CHEMICAL PARTITIONING OF TRACE METALS IN SEDIMENTS OF A TROPICAL ESTUARY

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CERTIFICATE

This is to certify that this thesis is a bonafide record of the research carried out by Shri.C.Kunhikrishnan Nair, initially under the guidance of the late Prof. (Dr) P.N.K. Nambisan, and presently under my guidance, in partial fulfilment of the requirements for the degree of **Philosophiae Doctor** of the Cochin University of Science and Technology.

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PREFACE

Chemical analysis of sediments is one of the reliable techniques employed for the monitoring of metals in aquatic environments. To-date a number of reports are available on the baseline values of `total metals' from different environments. Concurrently consistent efforts have been directed at developing techniques that could yield better information. Sequential chemical extractions that provide better insight into the environmental behaviour of trace metals by quantifying sediment bound trace metals susceptible to short-term processes, have caught the attention of many scientists. This thesis reports the attempts made by the author to explore the possibilities of a sequential chemical extraction scheme in delineating the behaviour of sediment bound trace metals, in the highly dynamic environments of a tropical estuary.

The thesis is presented in five chapters.

CHAPTER 1, the introduction, reviews the historical development of chemical partitioning technique as an effective tool in trace metal monitoring programmes. An update on scientific information about trace metals in the Cochin estuary is also provided together with the aims and objectives of the present investigation.

CHAPTER 2 describes the study area and details the materials and methods employed in this study.

CHAPTER 3 presents the data recorded on the physical and chemical parameters of the sediments such as moisture content, texture, organic carbon content and total trace metal concentration along with results and discussion. The seasonal and spatial variations observed have been critically analysed in relation to the varying estuarine conditions.

CHAPTER 4 presents the results and discussion on chemical partitioning of trace metals. The seasonal and spatial variations in distribution of the various fractions of iron, manganese, zinc, copper, cadmium, lead, cobalt, nickel and chromium have been discussed individually and the variations explained.

CHAPTER 5 deals with the interrelationship between metals, metal fractions and environmental parameters. Metal enrichment factors have also been worked out phase-wise. A critical commentary on the role of chemical partitioning of trace metals in the tropical estuarine environment is also presented.

The results of the present investigation have been/ are being published, as given below.

i) Heavy metal speciation in sediments of Cochin estuary determined using chemical extraction techniques. Sci. Total Environ., 102 (2), 113 - 128.

ii) Speciation of Mn, Fe, Cr, Ni, Zn and Co in the sediments of a tropical estuary (communicated to Environmental Geology and Water Science).

iii) Seasonal and spatial distribution of chemically determinable species of trace metals in sediments of Cochin estuary. (under preparation)

iv) An investigation on total trace metals in sediments of the Cochin estuary.(under preparation)

v) State of art in metal speciation - new perspectives. (under preparation)

vi) Exchangeable and organically bound trace metal levels in sediments in relation to estuarine chemical reactivity. (under preparation)

vii) Implications of metal fractionation in sediments - strategies in assessing trace metal levels in aquatic environments. (under preparation)

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CHAPTER 1

INTRODUCTION

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1.1 TRACE METALS

The term "trace metal" is widely recognised and used to denote those metals that are distributed in earth's crust in very low concentrations. The popular elements of this group are cadmium, chromium, cobalt, copper, lead, nickel and zinc. Often, iron and manganese also find a place in the study of trace metals, as the environmental chemistry of the trace metals is closely related to that of iron and manganese (Jenne,1968). Industrially important, these metals and their compounds find a variety of uses in all fields of human endeavour, like agriculture, engineering, health, hygiene and so on. Nriagu and Pacyna (1988) have recently reviewed the trends in the production of several of such industrially important metals and have concluded that there has been a significant increase, during the past 55 year period (1930-85), in the amount of the different metals produced. The increase in production and supply of trace metals is generally viewed with great concern as it has been established that most of these trace metals are potentially toxic to living organisms.

Trace metals are known to play a dual role in living organisms. Many of these elements are essential for the sustenance of life, although required only in very small quantities. At higher levels of uptake, most of these metals turn toxic. The difference between the nutritive function and toxicity is only a matter of variations in concentration of the metals in the organisms and generally the difference is large enough to cause any practical concern (Waldichuk, 1985). However, there are some metals like cadmium and lead whose essentiality is not yet known but toxicity is well established even at very low concentrations.

One oft-quoted property of the trace metals is their persistence in aquatic environments. Once the metal is released into a system, it remains there for relatively long periods as it cannot be destroyed or disintegrated. Although the form in which it remains in the system may vary depending on the biogeochemical processes prevalent in the system, the total metal content would be the same unless and until it is transported to another regime.

The tragedies of Minamata and Niigata in Japan [where over 50 mortalities and over 100 permanently disabled victims of mercury poisoning caused by the consumption of mercury contaminated shellfish and finfish (Goldwater,1971) were reported] served to arouse serious concern over the `health' of oceans and in particular over metal pollution in the aquatic environment. Public concern over metal-toxicity further aggravated with the reports that the affliction known as "itai-itai", again reported from Japan, was caused by the consumption of food contaminated by cadmium (Ui, 1972). There were reports on the toxic effects of other metals also, especially that of lead (Chisolm, 1971), which entered the atmosphere from smelters and through the use of tetraethyl lead in gasoline. These reports have provided a stimulus for initiating more comprehensive studies aimed at identifying known or suspected areas of pollution and for complementary investigations of the chemical behaviour of trace metals in soils, sediments and water (Wittmann,1979; Fowler, 1990).

1.2 METAL ASSOCIATION IN SEDIMENTS

Processing of ores and production of metals lead to the generation of metal containing wastes that get redistributed in the environment under the influence of the natural agents - wind and water. Eventually, under the influence of the hydrological cycles these metals find their way to the surface waters (Forstner, 1979a). Transport and fate of trace metals depend greatly on the physical and chemical factors controlling the system. Trace metals from a number of non-point diffusive sources, such as, geologically weathered products, urban and rural runoff, domestic sewage, etc. are transported to surface waters. The sediment, the unconsolidated accumulation of particles covering the floor area of the waterbody usually acts as a repository for these trace metals. In sediments, trace metals are associated within a variety of accumulative phases. Gibbs (1973) suggested four groups of metal associations; later workers (Forstner and Patchineelam, 1976; Engler et al. 1977; Jenne and Luoma, 1977; Salomons and Forstner; 1980; Harrison et al. 1981) expanded this categorisation to include all main types of metal associations as may occur in sediments, soils and deposited dusts. Broadly, five categories of accumulative phases are recognised:

i) adsorptive and exchangeable phase
ii) carbonate bound phase
iii) easily reducible phase (Fe/Mn oxide phase)
iv) organic/ sulfide bound phase and
v) detrital or residual phase.

