097	0.291	0.471	0.053	-0.370	-0.536	1.000		
Clay	0.015	-0.006	0.452	0.219	-0.189	0.465	**-0.973**	0.326	1.000	
OC	0.434	0.191	**0.751**	0.557	0.242	0.379	**-0.900**	0.642	**0.832**	1.000

Bold figures are statistically significant at $p < 0.05$, $n = 9$.

Table 5.3: Correlation between metals, sand, silt, clay and organic carbon (OC) in different fractions of the surface sediments of Zuari Estuary for pre-monsoon season.

Exchangeable

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	0.514	1.000								
Cu	**-0.389**	-0.576	1.000							
Zn	0.543	**0.828**	-0.240	1.000						
Cr	-0.030	-0.185	0.521	-0.021	1.000					
Co	0.363	0.274	0.417	0.622	0.522	1.000				
Sand	0.129	-0.051	-0.146	-0.191	-0.589	-0.448	1.000			
Silt	0.066	0.141	-0.128	0.397	0.273	0.324	**-0.793**	1.000		
Clay	-0.233	-0.022	0.299	0.006	**0.669**	0.428	**-0.910**	0.469	1.000	
OC	0.128	-0.003	0.169	0.162	0.496	0.529	**-0.801**	0.534	**0.789**	1.000

Table 5.3 (continued).

Carbonate

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	0.626	1.000								
Cu	**0.954**	0.509	1.000							
Zn	**0.797**	0.621	**0.753**	1.000						
Cr	0.616	**0.701**	0.512	**0.831**	1.000					
Co	**0.780**	0.487	**0.724**	**0.676**	0.473	1.000				
Sand	-0.220	-0.434	-0.174	-0.342	-0.207	-0.211	1.000			
Silt	0.442	**0.664**	0.489	0.558	0.373	0.425	**-0.793**	1.000		
Clay	0.017	0.176	-0.081	0.115	0.046	0.016	**-0.910**	0.469	1.000	
OC	-0.208	0.274	-0.291	0.144	0.228	0.013	**-0.801**	0.534	**0.789**	1.000

Fe-Mn oxide

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	**0.769**	1.000								
Cu	0.565	0.481	1.000							
Zn	**0.836**	**0.671**	0.535	1.000						
Cr	0.484	0.580	0.223	0.124	1.000					
Co	0.501	0.427	0.422	0.631	-0.049	1.000				
Sand	-0.485	-0.095	-0.174	**-0.714**	0.168	-0.467	1.000			
Silt	0.553	0.089	0.489	**0.719**	-0.366	0.559	**-0.793**	1.000		
Clay	0.326	0.076	-0.081	0.545	0.005	0.297	**-0.910**	0.469	1.000	
OC	0.271	-0.056	-0.291	0.542	-0.244	0.189	**-0.801**	0.534	**0.789**	1.000

Organic bound

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	**0.686**	1.000								
Cu	**0.759**	**0.781**	1.000							
Zn	**0.721**	**0.688**	**0.929**	1.000						
Cr	0.188	0.389	0.245	0.292	1.000					
Co	-0.007	-0.425	-0.329	-0.150	-0.564	1.000				
Sand	**-0.850**	-0.436	**-0.652**	**-0.708**	-0.406	0.066	1.000			
Silt	0.629	0.368	**0.714**	**0.747**	0.323	-0.039	**-0.793**	1.000		
Clay	**0.805**	0.382	0.459	0.518	0.368	-0.069	**-0.910**	0.469	1.000	
OC	**0.767**	0.306	0.499	0.509	0.260	-0.170	**-0.801**	0.534	**0.789**	1.000

Table 5.3 (continued).

Residual

	Fe	Mn	Cu	Zn	Cr	Co	Sand	Silt	Clay	OC
Fe	1.000									
Mn	**0.759**	1.000								
Cu	0.574	0.601	1.000							
Zn	**0.843**	0.522	0.530	1.000						
Cr	-0.010	-0.216	-0.114	-0.069	1.000					
Co	0.475	0.525	**0.776**	0.380	-0.413	1.000				
Sand	-0.519	**-0.887**	-0.582	-0.314	0.294	-0.521	1.000			
Silt	0.422	**0.677**	0.120	0.122	-0.366	0.373	**-0.793**	1.000		
Clay	0.465	**0.825**	**0.762**	0.372	-0.177	0.502	**-0.910**	0.469	1.000	
OC	0.482	**0.740**	**0.775**	0.388	-0.427	**0.784**	**-0.801**	0.534	**0.789**	1.000

Bold figures are statistically significant at $p < 0.05$, $n = 10$.

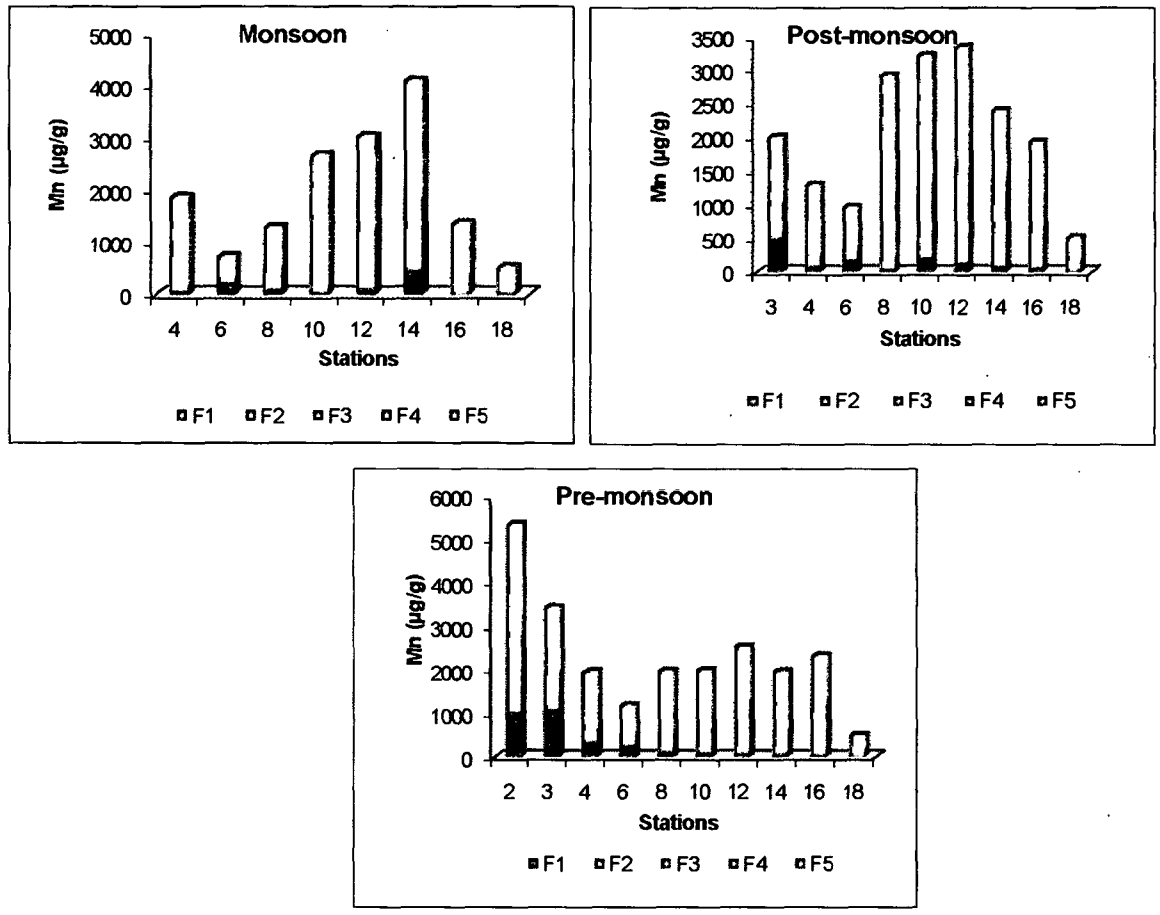
While describing the relations, "Significant" word is used for the values that are statistically significant ($p<0.05$) and are made bold in the tables and "Good" word is used for the values for which $p \leq 0.1$. During monsoon, correlation obtained between different metals, sand, silt and clay in five fractions indicate good correlation of Fe with Mn, Cu and Co and significant correlation with clay and organic carbon in exchangeable fraction (Table 5.1). Fe does not show any significant correlation with metals or with sand, silt and clay in carbonate bound fraction. It shows a good correlation with Zn and Co in the Fe-Mn oxide fraction and in organic bound, it shows a significant correlation with Mn, Cr, Co, clay and organic carbon and a good correlation with Cu. It also shows a good correlation with Cu and Co in the residual fraction. In case of post-monsoon season, Fe does not show significant correlation with most of the metals in the exchangeable and carbonate bound fractions but shows a good correlation with Cr in exchangeable fraction and with Mn in carbonate fraction (Table 5.2). It displays significant correlation with Mn, Zn, Co and good correlation with silt in Fe-Mn oxide bound fraction. Fe exhibits significant correlations with Mn, Cu, Zn, Cr, Co, clay and organic carbon in organic bound fraction. It also shows a significant correlation with Cu, Zn and Cr in residual fraction. During pre-monsoon, Fe show good correlation with Mn and Zn in the exchangeable fraction and significant

correlation with Cu, Zn and Co and good correlation with Mn and Cr in carbonate fraction. In Fe-Mn oxide fraction, it exhibits significant correlation with Mn and Zn and good correlation with Cu, Cr, Co and silt. Fe shows a significant correlation with Mn, Cu, Zn, clay, organic carbon (OC) and good correlation with silt in organic bound fraction. It shows a significant negative correlation with sand in the same fraction. In the residual fraction, it exhibits significant correlation with Mn and Zn and good correlation with Cu, Co, clay and organic carbon (Table 5.3).

Strong relationship between iron and other elements can be due to the high adsorption capacity of its oxide which has been already reported earlier by Algan et al. (2004) and Niencheski et al. (2002). The distribution of Fe in residual fraction during all the three seasons largely agrees with the distribution of total Fe metal content in the surface sediments representing higher concentration in the lower estuary between stations 10 to 14 and also in the upstream end of upper estuary. Its significant correlation with finer sediments, organic carbon and metals viz. Mn, Cr, Co, Cu and Zn during all the seasons in organic fraction indicates their strong association in the sediments.

b. Manganese (Mn)

Significant amount of Mn is available in the bioavailable phases (exchangeable, carbonate bound and Fe-Mn oxide) in all the three seasons (Fig. 5.2). The level of Mn is found to be higher in Fe-Mn oxide bound fraction in all the three seasons and the concentration ranges from 89 to 2333 µg/g (Avg. 996), 96 to 2223 µg/g (Avg. 953) and 119 to 2064 µg/g (Avg. 959) during monsoon, post-monsoon and pre-monsoon respectively. On an average Mn is recorded to be around 40 % in this fraction in all the three seasons. The next important phase is the carbonate bound in which Mn ranges from 84 to 1410 µg/g (Avg. 485) during monsoon, 167 to 1434 µg/g (Avg. 639) during post-monsoon and 183 to 1799 µg/g (Avg. 749) during pre-monsoon season. It accounts for 22 % during monsoon, 29 % during post-monsoon and 31 % during pre-monsoon season in this fraction.