Characterisation of the distribution of trace metals among the various accumulative phases of the sedimentary particles is of great interest to sediment and water chemists for a number of reasons (Bernhard et al. 1986). A quantitative knowledge of the selective distribution of trace metals in sediments can be of value in assessing the potential impact of sediment re-suspension on water quality (Brannon et al. 1977). The selective distribution of trace metals may also be helpful in evaluating the relative influence of these metals on biological communities (Luoma and Jenne, 1976). By studying the distribution of metals between the different sediment phases, their contamination risks can be ascertained because the more mobile fractions introduced by man's activities remain bound to the exchangeable, the carbonate and the easily reducible phases (Calmano and Forstner, 1983; Forstner, 1985; Chester et al. 1985; Samanidou and Fytianos, 1987; Yoshimura et al.1988; Elsokkary and Muller, 1990). The metal levels in the inert fraction, being detrital and of lattice origin, can be taken as a measure of the geochemical contamination of the sediment sample as proposed by Salomons and Forstner (1980). The differentiation of the accumulative phases has been particularly useful in recognising the diagenetic reactions in deep sea sediments (Goldberg and Arrhenius,1958; Arrhenius and Korkish, 1959; Chester and Hughes, 1967 & 1969; Heath and Dymond, 1977; Rapin, 1983; Kumar and Roonwal, 1987; Chester et al. 1988).

Though the significance of identifying the accumulative phases has been well recognised, physical methods of identification suffer serious limitations because of the extremely low quantities present in the matrix. Toxic metals generally exist, even in polluted sediments and soils, at concentrations rarely exceeding 1000 mg/kg. Their existence as a discrete mineral phase is unlikely except when they result from dispersion from an area of mineralization and even if present in this form their abundance is too low to identify by presently available techniques (Harrison, 1987). Therefore, the best approach to obtain information on those fractions that are relevant for geochemical/biological processes is to separate the various chemically extractable fractions (Nissenbaum, 1972; Agemian and Chau, 1977; Waldichuk, 1985; Tessier and Campbell, 1987; Luoma, 1989, Ure, 1990; Dudka and Chlopecka, 1990).

1.3 CHEMICAL PARTITIONING

The use of chemical extractants to quantify the element in a particular solid phase was originally attempted in soil studies (Jackson, 1958; Jenne et al. 1986; Bermond and Sommer, 1989), where the "pool" of nutrients of different solubilities and mobilities were selectively sampled and determined using extractants of different strengths. Because of the similarities between sediments and soil, extraction procedures used in soils have often been borrowed or adapted for sediment analyses (Tessier et al. 1979). A number of extraction procedures, varying in manipulative complexity, have been proposed for the partitioning of the metal phase. Some of these techniques (Agemian and Chau, 1976; Loring, 1976; Malo, 1977) employ a single extractant and are designed to effect separation between residual and non-residual metals. These methods are rapid and simple and afford a better contrast between the anomalous and normal samples than the determination of total metal concentrations. The sequential extraction procedures (Nissenbaum, 1972; Presley et al. 1972; Gibbs, 1973; Gupta and Chen, 1975; Luoma and Jenne, 1976; Engler et al. 1977; Tessier et al. 1979; Harrison et al. 1981) employ a series of extractions with reagents of increasing power, under specified conditions, so that the individual phases can be more precisely isolated. The scheme of sequential extractions, although more time-consuming, provides detailed information on the origin, mode of occurrence, biological and physico-chemical availability, mobilization and transport of trace metals (Tessier et al. 1979; Campbell and Tessier, 1989; Gunn et al. 1989; Teraoka and Nakashima, 1990). The various extractants employed hitherto have been compiled and presented in Table 1.1.

Though the differentiated analysis in a sequential chemical extraction provides much more information than that from single extraction the extraction schemes are not free of flaws (Van Valin and Morse, 1982; Etcheber and Bourg, 1983; Rapin et al. 1986; Kheboian and Bauer, 1987). Transformation of phases during sample preparation (Jenne et al. 1980; Thompson et al. 1980; Trefry and Metz, 1984; Kersten and Forstner, 1987), re-adsorption and sometimes precipitation of metals (Rendell et al. 1980; Belzile et al. 1989), variability introduced by the duration, temperature, sequence of extraction and solid - extractant ratio (Calmano and Forstner, 1983; Miller et al. 1986), failure to validate the result with well defined samples (Nirel and Morel, 1990) etc. are some of the problems cited in the literature. Selectivity of some of the reagents being used is also in doubt (Engler et al. 1977; Nirel and Morel, 1990; Ure, 1990). The use of barium chloride - triethanolamine buffer or magnesium chloride for the determination of exchangeable metals is prone to interferences arising out of the formation of organic chelates in the former case and of chloro-complexes (Calmano and Forstner, 1983) in the latter case. Substantial precipitation of trace metals, presumably due to the formation

Table 1.1 Reagents for the extraction of metal phases

	Phase/Reagent	References
A.	EXCHANGEABLE PHASE	
a)	Ammonium acetate	Calmano and Forstner, 1983; Chapman, 1965; Engler et al. 1977; Gupta and Chen, 1975; Hong and Forstner, 1983; Jackson, 1958; Lee, 1985; Rapin, 1983; Samanidou and Fytianos, 1987; Stenekar et al. 1988; Teraoka and Nakashima, 1990; Yoshimura et al. 1988.
b)	Sodium acetate	Chapman, 1965
c)	Magnesium chloride	Bradley and Cox, 1990; Elliot et al. 1990; Gibbs, 1973; Lum et al. 1982; Tessier et al. 1979.
d)	Barium chloride-Triethanolamine	Forstner and Stoffers, 1981; Jackson, 1958
B.	CARBONATE PHASE	
a)	Sodium acetate-acetic acid	Bradley and Cox, 1990; Elliot et al. 1990; Lum et al. 1982; Nissenbaum, 1972; Samanidou and Fytianos, 1987; Stenekar et al. 1988; Tessier et al. 1979.
b)	Carbon dioxide treatment	Patchineelam, 1975
c)	Cation exchanger	Deurer et al. 1978; Forstner and Stoffers, 1981.

Contd.....

Table 1.1 contd......

	Phase/Reagent	References
C.	Fe/Mn PHASE	
a)	Hydroxylamine-hydrochloride/ acetic acid	Chester and Hughes, 1967; Kumar and Roonawal, 1987; Lee, 1985; Samanidou and Fytianos, 1987; Stenekar et al. 1988; Teraoka and Nakashima, 1990; Tessier et al. 1979; Yoshimura et al. 1988.
b)	Hydroxylamine-hydrochloride/ nitric acid	Bradley and Cox, 1990; Calmano and Forstner, 1983; Chao, 1972; Lum et al. 1982; Forstner and Stoffers, 1981.
c)	Ammonium oxalate-oxalic acid	Calmano and Forstner, 1983; Elliot et al. 1990; Patchineelam and Forstner, 1983; Schwertmann, 1964.
d)	Sodium dithionite-sodium citrate	Aguilera and Jackson, 1953; Engler et al. 1977; Holmgren, 1967.

Contd...

Table 1.1 contd....

	Phase/Reagent	References
D.	ORGANIC/SULFIDE PHASE	
a)	Hydrogen peroxide-ammonium acetate	Bradley and Cox, 1990; Calmano and Forstner, 1983; Engler et al. 1977; Hong and Forstner, 1983; Jackson, 1958; Lee, 1985; Lum et al. 1982; Patchineelam and Forstner, 1983; Rapin, 1983; Samanidou and Fytianos, 1987; Stenekar et al. 1988; Teraoka and Nakashima, 1990; Tessier et al. 1979; Yoshimura et al. 1988.
b)	Hydrogen peroxide-nitric acid	Gupta and Chen, 1975
c)	Organic solvents	Cooper and Harris, 1974
d)	Sodium hydroxide/sulfuric acid	Volkov and Fomina, 1974
e)	Sodium hypochlorite	Gibbs, 1973

Contd....

Table 1.1 contd.....

	Phase/Reagent	References
E.	RESIDUAL PHASE	
a)	Alkaline fusion	Gibbs, 1973; Jackson, 1958; Nissenbaum, 1972.
b)	Nitric/perchloric/ hydrofluoric acids	de Groot et al. 1982; Jackson, 1958; Lee, 1985; Teraoka and Nakashima, 1990.
c)	Nitric/hydrochloric acids	Bradley and Cox, 1990; Forstner, 1979b; Lum et al. 1982.
d)	Nitric/perchloric acids	Feijtel et al. 1988; Lithnor, 1975; Samanidou and Fytianos, 1987; Tiller et al. 1989.
e)	Nitric acid	Calmano and Forstner, 1983; Elsokkary and Muller, 1990; Knudtsen and O'Connor, 1987; Rapin, 1983.

of sulfide as a result of the disproportionation of dithionite, were observed during the use of dithionite-citrate couple for the determination of moderately reducible phases (Tessier et al. 1979).

Most of the limitations mentioned above could be rectified by careful selection of the extractants and the extraction conditions. However, the non-specificity of the extractants makes the procedure operational in character and the extracted "phases" are often operationally defined. Despite these drawbacks, sequential extraction procedures have yielded valuable insight into the geochemical processes occurring in the sediments (Chester and Hughes, 1969; Heath and Dymond, 1977; Singh and Subramanian, 1984; Kumar and Roonwal, 1987; Chester et al. 1988) as well as into the complexities of geochemical association of trace elements (Tessier et al. 1980; Lion et al. 1982; Allen et al. 1990; Bradley and Cox, 1990). These methods have been widely used in environmental studies to quantify those phases of the sediments that constitute the reservoir for potential release of contaminants into the water column (Lee, 1985; Chester et al. 1985; Carruesco and Lapaquellerie, 1985; Samanidou and Fytianos, 1987; Pardo et al. 1990; Allen et al. 1990; Clevenger, 1990; Elsokkary and Muller, 1990; Zhang et al. 1990). Sequential extraction procedures have also proved to be valuable in the description and prediction of biological trace metal uptake by sediment dwelling organisms and aquatic plants (Luoma and Bryan 1978; Luoma, 1983 & 1989; Langston and Bryan, 1984; Tessier et al. 1984; Gunn et al. 1989)

In spite of the proven advantages in elucidating the environmental effects of trace metals, the sequential extraction techniques have been used, only rarely, in estuarine sediment studies. The information on chemical partitioning of trace metals in sediments is particularly important for estuaries, where because of the rapidly changing hydrochemical conditions of water column, a steady state vertical distribution of elements cannot be used to understand their reactivities (Hart and Davies, 1981; Amdurer et al. 1983). Further, these waters receive large amounts of natural and anthropogenic inputs of potentially harmful substances (Yeats et al. 1978; Satyanarayana et al. 1985a; Qasim and Sen Gupta, 1988; Grigg, 1990). With their often restricted circulation, it is imperative to know what controls the movement of these chemicals through the system in order to predict whether they will be concentrated locally and in what form or if they will be diluted to the ocean (Duinker, 1986; Chester,1990).

1.4 ESTUARINE VARIABILITY

The term `estuarine variability' encompasses the spatial diversity and temporal changeability (Wolfe and Kjerfve, 1986) recorded in physical, chemical and biological properties of the estuary in response to exogenous inputs of materials or energy that may themselves vary over wide ranges of magnitude and exhibit different periodicities over a broad range of time scales. Estuaries are mixing zones between fresh river water and saline coastal water. Physical, chemical and biological processes within an estuary vary over a broad spectrum, both in space and time (Morris, 1990; Dyer, 1991). Spatial variations depend on the topography of the estuary, on the gradients in salinities and on the fine sediment concentration (Uncles et al. 1988; Wright and Phillips, 1988; van Leussan and Dronkers, 1990). With respect to temporal variations, several time scales can be distinguished (Bero and Gibbs, 1990): long-term (yearly), seasonal (monthly/fortnightly), intermediate (daily/diurnal) and short-term (hours/minutes). While annual and seasonal variations depend on the climatological factors, fortnightly and diurnal variations are caused by tidal actions (Holmes,1986; Vale,1990).

Within an estuary, the amount and direction of the flow and thus the water level and river width vary periodically with river inputs and tides (Bowden, 1980; Dyer, 1988). Sedimentation of suspended particulate matter, resuspension of this material and possible erosion of consolidated sediments change with the flow dynamics and influence the particulate matter concentration in the water column (Michaelis, 1990). These processes, thus leave significant impressions on the trace metal distribution within the estuary, since major part of trace metals in estuaries are bound to particulate matter (Luoma and Phillips, 1988; Vollmer et al. 1990).

It may be remarked that an estuary provides a particularly varied chemical environment for element cycling (Burton and Liss, 1976; Elderfield, 1978; Morris et al. 1982; Martin and Whitfield, 1983). Suspended matter carried by rivers is subjected to gradually altering salinities (and pH) within an estuary. This often causes precipitation of suspended material by flocculation (Sholkovitz, 1976 & 1978; Sholkovitz and Copland, 1981) and chemical exchange between the suspended sediment and estuarine waters that changes the chemistry of both (Van der Weijden et al. 1977). Gradients in the chemical environment, e.g., in the salt or oxygen content, may change the partitioning of trace metals with the possible consequence that for instance, the transport mechanism vary with time and location (Carey, 1990).

The major nutrient elements as well as some of the essential trace metals are much more abundant in river water than in sea water (Martin and Whitfield, 1983). The uptake and release of metals between the organisms and water body regulate the metal fluxes within the estuary (Salomons and Mook, 1980; Windom et al. 1991). In general, estuaries have a high biological productivity but the species composition vary greatly with the changing salinity pattern. While the fresh water plankton die off with increasing salinity, the marine plankton die with the growing influence of fresh water. The detritus thus formed contribute substantially to the suspended load, especially in the maximum turbidity zone (Michaelis, 1990). The organic rich particulate matter settles to the bottom and leads to the formation of anoxic interstitial waters which strongly influence the partitioning of trace metals between the various components of the system.

Estuaries, adjacent to centres of urbanization and industrialisation, are likely to receive bio- degradable and stable compounds of anthropogenic origin, containing trace metals (Allan, 1990). Early interest in the study of trace metals in estuaries arose mainly from the fact that the estuaries represented an important stage in the supply of trace metals to the oceans (Aston, 1978). The behaviour of trace metals, besides showing distinct seasonal and diurnal variation within an estuary (Bewers and Yeast, 1980; Windom et al. 1991), varies from one estuary to the other (Turner et al. 1990). Seasonal and annual variations in river flow affect the transportation processes that distribute the metals within the system (Nichols et al. 1986; Ackroyd et al. 1987; Kappenberg et al. 1990). The seasonal and annual changes in salinity pattern also influence the adsorption, desorption and chemical partitioning of trace metals. The biological and geochemical activity of a particular trace metal is strongly influenced by its chemical partitioning within the sedimentary phases. Trace metals would not remain permanently bur~~r~~ied in sediments (Yen and Tang, 1977). A matter of particular concern is that of the decaying organic matter which may eventually set free many of the toxic metals that get resuspended by tides, storms and dredging. It is quite possible that the toxic metals released in this way could damage the estuarine and nearshore aquatic life (Dyrssen and Wedborg~~e~~, 1980) and hence intensive studies are needed to determine the release rates of trace metals from estuarine sediments. The chemical partitioning of sediment bound metals can offer much information in this direction (Hart and Davies, 1981).