F1: Exchangeable, F2: Carbonate, F3: Fe-Mn oxide, F4: Organic bound, F5: Residual

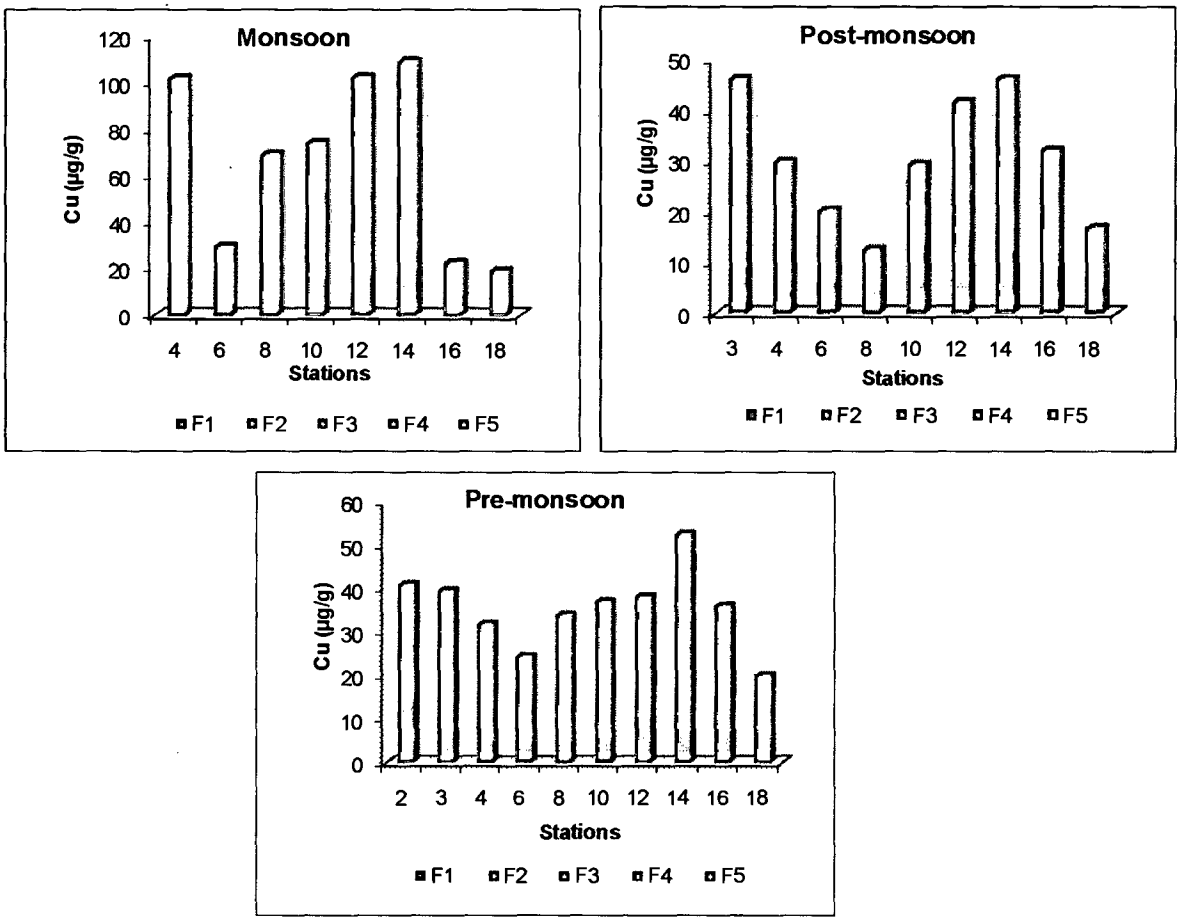
Fig. 5.2: Extractable contents of Mn in surface sediments of Zuari Estuary using Tessier sequential extraction protocol.

The higher level of Mn in this fraction is most likely due to the similarity in ionic radii to that of calcium that allows them to substitute for calcium in carbonate phase (Pederson and Price, 1982; Zhang et al., 1988). Significant amount of Mn is also available in the exchangeable fraction especially during pre-monsoon season, which ranges from 25 to 1122 µg/g (Avg. 343). Tessier et al. (1979) and Jingchun et al. (2006) have reported high concentration of exchangeable Mn in the sediments elsewhere. Heavy metal concentration in the exchangeable fraction is known to play an important role in the evaluation of environment and act as a pollution indicator (Forstner and Wittmann, 1979) for its environmental mobility and bioavailability. Also, Hseu (2006) stated that metals associated with the two fractions i.e. exchangeable and carbonate bound are more labile and

readily leachable or bioavailable. Lower concentration of Mn (µg/g) (Avg. 17) is available in the organic bound fraction, and ranges from 3 to 49 µg/g, 4 to 33 µg/g and 6 to 31 µg/g during monsoon, post-monsoon and pre-monsoon respectively, can be due to weak affinity of Mn for organics (Bendell-Young and Harvey, 1992). The average concentration of Mn in the residual phase is 316 µg/g during monsoon, 308 µg/g during post-monsoon and 295 µg/g during pre-monsoon season. The higher concentration of Mn in the non-residual phase can be directly related to the input from anthropogenic activities like mining, which is being carried out in the catchment area of Zuari Estuary. During monsoon, higher concentration of Mn is observed in the lower half of the estuary with a decreasing trend towards the mouth in case of all the fractions. During other seasons, higher concentrations were observed in the upstream end and also in the lower half of the estuary with a decreasing trend towards the mouth. Mn exhibits significant correlation with Cu, clay and organic carbon in the exchangeable fraction and it shows a good correlation with Cr during monsoon season (Table 5.1). In carbonate fraction, it shows a significant correlation with Zn, clay and organic carbon and shows a good correlation with Cu, Co and silt. It displays significant correlation with Co and good correlation with Cr, organic carbon and clay in Fe-Mn oxide bound fraction, while in organic bound fraction, it shows a significant correlation with Cu, Cr, Co, clay and organic carbon and a good correlation with Zn. It exhibits good correlation with Cr and silt in residual fraction in the same season. In case of post-monsoon, Mn shows a significant correlation with Zn in the exchangeable fraction and with Co, silt, clay and organic carbon in the carbonate bound phase (Table 5.2). Sand shows a significant negative correlation with Mn in this fraction. In Fe-Mn oxide phase, Mn shows a significant correlation with Co while in organic bound phase, it exhibits significant correlation with Cr and Co and displays good correlation with Cu, Zn, clay and organic carbon in this fraction. In residual fraction, it does not show any significant correlation with metals or with sand, silt and clay. During pre-monsoon, it shows a significant correlation with Zn in exchangeable fraction and with Cr and silt in carbonate fraction. It also shows a good correlation with Cu, Zn and Co in the

carbonate fraction. It exhibits significant correlation with Zn and good correlation with Cu and Cr in Fe-Mn oxide phase. In organic bound fraction, it displays significant correlation with Cu and Zn while in case of residual fraction it exhibits significant correlation with silt, clay and organic carbon and good correlation with Cu, Zn and Co indicating their association (Table 5.3).

c. Copper (Cu)



F1: Exchangeable, F2: Carbonate, F3: Fe-Mn oxide, F4: Organic bound, F5: Residual

Fig. 5.3: Extractable contents of Cu in surface sediments of Zuari Estuary using Tessier sequential extraction protocol.

Substantial amount of Cu is present in the residual fraction, which ranges from 14 to 98 µg/g (Avg. 56) during monsoon, 8 to 37 µg/g (Avg. 22) during post-monsoon and from 14 to 45 µg/g (Avg. 28) during pre-monsoon season. On an average more than 70 % of Cu is available in this fraction in all the three

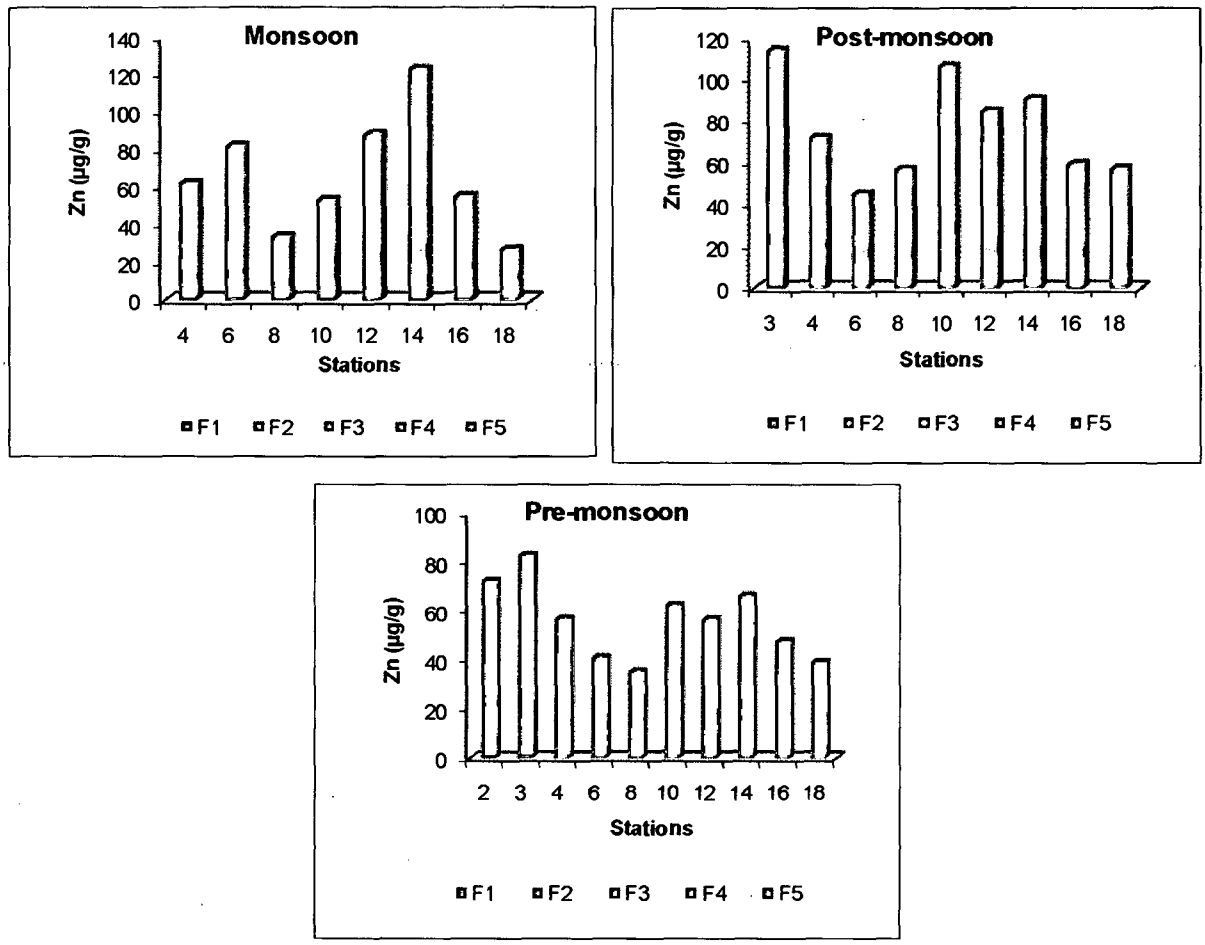
seasons. The higher concentration of Cu in the residual fraction is due to natural sources such as weathering of rocks and decomposition of detritus biota (Badri and Aston, 1983). Next to residual fraction, Cu is associated with organic bound fraction that varies from 1 to 14 µg/g (Avg. 7), 1 to 12 µg/g (Avg. 5) and 2 to 7 µg/g (Avg. 4) during monsoon, post-monsoon and pre-monsoon seasons respectively. Cu forms highly stable complexes with the organic matter (Li et al., 2001). Cu bound to other three fractions is comparatively low which can be seen from the figures (Fig. 5.3). The average concentration of Cu in the exchangeable and carbonate bound fraction is around 1 µg/g during all the three seasons, while in case of Fe-Mn bound, Cu varies from 1 to 6 (µg/g), 1 to 3 (µg/g) and 0 to 3 (µg/g) in the respective seasons. Organic and exchangeable bound Cu is observed to be higher in the lower half of the estuary. Distribution of Cu in the residual fraction is similar to that of Fe in the same fraction. Cu does not show any significant correlation with metals in exchangeable fraction during monsoon season (Table 5.1), but shows a good correlation with Fe, clay and organic carbon. Correlation analysis indicated significant correlation of Cu in carbonate fraction with Co and good correlation with Zn in the same season. In case of Fe-Mn oxide fraction, it shows a significant correlation with Zn, silt, clay and organic carbon and good correlation with Cr and Co. It exhibits significant negative correlation with sand in the same fraction. In organic bound, Cu exhibits significant correlation Mn, Zn and organic carbon and good correlation with Fe, Cr, Co and clay, while in case of residual fraction it displays good correlation with Fe, Zn and organic carbon and to some extent with clay in the same season. In case of post-monsoon, Cu does not show significant correlation with metals in the exchangeable fraction as well as in carbonate fraction. However, it exhibits significant correlation with Zn and Cr in Fe-Mn oxides fraction and with Fe, Zn, silt, clay and organic carbon in organic bound fraction (Table 5.2). In residual fraction, it shows a significant correlation with Fe, Zn, Cr and organic carbon. It exhibits good correlation with Co in organic bound and also in residual fraction. During pre-monsoon, Cu shows a good correlation with Cr in the exchangeable fraction. It exhibits significant correlation with Fe, Zn and Co and good correlation

with Cr and Mn in carbonate fraction. Cu shows a good correlation with Fe, Mn, Zn and silt in the Fe-Mn bound whereas in organic bound, it exhibits significant correlation with Fe, Mn, Zn and silt and good correlation with clay and organic carbon. In the residual fraction Cu shows a significant correlation with Co, clay and organic carbon and a good correlation with Fe, Mn and Zn (Table 5.3).