The multi-component heterogeneous nature of sediments provides little scope in predicting the partitioning of metals from fundamental theories and hence the quantification has to be made based on empirical observations. Most of the studies reported in literature on chemical partitioning relate to Europe and North America. As far as tropical systems are concerned, very few authentic data are available (Windom et al. 1988). In this respect, the Cochin estuary situated on the west coast of India constitutes an excellent model, under tropical climate for the study of the partitioning of trace metals, especially in view of increasing evidences on the toxic effects of metal contamination in this coastal water body.

1.5 COCHIN ESTUARY

The Cochin estuary extending between 09°40′ - 10° 12′N and 76° 10′ - 76° 30′E is a typical tropical positive estuary as per Pritchard's classification (Pritchard, 1967; Fairbridge, 1980), as the runoff plus precipitation exceeds evaporation. The climate of the region is tropical maritime with a characteristic monsoonal season (Ananthakrishnan et al. 1979). Two major rivers discharge fresh water into the estuarine system; the Periyar river flows into the northern parts and the Muvattupuzha river into the southern parts. The estuary is connected to the Lakshadweep sea (a part of the Arabian sea) through a permanent opening, the barmouth at Cochin. The Cochin barmouth is 450 m wide and is dredged to a depth of 10-13 m through which tides act within the estuary. Cochin is a major port on the south west coast of India.

The considerable research effort expended in elucidating the physical, biological and chemical characteristics of the Cochin estuarine system during the last three decades, is indicative of the economic and social importance enjoyed by the Cochin harbour area and its adjoining backwater system. The hydrography of the estuary was investigated by several investigators including, George and Kartha (1963), Cherian (1967); Qasim and Gopinathan (1969), Josanto (1971), Haridas et al. (1973), Shynamma and Balakrishnan (1973), Narayana Pillai et al. (1973), Balakrishnan and Shynamma (1976), Anto et al. (1977), Rama Raju et al. (1979), Udaya Varma et al. (1981 & 1987) Lakshmanan et al. (1982), Sankaranarayanan et al. (1986), Anirudhan et al. (1987), Pillai (1989), Sarala Devi et al. (1979), Anirudhan and Nambisan (1990) and Pylee et al. (1990). The information available includes spatial and seasonal distributions of temperature, salinity, dissolved oxygen, pH, alkalinity, and suspended solids of surface and bottom waters of the region as a whole or a part. Nair et al. (1975), Kurian et al. (1975), Gopalakrishna Pillai (1979), Anwar Batcha (1985), Madhusoodana Kurup (1983), Joseph (1989) and several others investigated the biological characteristics of the estuary as the fishery resources from this extensive water body formed the back-bone of the regional economy. The greater awareness on the potential health hazards due to the industrial and domestic effluents added to this estuary prompted several research workers to take up toxicological studies (Lakshmanan, 1982; Sivadasan, 1987; Baby, 1987; Latha Thampuran, 1987; Krishnakumar, 1987; Prabhudeva, 1988) and considerable data is now available on the toxic effects of several of the pollutants, especially of trace metals on several of the native fauna of the Cochin estuary and adjoining marine environments (Lakshmanan and Nambisan, 1977, 1979, 1980, 1983, 1985a, 1985b & 1989; Nambisan et al. 1977; Abraham et al. 1986; Menon, 1986; Baby and Menon, 1986; Sivadasan et al. 1986; Prabhudeva and Menon, 1987; Suresh and Mohandas, 1987; Sathyanathan et al. 1988; Sivadasan and Nambisan, 1988; Krishnakumar et al. 1990).

Like any other estuary located in the vicinity of metropolitan cities and industrial conglomerates, Cochin estuary also is subjected to increasing human interferences (Gopalan et al. 1983; Balchand, 1984; Balchand and Nambisan, 1986; Lakshmanan et al. 1987; Paul and Pillai, 1983a; Joy et al. 1990). Nearly 70 percent of the chemical industries of Kerala State is situated on the banks of river Periyar and the effluents from these industries (fertiliser, pesticide, fungicide, metallurgical, rare earth and catalyst plants) form an important source of pollutants to this estuary. The point source of pollutants identified on the Muvattupuzha river is a newsprint factory, but its effluents seldom reach the estuary proper (Balchand and Nambisan, 1986). In addition to the industrial effluents, the estuary receives organic wastes also, from domestic sewage works, coconut husk retting yards, fish processing units etc. Storm water channels also contribute substantially to the pollutant load of this waterbody. The net effect of these discharges have caused irreparable damage to the flora and fauna of this waterbody (Jayapalan et al. 1976, Unnithan et al. 1977; Vijayan et al. 1976; Sarala Devi et al. 1979; Remani et al. 1980; Venugopal et al. 1980; Remani et al.1981; Gopalan et al. 1983; Remani et al. 1983; Joseph et al. 1988; Sarala Devi and Venugopal, 1989; Ouseph, 1990) and the productivity of this region has been seriously affected.

Control and improvement of water standards in an estuarine system requires an insight into the various physico-chemical parameters that define the water quality. Several workers have recently addressed this problem in Cochin estuary and data is now available on the status of nutrients (Sankaranarayanan and Qasim, 1969; Manikoth and Salih, 1974; Sankaranarayanan and Punampunnayil, 1979; Sankaranarayanan et al. 1984; Lakshmanan et al. 1987; Anirudhan, 1988; Anirudhan and Nambisan, 1990; Sarala Devi et al. 1991) and organic compounds (Nair et al. 1989; Balchand et al. 1990) in waters and sediments of Cochin estuary. Perhaps the most widely studied toxicants in the Cochin estuary are the trace metals. Earlier reports on the trace metal distribution in water, sediments and biota of Cochin estuary were due to Sankaranarayanan and Rosamma (1978), Sankaranarayanan et al. (1978), Murty and Veeraya (1981) Venugopal et al. (1982), Jayalakshmy and Sankaranarayanan (1983) and Paul and Pillai (1983a; 1983b). Sankaranarayanan and Rosamma (1978) observed high levels of zinc, chromium etc. in the particulate matter of estuarine waters. Sankaranarayanan et al. (1978) recorded high concentrations of zinc, copper, iron etc. in oysters of this region. Murty and Veeraya (1981) reported high spatial variability in the distribution of trace metals (iron, manganese, nickel, cobalt, copper and titanium) in the sediments of the southern parts of the estuary and brought out its dependency on the particle size distribution. Venugopal et al. (1982) studied the levels of copper, manganese, cobalt, nickel and zinc in the sediments from the northern part of the estuary and reported noticeable spatial and seasonal variability. The level of trace metals in water, suspended solids and sediments from the industrial zone and backwater zone was studied by Paul and Pillai (1983a). They have also attempted (Paul and Pillai, 1983b) to study the human exposure to trace metals through contaminated food and concluded that the human population in this region was not exposed to high levels of toxic metals in spite of high levels of contaminants in the environmental samples.

Recently Sivadasan (1987) elaborated on the seasonal distribution of toxic metals, copper, zinc and mercury in an estuarine crustacean. Ouseph (1987) measured the levels of zinc, mercury, chromium, lead and cadmium in the sediments of Cochin estuary and concluded that high content of mercury, zinc and cadmium reach the estuary through industrial wastes.

The speciation studies on the trace metals cadmium, copper and zinc in estuarine waters (Shibu et al. 1990) revealed the influence of environmental factors such as, influx of riverine inputs of metals , introduction of industrial effluents and sewage, modification arising out of anthropogenic activities and hydrographic changes related to complexity of water use on metal speciation and fate in the estuary. Levels of iron, manganese, zinc, copper, cadmium, lead, chromium, cobalt and nickel in surficial sediments of the estuary were studied by Nair et al. (1990). These studies revealed that the metal behaviour in the surficial sediments is influenced by natural as well as anthropogenic factors. Most of the metals considered were found to be significantly enhanced in the lower reaches of the northern parts of the estuary. These high values were attributed to industrial effluents from the factories on the banks of the Periyar river. The studies have also indicated the predominant role of seasonal hydrographic changes in regulating metal levels in the sediments.

1.6 SCOPE OF THE PRESENT STUDY

Although there are a number of references on the trace metal distributions in the sediments of Cochin estuary, no attempt has so far been made to assess chemical partitioning of trace metals in sediments. Indeed, such information is not available for any estuary on the Indian coast, although a few reports on partitioning of heavy metals in deep sea sediments are available (Murty et al. 1973, 1977 & 1980; Rao et al. 1976 & 1978). Initial studies by the author (Nair et al. 1991) have indicated significant spatial variability in the distribution of the different metal forms in the sediments of this region and therefore, an attempt has been made to improve the data base by following a scheme of intensive sampling and analytical determinations. Since the characteristics of estuarine systems are greatly influenced by the monsoonal cycle, a seasonal study is expected to throw much light on the behaviour of metals within the estuarine zone. It would also help to establish the background levels of toxic metals in their different chemical forms for assessment of the extent of environmental pollution. Although total elemental concentrations are rarely sufficient to describe the environmental processes adequately, total amounts are useful for the estimation of the quantitative influence of the various fractions determined.

This report characterises the regional distribution and temporal variability of five different forms (`exchangeable', `carbonate bound', `iron-manganese oxide bound', `organic/ sulphide bound' and `residual') of iron, manganese, zinc, copper, cadmium, lead, cobalt, nickel and chromium in surficial sediments within a broad salinity transition zone where the Periyar and Muvattupuzha rivers enter into the Cochin estuary. The aim of this case study is, thus, to demonstrate the usefulness of the sequential chemical extraction technique in assessing the behaviour of trace metal in estuarine sediments. The study successfully tests whether metal contamination and partitioning differ between an urbanized/industrialized estuarine area and an estuarine region subjected mainly to agricultural runoff. The influence of salinity changes on metal concentration and metal partitioning patterns have also been assessed within the estuary. Specific temporal and chronic influences of local metal inputs on monthly/seasonal variations in metal concentrations are delineated.

The data collected provide a measure of the persistence and bioavailability of trace metals in surficial sediments of Cochin estuary. This information in turn gives a general indication of potential for food chain bio-magnification of these contaminants and an early warning of changes in environmental pollution which will ultimately affect organisms at higher trophic levels.

CHAPTER 2

MATERIALS AND METHODS

2.1 DESCRIPTION OF THE STUDY AREA

2.2 SAMPLING PROCEDURE

2.3 LABORATORY PROCEDURES

2.4 STATISTICAL ANALYSIS

2.1 DESCRIPTION OF THE STUDY AREA

The area of the study, the Cochin estuary and the stations sampled are shown in Fig. 2.1. The Cochin estuary is the largest of the estuaries on the Kerala coast. The hydrography of the estuary is controlled mainly by discharges from Periyar and Muvattupuzha rivers and also by tidal action through the Cochin barmouth. The saline water intrusion to the southern parts of the estuary is regulated by the Thanneermukkam bund (marked as BUND in Fig. 2.1), a salt water barrier commissioned in 1975. Four more rivers, namely, Achancoil, Meenachil, Manimala and Pamba discharge their waters at the southern parts