The distribution of Cu and significant correlation obtained indicated that similar to Fe, it is also associated with finer sediments, organic carbon and metals in residual and organic bound fractions.

d. Zinc (Zn)

Like Fe and Cu, significant amount of Zn is also available in the residual fraction (above 60 %), which varies from 13 to 93 µg/g (Avg. 46) during monsoon, 26 to 89 µg/g (Avg. 55) during post-monsoon and 18 to 61 µg/g (Avg. 37) during pre-monsoon seasons and least quantity is available in the exchangeable fraction (Avg. 1), which varies from 0 to 1 µg/g during monsoon and 0 to 2 µg/g in both during post-monsoon and pre-monsoon (Fig. 5.4). The low concentration of Zn in exchangeable fraction can be probably due to the fact that metals in this form can easily be absorbed and utilized by organisms in the aquatic environment (Campbell, 1995). Similar results have been reported by Pizarro et al. (2003). Among the non-residual fractions, the Fe-Mn oxide phase is much more important than the other fractions in which the concentration of Zn ranges from 5 to 17 µg/g (Avg. 10), 6 to 22 µg/g (Avg. 12) and 9 to 15 µg/g (Avg. 11) during monsoon, post-monsoon and pre-monsoon respectively. The association of Zn with the Fe and Mn oxides of soils and sediments has been widely recognized by Kuo et al. (1983) and Gonzalez et al. (1994). These studies have shown that the Zn adsorption onto these oxides has high stability constants. The availability of Zn in different fractions in Zuari estuarine sediments is in the following ascending order, exchangeable < carbonate < organic bound < Fe-Mn oxide < residual in case of all the three seasons.



F1: Exchangeable, F2: Carbonate, F3: Fe-Mn oxide, F4: Organic bound, F5: Residual

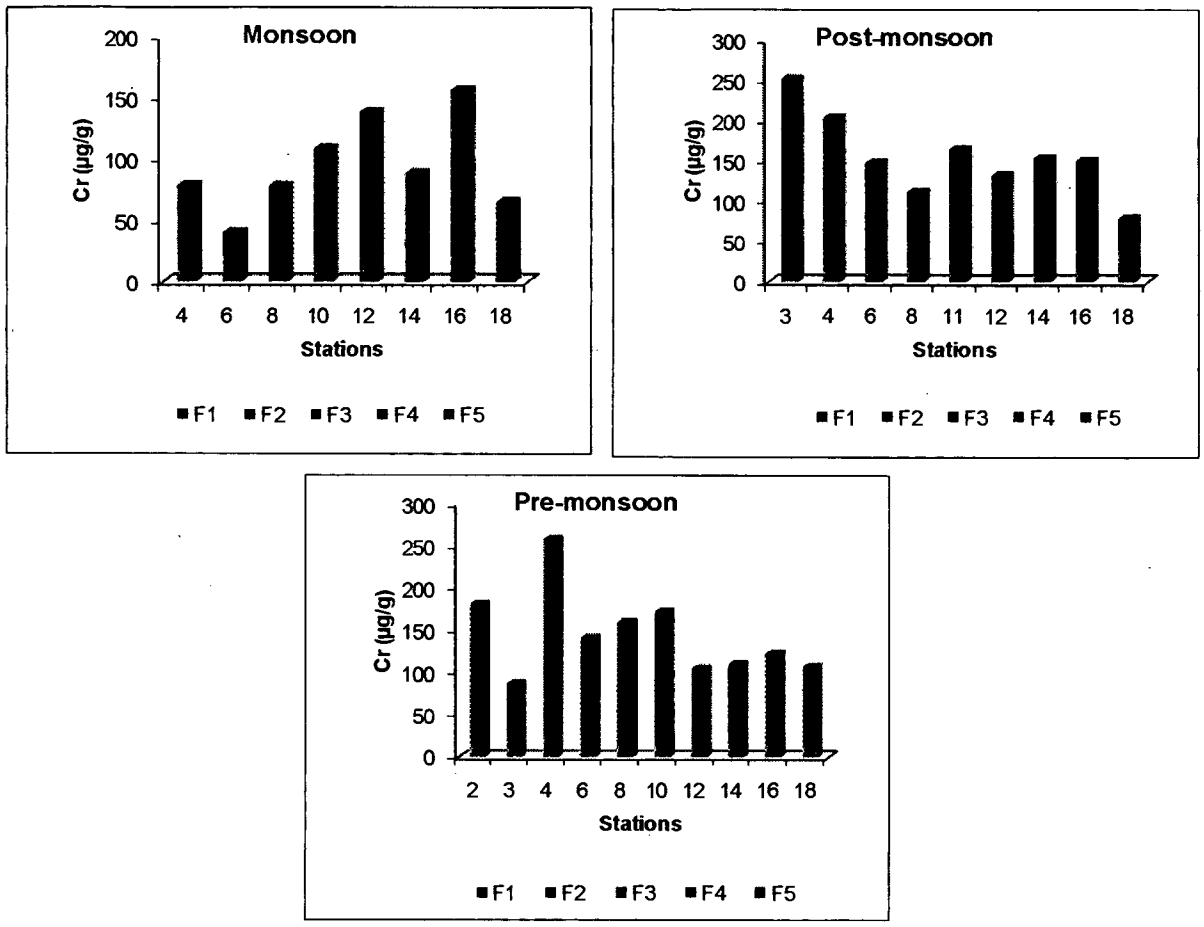
Fig. 5.4: Extractable contents of Zn in surface sediments of Zuari Estuary using Tessier sequential extraction protocol.

In organic bound fraction, Zn content varies from 3 to 12 µg/g (Avg. 5), 2 to 8 µg/g (Avg. 5) and 2 to 5 µg/g (Avg. 4) during monsoon, post-monsoon and pre-monsoon respectively, whereas, in carbonate bound it varies from 3 to 4 µg/g (Avg. 3), 1 to 11 µg/g (Avg. 4) and 3 to 5 µg/g (Avg. 4) during respective seasons. Results obtained indicated that Zn has higher potentials for mobilization from the sediments than Cu because of its higher concentration in the Fe-Mn oxide fraction in all the three seasons. Zn is observed to be comparatively less in the exchangeable fraction than in the rest of the fractions. Exchangeable Zn is observed to be higher in the upstream end of the estuary in all the three seasons. During monsoon, carbonate (Stn. 12 and 14), Fe-Mn oxide bound (Stn. 12, 14 and 16), organic bound (Stn.10, 12 and 14) and residual bound Zn (Stn. 12 and

14) are observed to be higher in the lower half of the estuary with a decreasing trend towards the mouth with minor variations. In case of other two seasons, the distribution of Zn in the first three fractions is almost similar with relatively higher concentrations in the upstream and at station 10 in case of post-monsoon in Fe-Mn oxide fraction. Organic bound Zn is observed to be comparatively higher in the lower half of the estuary in all the three seasons and residual bound Zn largely follows the trend of Fe and Cu in all the seasons.

e. *Chromium (Cr)*

In general, residual fraction is the main carrier for Cr in all the three seasons, in which Cr content varies from 12 to 134 µg/g (Avg. 66), 63 to 198 µg/g (Avg. 125) and 63 to 228 µg/g (Avg. 121) respectively during monsoon, post-monsoon and pre-monsoon seasons. This fraction is followed by Fe-Mn oxide bound, in which Cr varies from 4 to 15 µg/g (Avg. 12) during monsoon, 4 to 37 µg/g (Avg. 15) during post-monsoon and 6 to 14 µg/g (Avg. 11) during pre-monsoon. The association of Cr in Fe-Mn hydroxide phase may be the result of the insoluble Cr^{+3} hydroxide (Eary and Rai, 1988 and Morel, 1983), which is eventually incorporated into Fe-Mn matrix during precipitation and Fe containing Mn phase of the particle provide more surface sites for Cr to be adsorbed (Sager, 1992). The next important phases are organic bound and exchangeable. The Cr (µg/g) content varies from 1 to 22 (Avg. 9), 2 to 14 (Avg. 7) and 3 to 10 (Avg. 6) in organic bound and from 6 to 9 (Avg. 7), 5.8 to 6.4 (Avg. 6) and 5 to 6 (Avg. 6) in exchangeable fraction during monsoon, post-monsoon and pre-monsoon seasons respectively. Comparatively less content of Cr (µg/g) is available in the carbonate fraction viz. monsoon (avg.1), post-monsoon (avg. 3) and pre-monsoon (avg. 2) (Fig. 5.5). In general, the distribution of Cr in the different fractions is in the following order, carbonate < exchangeable < organic bound < Fe-Mn oxide < residual.