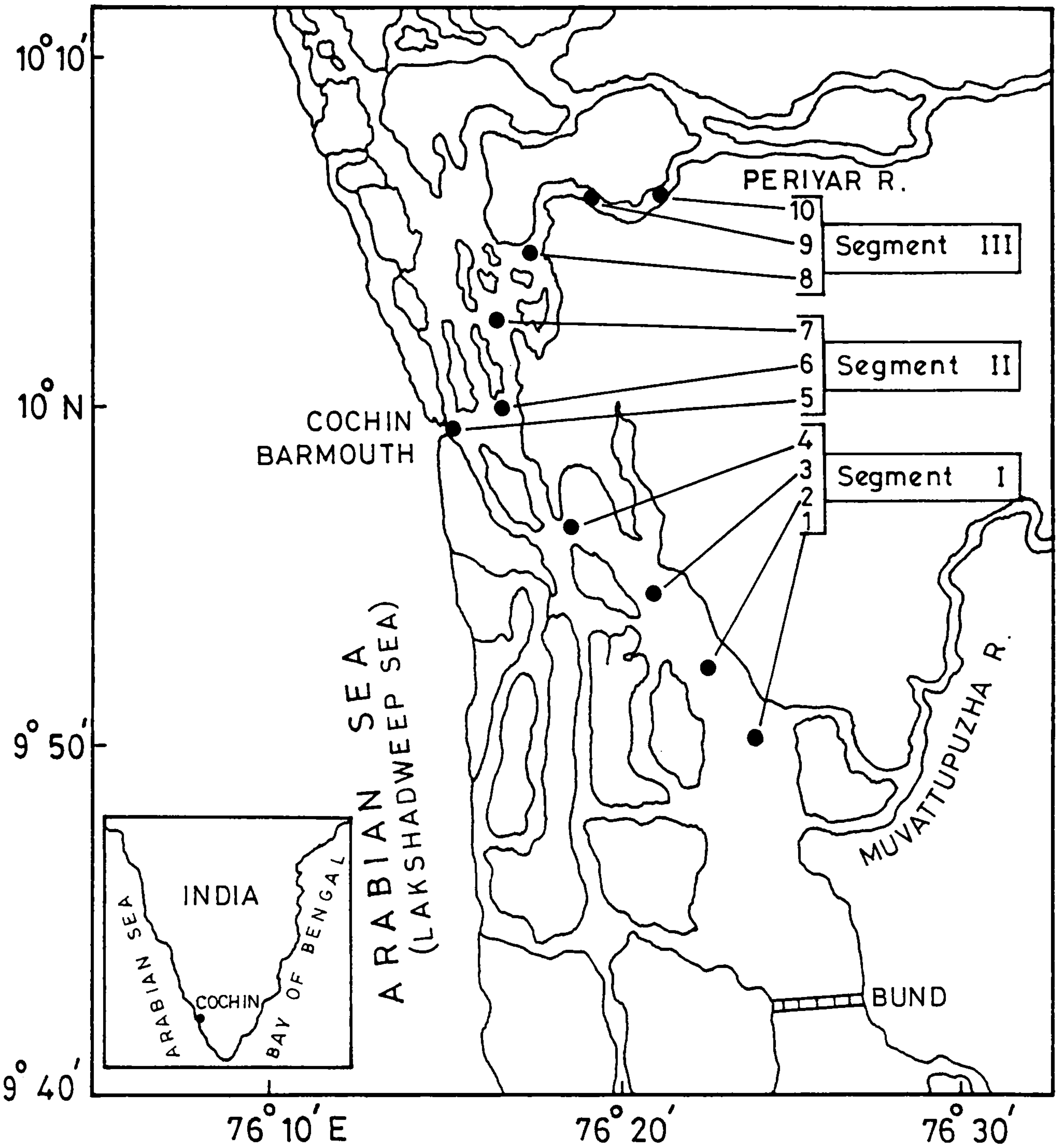

Fig. 2.1 Map of the Cochin estuary showing location of sampling sites (Segment I- Stations 1 to 4; Segment II- Stations 5 to 7 and Segment III- Stations 8 to 10).

as the bund is opened with the

onset of monsoon rains. Hydrographical conditions of this estuary have been altered by the inter basin transfer of water from Periyar river to Muvattupuzha river to facilitate a hydroelectric project.

A large number of heavy industrial units are situated on either banks of Periyar river and hence the northern part of the estuary receives large quantities of treated and untreated industrial effluents. This part receives also the effluents from the sewage treatment plant of Cochin metropolitan city. On the other hand, the southern part of the estuary receives water that drains through vast expanses of agricultural land and point sources of trace metal pollution can hardly be detected.

Samples were collected from ten stations(Stations 1 to 10) sited in the Cochin estuary (Fig. 2.1) at monthly intervals between November 1988 and December 1989. The selection of the sites was based on specific geographical features, water flow regimes and anthropogenic activities. The stations may be subgrouped, under three segments for critical appraisal, as :

Segment I - Stations 1 to 4 - Southern arm of the estuary
Segment II - Stations 5 to 7 - Lower and middle estuary
Segment III- Stations 8 to 10- Northern arm of the estuary

Segment I, the southern arm of the estuary extends up to the southern limit of salt water intrusion and to which point the Muvattupuzha river debou~~n~~ches into the estuary.

Segment II extends from the barmouth up to 10 km on the northern arm of the estuary and contains that part of the estuary that is saline throughout the year.

Segment III extends beyond segment II on the northern arm of the estuary. For most of the time these stations contain only freshwater; saline water intrusion could be recorded only during the periods of very low river discharge. Station 9 located in this segment is the recipient of industrial effluents, and Station 10 located above the industrial zone is free from the influence of industrial pollutants.

2.2 SAMPLING PROCEDURE

The surveys were conducted by means of an exclusively fibre glass dinghy "Flying Fish" of the School of Marine Sciences, Cochin University of Science and Technology. A stainless steel, plastic lined van Veen grab was used to collect the sediments. At each location five to six grab-full of sediments were sampled and the top 5 cm layer was carefully skimmed from all the grabs using a polyethylene spoon, homogenized, and stored at -5° C, in polyethylene containers.

2.3 LABORATORY PROCEDURES

All glassware and plasticware used in the experiments were previously washed, soaked in nitric acid 20% (v/v) and then rinsed with double distilled deionized water. All reagents used were of analytical grade and were checked and excluded for possible trace metal contamination. Reagent solutions and standard solutions were prepared with deionized double distilled water.

i) Chemical partitioning

Trace metals in the sediments were partitioned according to the scheme depicted in Fig 2.2.

The metal species determined were:

Fraction 1. Exchangeable fraction
Fraction 2. Carbonate bound
Fraction 3. Easily reducible fraction (metals combined with Fe-Mn oxyhydrates)

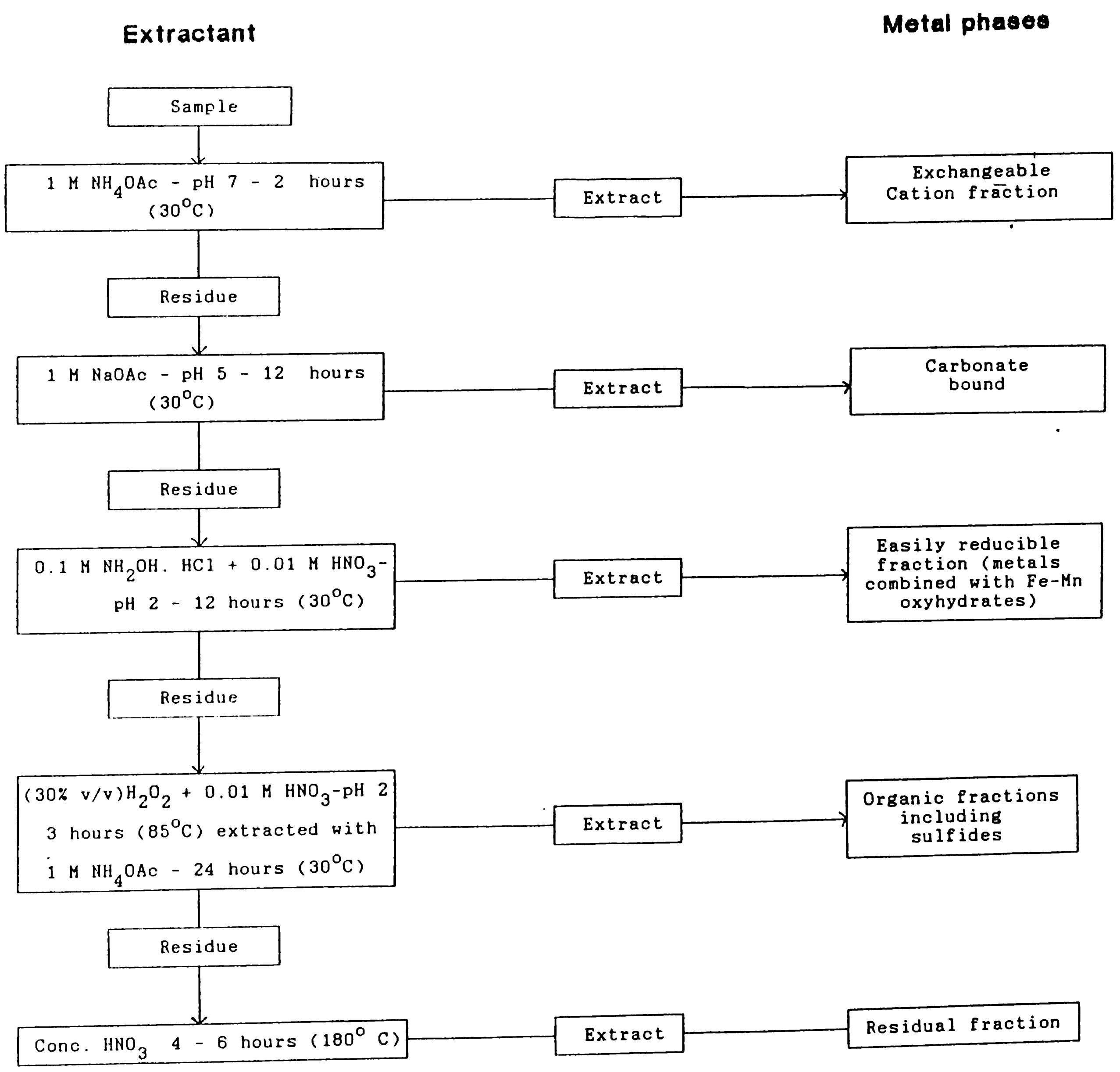

Fig. 2.2 Sequential extraction scheme

Fraction 4. Organic fraction including sulfides
Fraction 5. Residual fraction

8 to 10 g aliquots of the field samples were used for the sequential chemical extraction. The extractions were done in 250 ml Erlenmeyer flasks with continuous agitation. The phases were separated by centrifugation at 6000 rpm for 10 minutes. The supernat~~e~~ant liquid was removed with a pipette and analysed for trace metals (by AAS) whereas the residue was carefully transferred back to the container with the next extractant to be used. Washings in between the extractions were dispensed with to avoid excessive solubilisation of solid phases. The samples were analysed in duplicate and the analysis was repeated when the values differed by over 10 percent. The mean of the two determination has been reported.

(ii) Moisture percentage

Concurrent to partitioning studies, aliquots of sediment samples were carefully weighed out for moisture determination also. The samples were dried at 105° C in an electric oven to constant weight (Hakanson and Jansson, 1983). The moisture was expressed as the percentage weight of water in the total wet weight of the sample. From the percentage moisture values, the sediment metal values were recalculated and the same was expressed in terms of oven dry weight basis.

(iii) Total metals

The oven dry samples were ground to a fine powder in an agate mortar and 1 g aliqot of these samples were used for the determination of total metals. Each sample was carefully digested with 10 ml of a 5:1 mixture of nitric acid and perchloric acid (Lithnor, 1975). The digest was made up to 50 ml and was centrifuged. Trace metals were determined in the supernatent liquid.

(iv) Trace metal analysis

Trace metal concentrations were determined by atomic absorption spectrophotometry (Perkin Elmer Model 2380) involving direct aspiration of the aqueous solution into an air-acetylene flame. A standard addition technique was used for the determination of cadmium, copper, chromium, cobalt, nickel, zinc and lead in the first four fractions extracted. For iron and manganese, the extractants were suitably diluted with deionised double distilled water. Blank corrections were applied wherever necessary.

(v) Precision

In order to determine the precision of the analytical techniques and the reproducibility of data, five sediment samples were selected at random. From each of the five sediment samples, six aliquots each were separately weighed out and subjected to sequential chemical extractions and determination of trace metals. Then the mean, standard deviation and coefficient of variations were worked out. The maximum percentage coefficient variation recorded for the various analytes determined are presented in Table 2.1. The precision was generally low when the concentration approached the detection limits , but improved for higher concentrations. It was observed that the reproducibility of the data was quite good within the operational limits and comparable with values reported in literature for similar studies (Adams et al. 1980; Chester et al. 1988). The precision was much better as the amount of analyte determined increased within limits.

The precision was also checked by summation of the values of all fractions and comparing the same with total metal concentration determined. It was found that the two sets of

Table 2.1 Maximum percentage coefficient variation recorded for the analytes determined.

Metal	M1	M2	M3	M4	M5	Total
Cadmium	10.5	12.3	15.3	8.5	7.0	4.0
Chromium	14.8	15.0	12.8	8.5	6.0	3.8
Cobalt	12.3	11.8	13.4	7.5	5.5	3.3
Copper	8.5	7.3	2.5	6.4	2.8	2.0
Iron	9.7	8.4	12.1	6.8	4.5	3.0
Lead	10.2	9.7	8.8	6.7	4.7	3.5
Manganese	6.2	5.4	4.8	4.7	3.3	2.6
Nickel	8.8	7.3	9.2	6.3	5.1	3.8
Zinc	7.3	6.5	8.3	5.4	3.2	2.2

M1 to M5 denotes the five fractions determined values agreed within 10 percent for ninety percent of the samples. In this thesis, the summation values are presented as `total values' because of the convenience in computing the percentage values.

(vi) Complementary analysis

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

pH : Elico pH meter
Salinity : Argentometry (Strickland and Parsons, 1977)
Dissolved oxygen : Iodometry (Strickland and Parsons, 1977)
Suspended solids : Gravimetry (Butler and McManus, 1979)

The sediments were analysed to determine the organic carbon content by the dichromate method (Walkley and Black, 1934, as modified by El Wakeel and Riley, 1957). The texture analysis was performed as per the technique described by Krumbein and Pettijohn (1938). Exchangeable calcium and magnesium were determined in the ammonium acetate extract by EDTA titration, using Patton and Reeder's indicator for calcium and Solochrome Black T as indicator for calcium plus magnesium (Basset et al. 1978). Magnesium was determined by difference. Total phosphorus was determined in the nitric - perchloric acid extract using phosphomolybdic acid method (Strickland and Parsons, 1977).

2.4 STATISTICAL ANALYSIS

The data management was performed using an HCL PC/XT. Initially the average, standard deviation and percentage coefficient variation for all the parameters recorded were computed to get an idea of the spread of the data. Both spatial and monthly variations were evident. The data were further pooled and season-wise as well as station-wise averages were worked out. The data were subjected to analysis of variance to bring out the significant variations in space and time. Not only the variations but also the interactions were found to be significant. As such the average values had to be interpreted cautiously. In this thesis the spatial variations were discussed mainly on the basis of annual mean concentrations recorded at each station. For discussing seasonal variations, four seasons namely, Winter (December, January, February), Pre-monsoon (March, April, May), Monsoon (June, July, August) and Post-monsoon (September, October, November) have been recognised. Each monthly data was considered as a replicate and the seasonal averages were worked out. The seasonal mean values are presented graphically, station-wise, to bring out the seasonal and spatial variation in metal partitioning. The original data has been utilised to work out the correlations between the parameters investigated.

CHAPTER 3

PHYSICO-CHEMICAL CHARACTERISTICS OF SEDIMENTS

3.1 INTRODUCTION

3.2 MATERIALS AND METHODS

3.3 RESULTS AND DISCUSSION

- 3.3.1 HYDROGRAPHICAL FEATURES
- 3.3.2 SEDIMENT CHARACTERISTICS
- 3.3.3 TRACE METALS
- 3.3.4 CORRELATION BETWEEN VARIABLES
- 3.3.5 THE GEOCHEMICAL BACKGROUND

3.1 INTRODUCTION.

Monitoring of trace metal concentration in sediments is an integral part of any environmental management programme such as mineral exploration (Hawkes and Webb, 1962), pollution assessment (WHO, 1982; Forstner and Wittmann, 1979; Hakanson and Jansson, 1983; Sinex and Wright, 1988; Hoshika et al. 1991), geochemical flux calculations (Burton, 1978; Martin and Maybeck, 1979; Salomons and Forstner, 1984; Seidemann, 1991) and determination of effectiveness of pollution control programmes (Salomons and Eysink, 1981) . Several investigations have been carried out to assess the trace metal content of sediments of the Cochin estuary (Murty and Veerayya, 1981; Venugopal et al. 1982; Paul and Pillai, 1983a; Ouseph, 1987; Nair et al. 1990). These studies differed in approach and were spatially non-comprehensive. Few studies have taken cognizance of the influence of varying hydrographical and sedimentological parameters. The large variations in metal concentrations which are a consequence of the differences in grain size, organic matter content, water content and sources of anthropogenic inputs, make the interpretation of metal concentration in sediments extremely difficult without adequate prior knowledge on sediment and environmental characteristics. River flow, tidal incursions, geomorphology, bathymetry etc. are important factors in an estuary which interact with each other to produce varying patterns of sediment accumulation (Feijtel et al. 1990). Therefore, defining the hydrographical features and sediment characteristics constitute an essential and useful basis for the study of trace metals. In this chapter, the data recorded during the survey (December 1988 to November 1989) on some important hydrographical parameters (salinity, dissolved oxygen, pH and suspended particulate matter) as well as sediment parameters (water content, grain size distribution, organic carbon content, exchangeable calcium, exchangeable magnesium, total phosphorus, total iron, and total trace metals) are presented and discussed.