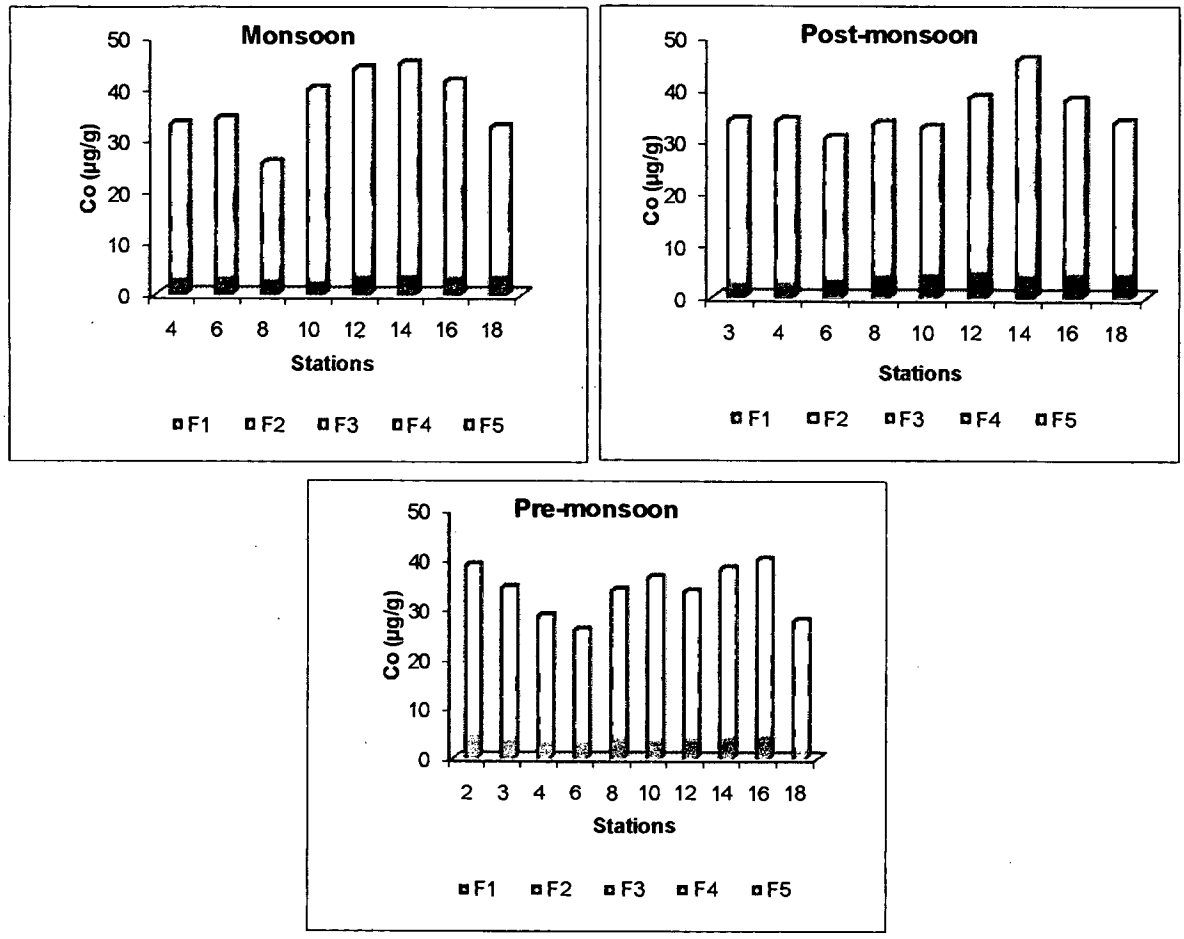
F1: Exchangeable, F2: Carbonate, F3: Fe-Mn oxide, F4: Organic bound, F5: Residual

Fig. 5.5: Extractable contents of Cr in surface sediments of Zuari Estuary using Tessier sequential extraction protocol.

Overall, Cr in the different fractions is observed to be higher in the upper estuarine region and also between stations 10 to 16, further downstream it shows a decreasing trend towards the mouth with few exceptions.

f. Cobalt (Co)

Significant amount of Co is available in the bioavailable phases even though individually, residual fraction accounts for more amount of Co (Fig. 5.6). During monsoon Co concentration ranges from 3 to 4 µg/g (Avg. 3), 3 to 6 µg/g (Avg. 4), 3 to 10 µg/g (Avg. 7), 5 to 8 µg/g (Avg. 6), 10 to 20 µg/g (Avg. 17) in exchangeable, carbonate, Fe-Mn oxide, organic bound and residual phases respectively.



F1: Exchangeable, F2: Carbonate, F3: Fe-Mn oxide, F4: Organic bound, F5: Residual

Fig. 5.6: Extractable contents of Co in surface sediments of Zuari Estuary using Tessier sequential extraction protocol.

In case of post-monsoon, it ranges from 3 to 5 µg/g (Avg. 4), 2 to 5 µg/g (Avg. 3), 6 to 11 µg/g (Avg. 8), 4 to 6 µg/g (Avg. 5) and 9 to 20 µg/g (Avg. 15) in the respective fractions. During pre-monsoon, Co (µg/g) ranges from 2 to 5 (Avg. 4), 2 to 6 (Avg. 4), 5 to 10 (Avg. 8), 2 to 5 (Avg. 3) and 10 to 20 (Avg. 16) respectively in the same fractions. Next to residual fraction, important phase is the Fe-Mn oxide phase (similar observations were made by Calmano and Forstner, 1983; and Jones and Turki, 1997). During monsoon and post-monsoon, exchangeable and carbonate bound Co shows an increasing trend towards the downstream region. Comparatively higher values of carbonate bound, Fe-Mn oxide and to some extent the residual bound Co are observed in the lower half of the estuary in all the three seasons.

5.2.2. Inter-Seasonal Variations

The inter-seasonal variations between the different parameters such as metals, sediment components along with near bottom water salinity and pH in five different phases / fractions were studied by using the isocon plots. Observations made from isocon plots are briefed below.

a. *Exchangeable Fraction*

When the average data of the different parameters during monsoon is plotted against post-monsoon, it can be seen from the isocon plots that Mn together with salinity and clay registered comparatively higher values during post-monsoon indicating the role of salinity and finer size sediment in maintaining higher concentration of Mn in this season, while Cr and silt content are higher during monsoon season signifying their association. Large run-off during this season must have brought elevated amount of silt along with Cr content from the catchment area into the estuary. While others fall on or near the iscon line indicating not much variation of these elements during the seasons although slightly higher concentration of Co and Cu along with pH are observed during post-monsoon season (Fig. 5.7). When the data set of monsoon is compared with the pre-monsoon season, Mn, Fe, Zn along with salinity and clay are observed to be higher during pre-monsoon season while silt and Cr are again higher during monsoon season. Co and Cu fall on or near the isocon line indicating very less variation during these seasons. Fe, Mn, Zn, silt and salinity was observed to be relatively higher during pre-monsoon season compared to post-monsoon season while others fall on or nearer to the isocon line indicating little variations between them.

In general, Mn and Fe are apparently higher during pre-monsoon season in exchangeable fraction indicating their anthropogenic input mainly from the activities related to mining. Metals in this fraction are likely to be affected by the sorption-desorption processes due to change in ionic composition of water. In

general comparatively higher concentrations of most of the metals during pre-monsoon season followed by post-monsoon and monsoon season could be due to desorption of metals from the suspended matter and finally deposition on the bed load surface sediment in the calmer conditions.

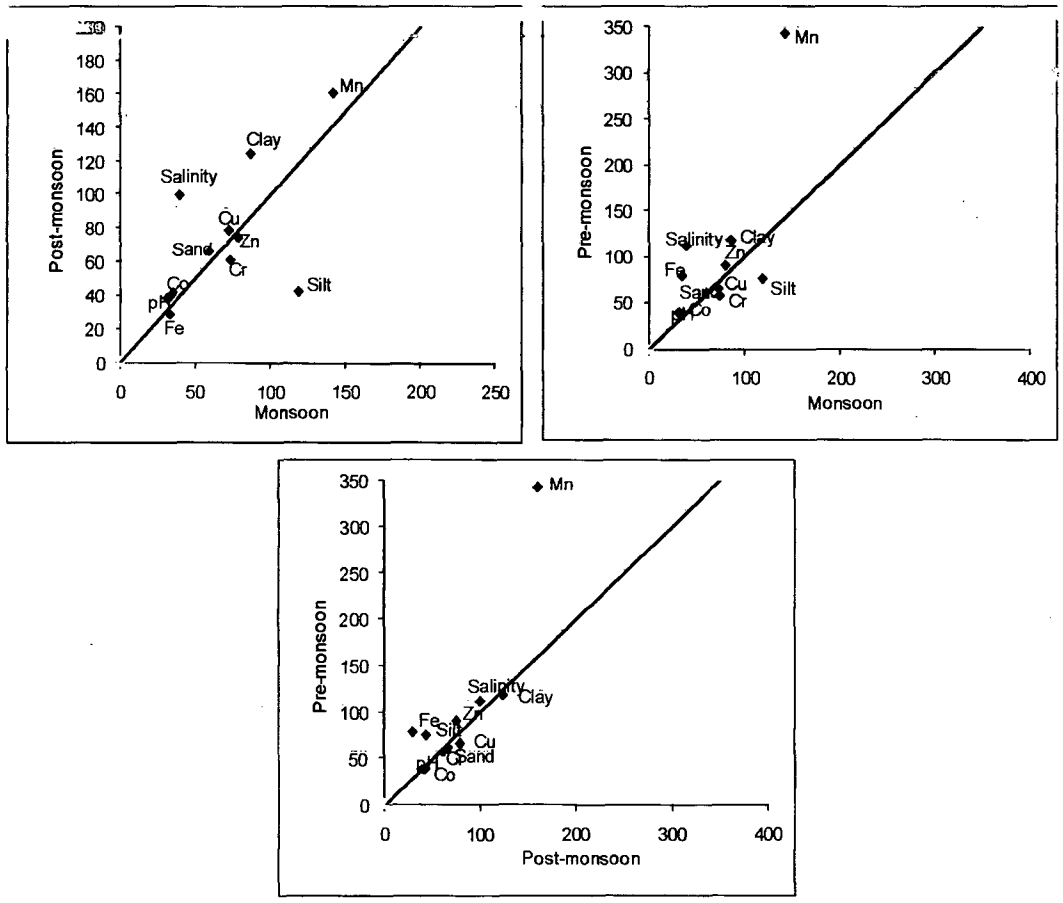


Fig. 5.7: Isocon plot for exchangeable fraction (Individual data points represent average concentrations of each parameter in the different seasons multiplied by the different factors to ensure all elements plot on the same scale).

b. Carbonate Fraction

When the data plotted for monsoon is compared with that of the post-monsoon season, Fe, Mn, Cu, Cr, Zn along with pH, salinity and clay are higher towards the post-monsoon season indicating enrichment during this season compared to monsoon season while Co and silt show higher concentration during monsoon season indicating their associations. Relatively higher concentrations of Mn, Zn,

Cu, Cr and salinity were observed in pre-monsoon season when compared to monsoon season, whereas, higher concentration of Fe and Co along with silt is observed during monsoon. Comparison of data between post-monsoon and pre-monsoon indicated that Mn is relatively higher during pre-monsoon season and Fe and Cr are higher during post-monsoon season in this fraction (Fig. 5.8). Zn, Co and Cu fall on or nearer to the isocon line indicating little variation between post-monsoon and pre-monsoon season.

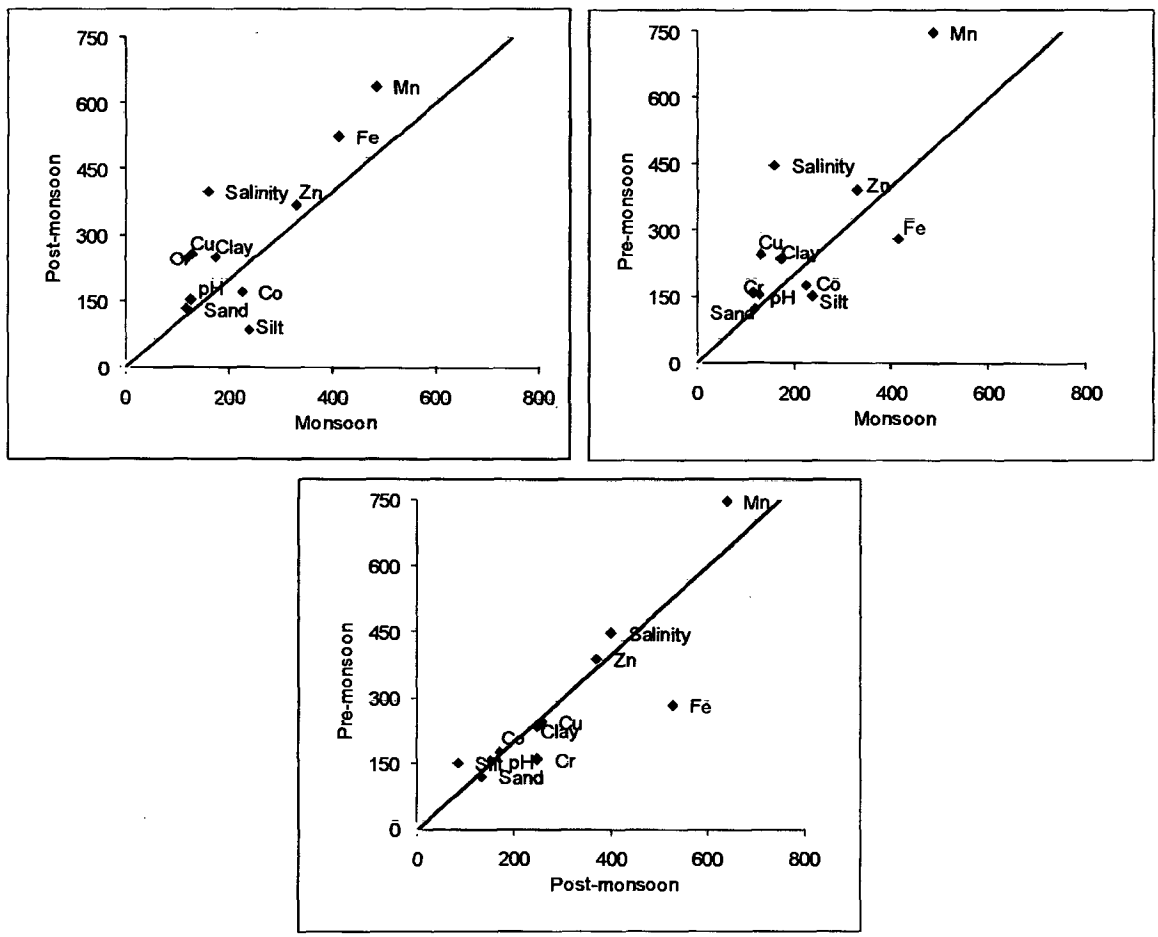


Fig. 5.8: Isocon plot for carbonate fraction (Individual data points represent average concentrations of each parameter in the different seasons multiplied by the different factors to ensure all elements plot on the same scale).

In general, relatively higher concentration of Mn was recorded during pre-monsoon season followed by post-monsoon and monsoon season in this fraction. This indicates the role of salinity in concentration and distribution of Mn. The adsorption of Mn on to carbonates is reported by several researchers. The

lower content of Mn during monsoon season in this fraction could be due to dissolution of carbonates in this season.

c. Fe - Mn Oxide Fraction

Most of the metals are slightly concentrated during post-monsoon season compared to the monsoon season (Fig. 5.9).

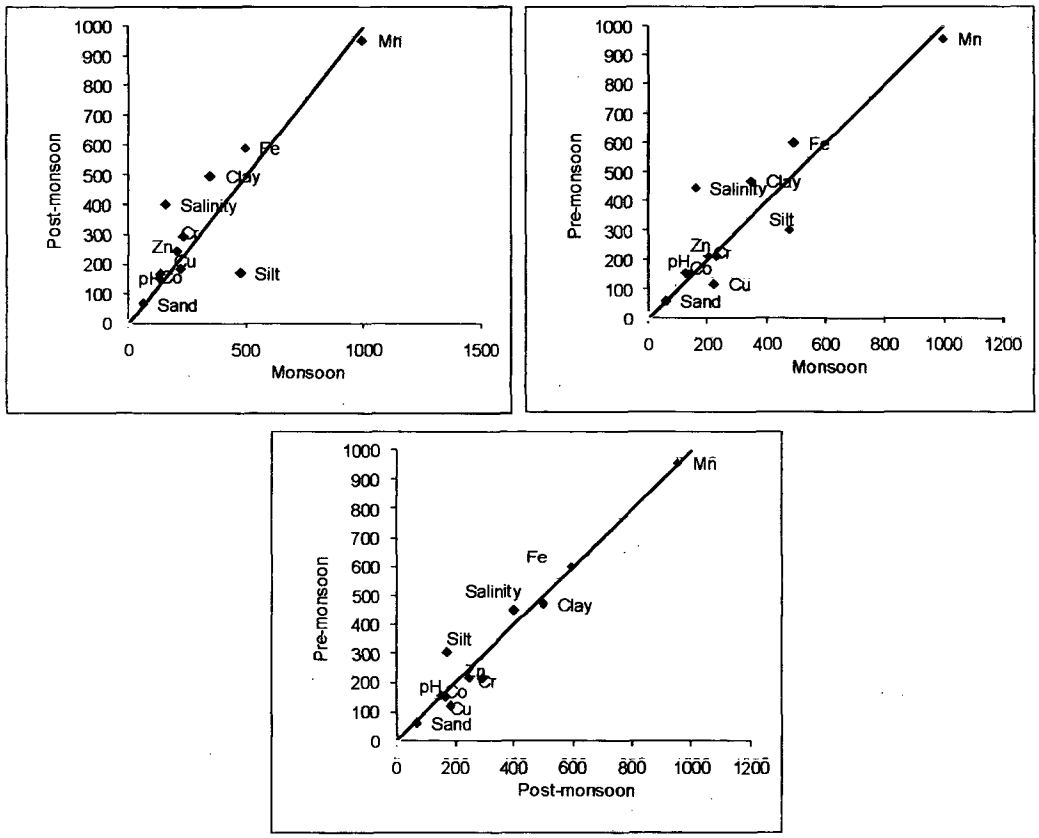


Fig. 5.9: Isocon plot for Fe-Mn oxide fraction (Individual data points represent average concentrations of each parameter in the different seasons multiplied by the different factors to ensure all elements plot on the same scale).

When data of monsoon is compared with the pre-monsoon season, Fe along with clay and salinity are observed to be relatively higher during pre-monsoon season and Cu and silt during monsoon season, while other metals did not show much variation. When data of post-monsoon and pre-monsoon is plotted little variations are observed for most of the metals. Slightly higher values of Cr and Cu are observed during post-monsoon season than pre-monsoon.

In general, isocon plots deciphered not much variation of metal content in different seasons in this fraction indicating the important role of Fe-Mn oxide in binding metal in each season.

d. Organic Bound Fraction

Although little variations of metal concentrations are observed in the plot of monsoon vs. post-monsoon and monsoon vs. pre-monsoon season, metals along with the silt content registered comparatively higher values during monsoon season than in other two seasons in this fraction (Fig. 5.10).

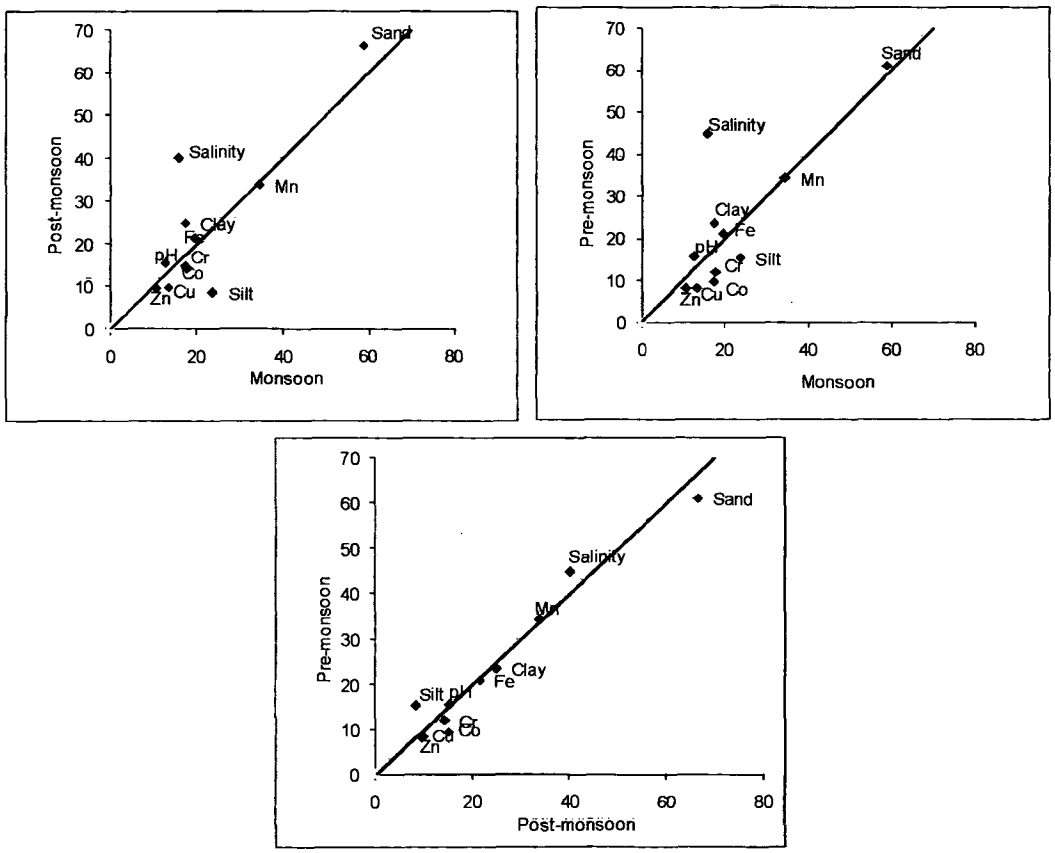


Fig. 5.10: Isocon plot for organic bound fraction (Individual data points represent average concentrations of each parameter in the different seasons multiplied by the different factors to ensure all elements plot on the same scale).

Co, Cr and Cu are observed to be slightly higher during monsoon season compared to pre-monsoon season. Also little variations are observed for almost all the metals between post-monsoon and pre-monsoon season except for Co,

which is slightly higher during post-monsoon season. Similar to Fe-Mn oxide, not much variation of metals are observed in this phase among the different seasons although slightly higher concentrations are reported during monsoon season.

e. *Residual Fraction*

Fe, Mn and Co falls on or nearer to the isocon line, indicating little or no variation of these elements between monsoon and post-monsoon seasons.

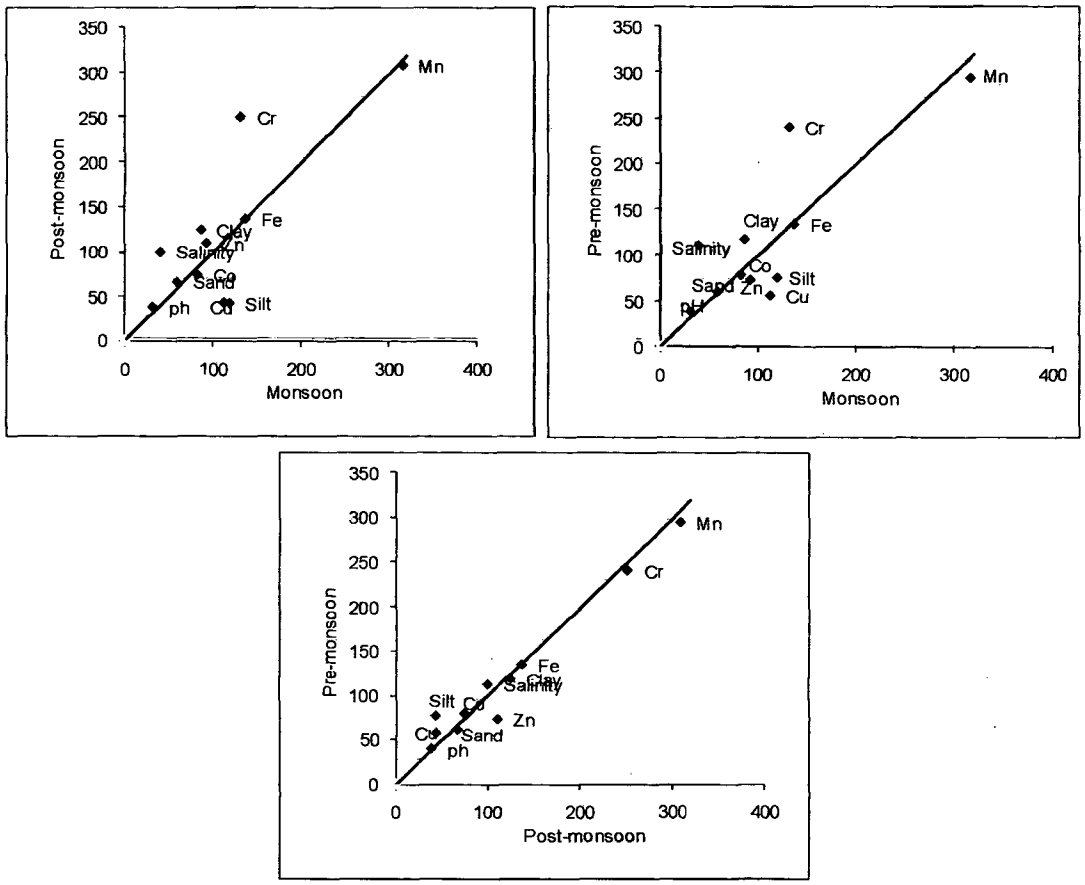


Fig. 5.11: Isocon plot for residual fraction (Individual data points represent average concentrations of each parameter in the different seasons multiplied by the different factors to ensure all elements plot on the same scale).

Cr along with salinity and clay and to some extent Zn is higher in the post-monsoon season and Cu and silt are higher in the monsoon season indicating their associations (Fig. 5.11). Comparison of data during monsoon with pre-monsoon indicates comparatively higher concentration of Cr along with salinity

and clay during pre-monsoon season and Cu and to some extent Mn and Zn during monsoon season. Very little variation in metal concentrations is observed between post-monsoon and pre-monsoon seasons although slightly higher concentration of Zn is observed during post-monsoon season compared to pre-monsoon season.

5.2.3 Factor Analysis

Varimax R-mode factor analysis for eigen value above 1 by using principal components extraction method was attempted for organic bound and Fe-Mn oxide fraction to identify common sedimentological and geochemical characteristics of the original data as these two fractions are important carriers of metals. Factor analysis extracted two / three common factors viz. Factor 1 (F1), Factor 2 (F2) and Factor 3 (F3) with significant loadings within each factor for all the three seasons, which are presented in the figure 5.12.

In Fe-Mn oxide phase, F1 accounts for 65.35 % of total variance during monsoon season. Cu, Zn, silt, clay and organic carbon are strongly loaded in this factor indicating association of Cu and Zn with finer fraction and organic matter. F2 accounts for 15.86 % of total variance. Strong loading of Mn, Cr, Co, clay and organic carbon is observed in this factor indicating their association with Mn oxides, finer sediments and organic matter whereas, F3 accounts for 10.26 % of total variance. The high loading of Fe and Zn in this factor indicates association of Zn with Fe-oxides. During post-monsoon, F1 accounts for 46.14 % of total variance. The strong loading of Cu, Zn and Cr is observed in this factor indicating their common source, probably anthropogenic input. In case of F2 association of metal is not seen but strong positive loading of clay, silt and organic carbon and strong negative loading of sand is observed. F3 accounts for 16.62 % of total variance, wherein Fe, Mn and Co and to some extent Zn and silt are loaded indicating their association with Fe-Mn oxides. During pre-monsoon, F1 accounts for 48.21 % of total variance, wherein association of Zn, clay, silt and organic carbon is seen indicating Zn's association with finer fraction and organic matter.

F2 accounts for 25.85 % of total variance. Strong loading of Fe, Mn and Cr is observed in this factor indicating their association. F3 accounts for 12.98 % of total variance. In this factor strong loading of Fe, Cu, Zn, Co and silt and also to some extent Mn is seen indicating their association.

Fe-Mn oxide fraction

Organic bound fraction

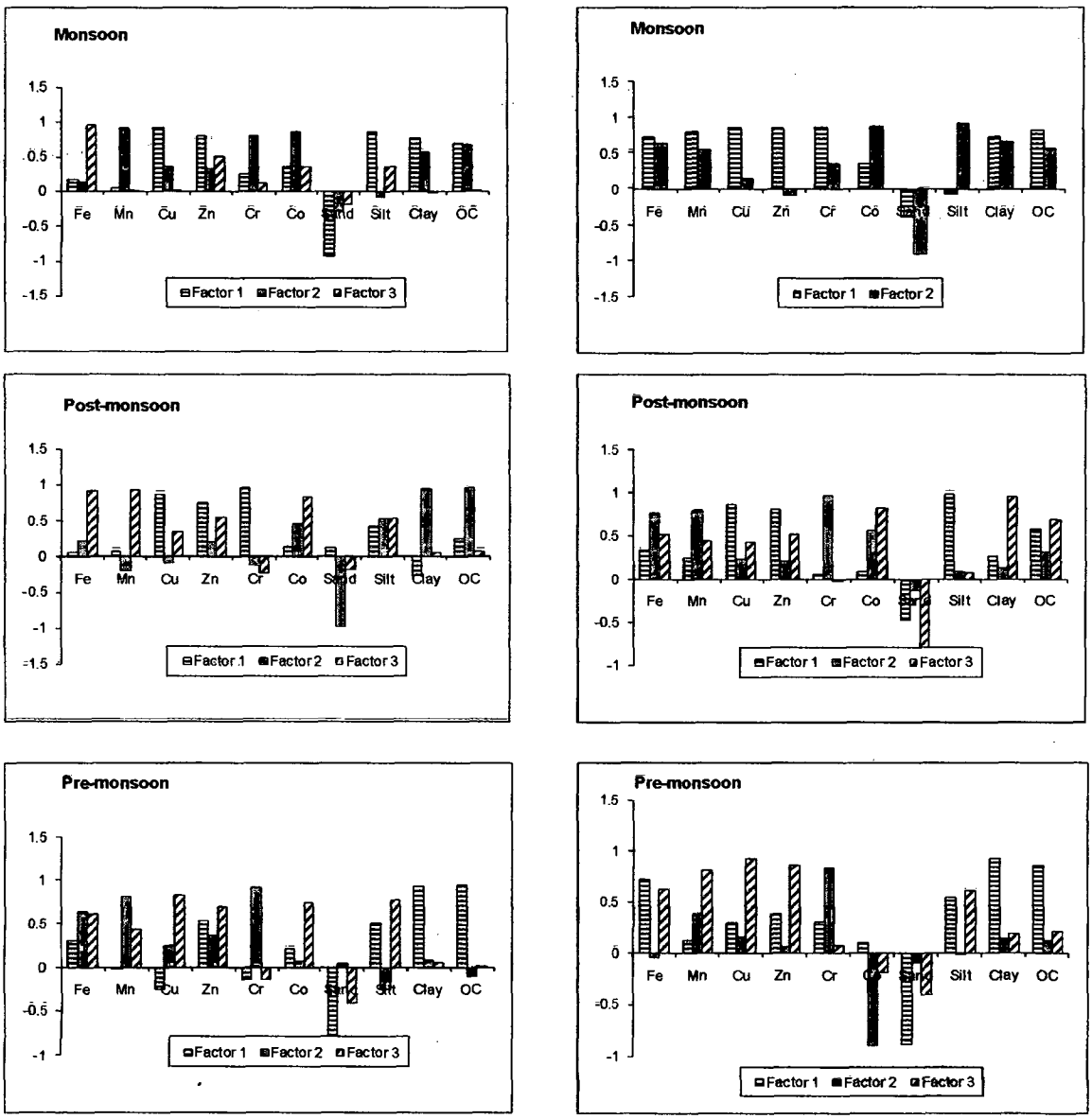


Fig. 5.12: R-mode factor analysis for Fe-Mn oxide and Organic bound fractions of surface sediments of Zuari Estuary in the different seasons.

In organic bound phase, during monsoon, F1 accounts for 72.89 % of total variance. Strong loading of Fe, Mn, Cu, Zn, Cr, clay and organic carbon in this factor indicates association of these metals with organic matter and finer fraction. F2 accounts for 16.36 % of total variance. In this factor, strong loading of Fe, Co, silt, clay and organic carbon is seen which indicates association of Co with Fe, finer sediments and organic carbon. During post-monsoon, F1 accounts for 67.58 % of total variance. Strong loading of Cu, Zn, silt and organic carbon is seen in this factor. The association of Zn and Cu with the organic matter is well established. The second factor i.e. F2 accounts for 16.34 % of total variance in which Fe, Mn, Cr and Co are strongly loaded. F3 accounts for 10.31 % of total variance, wherein Fe, Zn, Co, clay and organic carbon are strongly loaded in the same season. In case of pre-monsoon, F1 accounts for 58.14 % of total variance. Strong negative loading of sand and strong positive loading of Fe, silt, clay and organic carbon is observed indicating Fe's association with organic carbon and finer size sediment. F2 accounts for 15.77 % of total variance where strong loading of Cr alone is seen in this season where as F3 accounts for 11.21% of total variance. Strong positive loading of Fe, Mn, Cu, Zn and silt is observed in the organic bound phase.

5.3 Discussion

The residual fraction is the main carrier of most of the studied metals importantly for Fe and Cu, which comprises of detrital silicate, resistant sulfides and refractory organics (Tessier et al., 1979). Metals in this phase mostly remain stable and do not react during sedimentation and diagenesis, and therefore have less potential bioavailability. As mentioned earlier, this phase could be considered as inert phase corresponding to the part of metal that cannot be mobilized and as the geochemical background value for the elements in the sediments (Tessier et al., 1979). The second important phase is the Fe-Mn oxide phase for most of the metals except for Cu, for which it is the organic bound phase. Among the studied metals, Mn and Co is found to be relatively higher in the bioavailable fractions.

Fe-Mn oxide phase (reducible phase) consists of hydrous oxides of Fe (III) and Mn (IV) (Tessier et al., 1979; Kersten and Forstner, 1989) and is the major metal host in the estuarine sediments (Calmano and Forstner, 1983). This fraction along with exchangeable and carbonate fractions is an important bioavailable metal source (Luoma and Davis, 1983). Although an attempt has been made to study diagenetic processes in the Zuari Estuary, these could not be completely traced as the present work deals on the surface sediments. Diagenesis is a common process, which occurs in the estuarine environment. The higher concentration of Fe and Mn along with Cr, Zn, Co and Cu observed in the surface sediments of Zuari Estuary in the Fe-Mn oxide bound is largely controlled by the process of diagenesis. During early diagenesis, microbial mediated redox reactions quickly result in the reduction of insoluble Fe (III) and Mn (IV) oxides and release of Fe (II) and Mn (II) species to pore water (Canfield, 1989). Dissolution results in the release of metals associated with the oxide phases to the pore water and possibly to the overlying water to some extent (Petersen et al., 1995) and hence to the surface sediments. Higher concentration of Mn observed in this phase can be because of upward diagenetic mobilization from reducibly bound metals of near surface sediments. Metals originally bound to oxide phases must have initially transferred into monosulfides, but eventually be fixed as pyrites, through sulphidization process and the efficiency with which this transfer occurs differs significantly between metals (Huerta-Diaz and Morse, 1992). When the sulphidization of iron minerals is complete, pyrite will be the dominant host for metals. As long as the conditions within the sediment remain reducing, these pyrite bound metals will be unavailable for further reaction or uptake by biota. Cr and Zn which are in significant amount in the present study, are comparatively less in organic phase indicating that they must have remained in more labile phase throughout early diagenesis, or to be lost from sediment (Huerta-Diaz and Morse, 1992). Similar observations were reported earlier in the Tees Estuary (Jones and Turki, 1997). The oxidisable fraction is mainly dominated by Cu following residual fraction indicating its association with organic fraction. The affinity of Cu to organic substances is well known. Under oxidizing

condition significant amount of Cu reaching to the surface sediment can be transferred into the overlying water column and some must be reaching to the upper sediment layer (Petersen et al., 1995). A small amount of Zn can also be remobilized for the same reason (Petersen et al., 1995). Further mobilization of Cr, Zn, Co and Cu may occur due to microbial oxidation of organic substrate. However, most of the Cu and some of Cr and Zn are mainly fixed as pyrite (Huerta-Diaz and Morse, 1992) and remain immobilized as long as the sediments remain reducing. But processes such as mixing of sediment with oxygenated layer, materials dredged from the river channel may enhance oxidative degradation of organic matter, which would have lead to mobilization of Cr, Zn, Co and to lesser extent of Cu in the present study.

In order to understand the risk of the studied metals to the sediment dwelling organisms, the data set of both the total metals in sediment and metals in the bioavailable fractions (sum of first four fractions) (table 5.4) were compared with Sediment Quality Values (SQV) using SQUIRT (screening quick reference table) (Table 5.5).

Table 5.4: Average concentrations of total metal and bioavailable fractions in the three different seasons.

	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon
	Total metals			Sum of Bioavailable fractions		
Fe (%)	8.36	7.61	8.72	5964.41	7059.42	7086.62
Mn	3069.17	2936.72	3099.31	1640.14	1769.45	2067.64
Cu	96.88	34.34	44.78	10.20	8.86	7.20
Zn	90.18	101.95	70.39	19.64	21.58	19.59
Cr	113.47	178.89	267.43	28.98	30.46	24.06
Co	52.60	39.14	53.46	20.63	20.91	18.23

Except for Fe all values are in µg/g

Table 5.5: Screening Quick Reference Table (SQRT) for metals in marine sediments (Buchman, 1999).

Elements	Threshold Effect Level (TEL)	Effects Range Low (ERL)	Probable Effects Level (PEL)	Effects Range Median (ERM)	Apparent Effects Threshold (AET)
Fe	-	-	-	-	22 % (Neanthes)
Mn	-	-	-	-	260 (Neanthes)
Cu	18.7	34	108	270	390 (Microtox and Oyster Larvey)
Zn	124	150	271	410	410 (Infaunal community)
Cr	52.3	81	160	370	62 (Neanthes)
Co	-	-	-	-	10 (Neanthes)

Except for Fe all values are in µg/g

SQUIRT was developed by NOAA for screening purposes. Based on SQUIRT, the guideline values are categorized into five classes which are presented in the table 5.6 (Buchman, 1999).

Table 5.6: Sediment guidelines and terms used in SQUIRT.

Sediment Guidelines	
Threshold Effect Level (TEL)	Maximum concentration at which no toxic effects are observed
Effects Range Low (ERL)	10^{th} percentile values in effects or toxicity may begin to be observed in sensitive species
Probable Effects Level (PEL)	Lower limit of concentrations at which toxic effects are observed
Effects Range Median (ERM)	50^{th} percentile value in effects
Apparent Effects Threshold (AET)	Concentration above which adverse biological impacts are observed.

The implication of SQV is to achieve the information on toxicity of metals to the biota and thus understand the impact on environment. The total Cu falls under effects range low (ERL) to probable effect level (PEL) but the sum of the bioavailable fractions fall below threshold effect level (TEL) indicating no harm to the aquatic life. The values of total Zn itself are below TEL suggesting no risk to biota while total Cr values are nearer to PEL. However sum of the bioavailable fractions fall below TEL level indicating no potential bioavailability of this element. The percentage of Fe is also very low compared to apparent effect threshold (AET) indicating no harm and it is observed to be maximum in the residual fraction in all the three seasons. There are no reported values for Mn

and Co for first three classes but the values of both these metals exceeds the AET suggesting these two elements are potentially bioavailable and thus indicating their toxicity to environment. It is important to mention here that Mn is usually present in the oxide form and therefore can be the reason in maintaining higher concentration in the Fe-Mn oxide bound fraction. So it is advisable to exclude this fraction and check the bioavailability of this metal. Even after excluding this fraction, the Mn concentration was observed to be higher in the other three fractions (exchangeable + carbonate + organic bound), which exceeds the AET limit indicating its bioavailability.

To confirm the results obtained, mineral analysis of some of the selected samples of both bulk sediment and of the residual fraction (Fig. 5.13 & 5.14) was done which indicated that part of the minerals must have come in solution phase, which might affect the concentration of Fe and Mn to very less extent and therefore to be considered as insignificant. This indicates that the concentration of the other elements will not be affected.

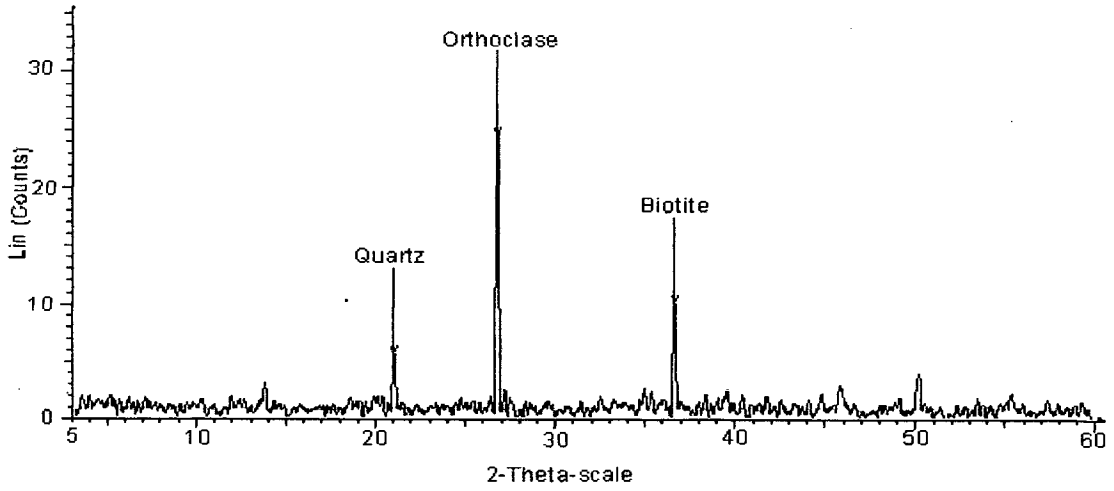


Fig. 5.13: XRD spectra of bulk sediment sample for station 7 during post-monsoon season.

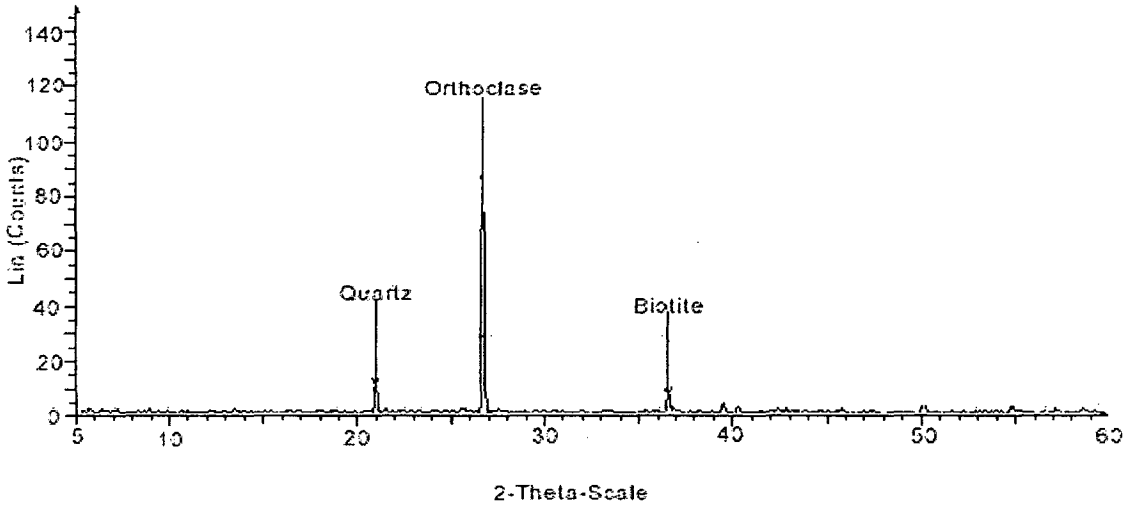


Fig. 5.14: XRD spectra of sediment from the residual fraction for station 7 during post-monsoon season.

Correlation analysis between the total metal content and the metal species indicated significant correlation ($p < 0.05$) between total Fe and residual Fe in all the three seasons viz. monsoon ($r = 0.93$), post-monsoon ($r = 0.95$) and pre-monsoon ($r = 0.94$). During pre-monsoon, total Fe is also significantly correlated with the Fe in Fe-Mn oxide ($r = 0.60$) and organic fraction ($r = 0.64$). Total Mn exhibits significant correlation ($p < 0.05$) with Mn in Fe-Mn oxide and organic bound in all the three seasons and with carbonate bound during monsoon ($r = 0.62$, $p < 0.1$) and post-monsoon ($r = 0.78$). In case of pre-monsoon, it also exhibits significant correlation with exchangeable ($r = 0.63$) and residual fraction ($r = 0.85$). Total Cr displays significant correlation ($p < 0.05$) with residual Cr in all the three seasons. It also shows a significant correlation with Fe-Mn oxide ($r = 0.59$, $p < 0.1$) and organic bound ($r = 0.70$) Cr during post-monsoon and pre-monsoon respectively. Significant correlation ($p < 0.05$, $p < 0.1$) of total Cu is observed with organic bound and residual Cu during the study period. It also exhibits significant correlation with exchangeable Cu during monsoon ($r = 0.77$) and post-monsoon ($r = 0.67$). Total Zn displays significant correlation with carbonate ($r = 0.68$, $p< 0.05$), Fe-Mn oxide ($r = 0.70$, $p < 0.05$) and residual ($r = 0.96$) Zn during monsoon. During post-monsoon it displays significant correlation with organic ($r = 0.56$, $p < 0.1$) and residual Zn ($r = 0.83$, $p < 0.05$). While during

pre-monsoon, it displays significant correlation with carbonate ($r = 0.61$, $p < 0.1$) and residual Zn ($r = 0.72$, $p < 0.05$). In general total Zn is mainly correlated with residual Zn in all the three seasons. Total Co exhibits significant correlation with Co in Fe-Mn oxide ($r = 0.85$, $p < 0.05$) during monsoon, residual ($r = 0.57$, $p < 0.1$) during post-monsoon and exchangeable ($r = 0.70$, $p < 0.05$) and residual ($r = 0.89$, $p < 0.05$) during pre-monsoon. In general, correlations obtained indicate that most of the metals viz. Fe, Cr, Cu, Zn and Co are mainly associated with the residual fraction, although they are available in the other fractions. However, total Mn is largely associated with the bioavailable fractions mainly with Fe-Mn oxide, organic and carbonate bound Mn indicating their association and its potential bioavailability.

A baseline study of Chemical speciation / partition in Zuari estuarine sediments indicates potential bioavailability and toxicity of Mn and Co (Dessai and Nayak, 2008). The higher Mn content can be directly related to mining and its associated activities in the catchment area. The open cast mining, especially of Mn ore, is more in the catchment area. As this ore is transported through the estuary, large amount is deposited in the estuarine sediments during loading and unloading of the barges and due to spill over from barges. Higher amount of Co in the bioavailable fractions along with Mn can be due to their association and probably because of their similar ionic radii. In general, total Co in surface sediments exhibit significant correlation with Mn in Fe-Mn oxide ($r = 0.88$, $p < 0.05$) during monsoon, Mn in exchangeable ($r = 0.57$, $p < 0.1$) and Fe-Mn oxide ($r = 0.97$, $p < 0.05$) during post-monsoon, exchangeable ($r = 0.72$, $p < 0.05$) and residual ($r = 0.80$, $p < 0.05$) during pre-monsoon season. This must have lead Co to remain in the bioavailable fractions together with Mn thereby increasing its toxicity to some extent. Similar observations have been reported by Tongtaveen et al. (2005) where they found association of Mn and Co in exchangeable, Fe-Mn oxide and organic bound fractions. Existing data clearly demonstrates the impact of mining on the Zuari Estuary to some extent and justifies the need to take up detailed study, especially on Mn with respect to its bioaccumulation.

SUMMARY

Estuaries are one of the important sub environments of the coastal zone. Estuaries are the favourable environments of deposition of sediments derived from various sources. Along the west coast of India estuarine processes are controlled largely by southwest monsoon facilitated seasons. Every component viz. total suspended matter, sand, silt, clay, organic carbon, metals and their species have gained importance in estuarine studies to understand natural processes as well as changing environmental conditions.

The Mandovi and Zuari Rivers together with connecting Cumbharjua Canal are considered as 'life line' of Goa as they play a pivotal role in Goa's economy, culture and means of livelihood. These rivers form an important tropical estuarine system along the west coast of India. Within the catchment area of both the rivers, the iron and manganese ores are mined using open cast method. Estuarine channels of both the rivers are used to transport large quantities of iron and ferromanganese ores to Marmugao harbour. The mining activities in this region influence the biological and geochemical conditions of the estuarine waters. Although the studies have proved that the Mandovi Estuary has been affected by mining and its associated activities, systematic studies on Zuari Estuary, especially concerning with the geochemistry of sediments, were not available. Present study is an attempt to fulfil this.

Estuarine sediments, both total suspended matter (TSM) and bed load are major repositories of metals and play a key role in the geochemical processes in estuarine environment. Thus measurement of metal concentration and distribution in aquatic environment leads to better understanding of their behaviour and most importantly for detecting their sources and level of pollution in the estuarine system. Factors such as grain size, organic matter, geomorphology, prevailing hydrodynamic conditions, and different point and non-point sources play a vital role in the concentration and distribution of metals in the estuarine system. Toxicity and biological availability of a particular element depend on its chemical form and hence the information on speciation is a must. Hence the principle objective of the present study was to investigate the geochemistry of both suspended and bed load sediments and to understand the abundance, distribution, factors / processes, source, toxicity

and bioavailability of metals to evaluate the scale of pollution in Zuari Estuary. To accomplish the objectives, field surveys were carried out in the three different seasons viz. monsoon, post-monsoon and pre-monsoon. Both water (near surface and near bottom) and bed load sediments were collected at 18 selected stations within the estuarine limits. Water samples collected were used to determine salinity, pH and TSM concentration. Geochemistry (both TSM and surface sediments), grain size, clay mineralogy, magnetic susceptibility of surface sediments was also carried out. In the present study an attempt has been made for the first time in Zuari Estuary to understand the partition / speciation of metals in surface sediments.

The results obtained in the present study reflect a distinct variation in salinity and pH indicating marine dominance over the estuary during post-monsoon and pre-monsoon season and a freshwater dominance during monsoon season. Several processes / factors such as river runoff, flocculation, resuspension, adsorption-desorption, remobilisation, dilution, grain size, geomorphology, seasons, salinity and tidal surge play a very important role in distribution of TSM and their associated metals in the Zuari Estuary. Abundance of metals observed during post-monsoon season compared to other two seasons can be attributed to flocculation process. Resuspension during pre-monsoon and fresh water influx during monsoon play significant role in distribution and concentration of TSM and its associated metals. Al normalized plots of metals show enrichment of metals in the upper estuarine region and then follows a general decreasing trend towards the downstream region in all the three seasons, signifying that the source is from the catchment area.

The distribution of surface sediment components viz. sand, silt, clay and organic carbon illustrates that the sand is dominating in the upper estuarine region while silt, clay and organic carbon are enriched in the lower estuarine region. Prevailing hydrodynamic conditions play a significant role in the deposition of sediments in the Zuari Estuary. Ternary diagrams plotted by using sand, silt and clay indicate relatively violent hydrodynamic conditions during monsoon compared to other two seasons. Slightly higher values of

organic carbon in the upper estuarine region coincide with the silt and clay. Kushawati tributary that joins the Zuari Estuary is responsible for bringing large amount of finer sediments and organic matter from the agriculture dominated catchment area. Clay mineralogical studies show presence of kaolinite, illite, chlorite and smectite in the surface sediments of Zuari Estuary and among them kaolinite is the dominant mineral. These minerals are predominantly derived from the drainage basin. The source of smectite can be either the catchment area or the offshore region. Presence of kaolinite in higher percentage indicates intense chemical weathering under warm and humid climate. Chemical alteration and transport of terrigenous supply to the estuarine sediments is revealed from the presence of higher chlorite and illite content. Clay mineralogy also helped in understanding the flocculation processes. Geochemistry of selected metals viz. Fe, Mn, Cr, Cu, Zn and Co in surface sediments showed slightly higher concentrations for most of the metals (Fe, Mn, Cr and Co) during pre-monsoon season. Cu is higher during monsoon season and Co is slightly higher in post-monsoon season. Spatial distribution of these metals showed higher concentrations in upstream end and upper half of the lower estuary. The source, salinity, sediment size, organic matter present in the sediment, Fe - Mn oxides, geomorphological setup, tide and associated currents, fresh water input all play an important role in distribution and abundance of metals within Zuari Estuary. Mining and its associated activities are largely responsible for maintaining higher concentration of metals in the upstream region while in the lower estuary, grain size and organic matter played significant role in retaining metals in sediments. Magnetic susceptibility measurements have shown higher magnetic concentration in the upper estuary and at few places of the upper half of the lower estuary indicating the anthropogenic influence. Magnetic grain size distribution shows dominance of finer grain in the lower estuary and coarser grain in the upper estuary. Magnetic mineral analyses of selected sediment samples reflect the dominance of haematite in the Zuari estuarine sediments. The iron ore in Goa mainly constitutes the haematite and is the major source in Zuari Estuary. Different pollution indices viz. geoaccumulation index, contamination factor, pollution load index and degree of contamination computed to evaluate the enrichment of metals or the level of pollution

indicate that Zuari estuarine sediments largely fall under unpolluted to moderately polluted class with respect to Fe and moderately to strongly polluted category with respect to Mn. With regard to other metals studied viz., Cr, Cu, Zn and Co, in surface sediments of Zuari Estuary, falls largely into practically unpolluted to moderately polluted class. Higher concentration observed for most of the metals in the present study when compared to the previous studies in Zuari Estuary indicates increase in anthropogenic influence.

Chemical speciation by sequential extraction procedure furnished information about mobility, bioavailability, diagenesis and toxicity of metals and has thus given a better insight into the ultimate fate of pollutants. Residual fraction is the main carrier for Fe, Cu, Zn and Cr to some extent indicating locked nature of these elements. The significant amount of metals in the residual fraction also point to weathering effect. After residual fraction, the next important phase for these elements is the Fe-Mn oxide phase indicating the role of Fe-Mn oxide in the distribution of metals except for Cu, which is mainly in organic bound phase. Mn and Co are observed to be relatively higher in the bioavailable phases. Mn is higher in the Fe - Mn oxide and carbonate bound, while Co is dominating in the residual fraction but is also observed to be higher in the bioavailable phases. Sum of the metal concentrations in bioavailable fraction when compared with the sediment quality values by using SQUIRT indicated low risk of Cu, Zn, Cr and Fe to the benthic dwelling organisms while Mn and Co are potentially available to the aquatic life. The mining of Mn ore with lesser Fe ore is carried out in the catchment area of Zuari Estuary and is mainly responsible for maintaining higher concentration of Mn which exceeds the toxicity limit. Co content in surface sediments exhibited significant correlation with Mn in Fe-Mn oxide during monsoon, Mn in exchangeable and Fe-Mn oxide during post-monsoon and exchangeable and residual during pre-monsoon season. The strong relation between Mn and Co and probably because of their close ionic radii must have lead to higher concentrations of Co in bioavailable fraction along with the Mn.

R-mode factor, cluster and correlation analysis helped in understanding the role of organic matter, sediments size and Fe - Mn oxide in the distribution and concentrations of metals in the estuary. Common features observed in the factor analysis for surface sediments and TSM indicates the role of transport of metals through the adsorption processes on to suspended matter and finally deposition in the bed sediment.

The present study helped in understanding various factors / processes responsible for the distribution and abundance of metals in the Zuari estuarine sediments. The risk of Mn indicated from both pollution indices and speciation studies should be considered and need thorough investigation by analysing the various biological samples to understand the extent of bioaccumulation of the metals. Continuous monitoring and further studies in Zuari Estuary are therefore suggested to ascertain long-term effects of anthropogenic impact.

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downstream up to the mouth with slightly higher value at station 16. Highest value was obtained for station 14.

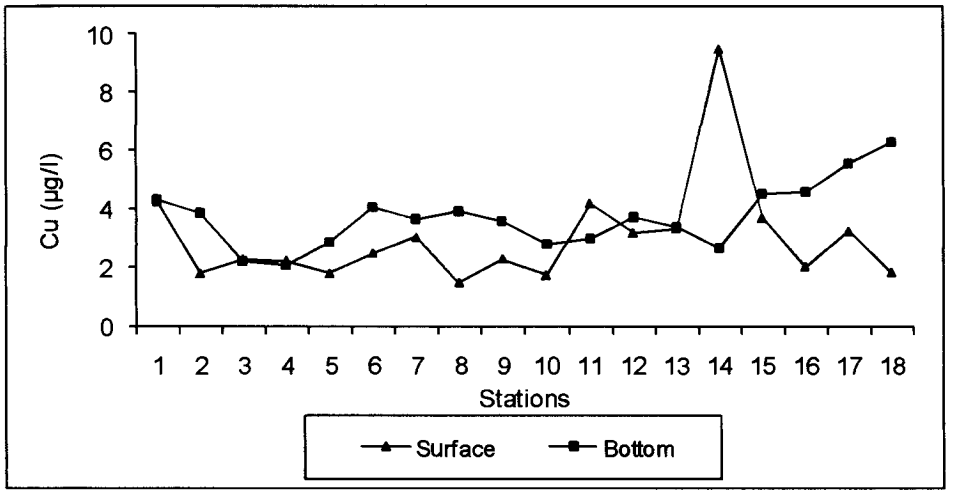

Fig. 3.9a: Distribution of Cu in surface and bottom TSM of Zuari Estuary during monsoon.

In bottom TSM, Cu content varies from 2.1 to 6.3 µg/l (Avg.3.7). It shows a decreasing trend from station 1 up to station 3 and then shows an increasing trend up to station 6. Decreasing trend was observed from station 6 to 10. Further downstream, it shows an increasing trend towards the mouth with slightly lower value at station 14.

During post-monsoon, Cu content ranges from 1.8 to 12.3 µg/l (Avg. 4.7) in surface TSM. Cu decreases from station 1 up to station 3. Slight increase in value is observed at station 4 which further shows a decreasing trend up to station 9. A drastic increase in value is seen from station 9 to 11 and then it shows a decreasing trend towards the mouth with minor fluctuations in between. In bottom TSM, Cu ranges from 3.9 to 14.8 µg/l (Avg. 6.9). Increasing trend of Cu is seen from station 1 up to station 5 which further decreases up to station 9. Increase in Cu content is seen from station 9 to 11 and then a decreasing trend towards the mouth is observed with minor fluctuations (Fig. 3.9b).