3.2 MATERIALS AND METHODS

Details are furnished in Chapter 2

3.3 RESULTS AND DISCUSSION

3.3.1 HYDROGRAPHICAL FEATURES

The annual mean values of salinity, dissolved oxygen, pH, and suspended solids recorded at the surface and bottom are presented in Tables 3.1 and 3.2, along with the summary statistics. The seasonal mean values are depicted in Fig. 3.1. The hydrographical features differed greatly between the stations and between seasons. Stations 5, 6 and 7 of Segment II had the highest salinity throughout the year whereas salinity intrusion seldom reached the Stations 8,9 and 10 of Segment III, except during the winter and the premonsoon months, when the river inflow was minimum. On the other hand, all the Stations in the southern arm of the estuary evidenced salinity intrusion except during the months of heavy rains and a characteristic horizontal salinity gradient was obvious. Both surface and bottom salinities decreased with the onset of the monsoon and a distinct stratification was recorded at the barmouth (Station 5) during the monsoon and the postmonsoon periods. Lakshmanan et al. (1982), Sankaranayanan et al. (1986) and several others have recorded similar observations. Thus, the available data on salinity unambiguously established the influence of the influx of fresh water from rivers and intrusion of sea water into the estuary via barmouth, on salinity distribution. The stratification recorded might play an important role in the settling of detritus and hence, in the metal fluxes.

Dissolved oxygen values of both surface and bottom waters exhibited significant spatial and seasonal variation in

Table 3.1 Summary statistics on hydrographical parameters (Salinity and dissolved oxygen)

Station	Mean	SD	C.V.%	Min.	Max.	Mean	SD	C.V.%	Min.	Max.
			Surface					Bottom		
					Salinity					
1	2.0	1.7	87.8	0.0	5.3	6.6	5.8	87.7	0.0	15.0
2	5.4	4.7	87.8	0.0	12.8	7.6	6.9	90.6	0.0	17.3
3	8.6	7.4	86.3	0.2	18.9	8.8	7.5	85.8	0.2	19.2
4	7.2	6.6	92.6	0.0	17.6	8.3	7.4	88.3	0.0	20.0
5	16.0	10.0	62.7	1.3	31.5	27.6	5.1	18.6	15.1	33.6
6	14.3	9.3	64.6	2.7	29.5	19.7	10.5	53.3	5.5	32.2
7	5.4	4.7	87.2	0.7	16.5	8.1	7.2	88.9	0.6	23.1
8	1.2	1.8	155.9	0.0	6.1	2.1	3.6	175.0	0.0	12.6
9	0.3	1.0	331.7	0.0	3.5	0.7	2.0	268.5	0.0	7.2
10	0.3	1.0	331.7	0.0	3.5	0.4	1.3	331.7	0.0	4.8
					Dissolved oxygen (ml/l)					
1	5.2	1.2	23.9	4.0	8.4	4.9	1.0	20.6	3.7	7.3
2	5.6	1.3	24.1	3.8	8.5	4.9	1.6	32.3	3.2	8.7
3	3.1	1.0	32.5	1.5	5.3	3.8	1.3	32.8	1.3	6.8
4	3.0	1.3	42.2	1.3	6.6	3.2	0.5	15.6	2.4	4.0
5	6.1	1.5	24.1	4.1	9.1	5.7	2.2	39.0	2.3	8.8
6	7.1	1.7	23.6	3.6	9.1	6.6	1.6	24.6	4.5	9.5
7	7.4	1.8	24.7	4.3	10.2	7.1	1.6	23.1	4.6	9.8
8	7.4	1.7	23.0	4.3	9.5	7.9	1.8	23.0	5.0	11.1
9	7.8	2.2	28.0	5.2	11.4	7.2	2.5	34.9	2.5	11.4
10	7.4	2.2	30.0	4.1	11.4	7.5	2.5	33.1	3.0	11.4

Table 3.2 Summary statistics on hydrographical parameters (pH and suspended solids)

Station	Mean	SD	C.V.%	Min.	Max.	Mean	SD	C.V.%	Min.	Max.
			Surface					Bottom		
					pH					
1	7.0	0.2	2.9	6.6	7.3	7.0	0.2	2.3	6.7	7.3
2	7.0	0.2	2.9	6.7	7.5	7.1	0.2	2.5	6.8	7.4
3	7.0	0.2	2.6	6.7	7.3	6.9	0.3	4.5	6.0	7.2
4	7.0	0.2	3.4	6.7	7.5	7.0	0.1	2.0	6.8	7.3
5	7.4	0.3	3.7	7.0	8.0	7.4	0.2	3.3	7.2	8.0
6	7.3	0.3	4.0	6.9	7.9	7.3	0.3	4.1	6.9	8.0
7	7.2	0.2	3.0	6.9	7.7	6.6	1.9	28.9	4.3	7.8
8	7.0	0.2	2.5	6.6	7.2	7.1	0.2	2.9	6.7	7.5
9	6.8	0.7	11.0	4.5	7.7	6.8	0.8	11.3	4.4	7.5
10	6.9	0.8	11.5	4.3	7.3	6.8	0.8	11.6	4.3	7.4
					Suspended solids (mg/l)					
1	5.9	4.6	77.7	1.4	15.2	14.5	8.9	61.6	5.0	36.4
2	9.2	4.9	53.2	4.4	20.3	16.1	7.0	43.8	4.2	27.4
3	21.8	13.4	61.5	1.2	54.4	24.0	14.2	59.1	5.2	56.4
4	14.2	7.4	51.8	4.7	26.1	23.7	9.0	37.8	10.4	36.1
5	20.6	23.4	113.8	7.7	97.2	68.8	49.7	72.2	9.3	201.1
6	17.3	12.8	74.0	3.5	48.3	72.9	75.7	103.9	14.3	289.1
7	11.4	12.7	111.1	1.5	41.0	11.2	5.5	49.0	2.8	21.3
8	6.7	6.5	97.1	1.5	25.4	7.7	3.7	47.7	2.2	15.2
9	8.0	8.9	110.2	1.3	32.9	8.9	10.4	116.5	2.2	41.8
10	7.3	8.6	117.7	1.3	29.4	9.9	8.7	88.6	2.1	32.1

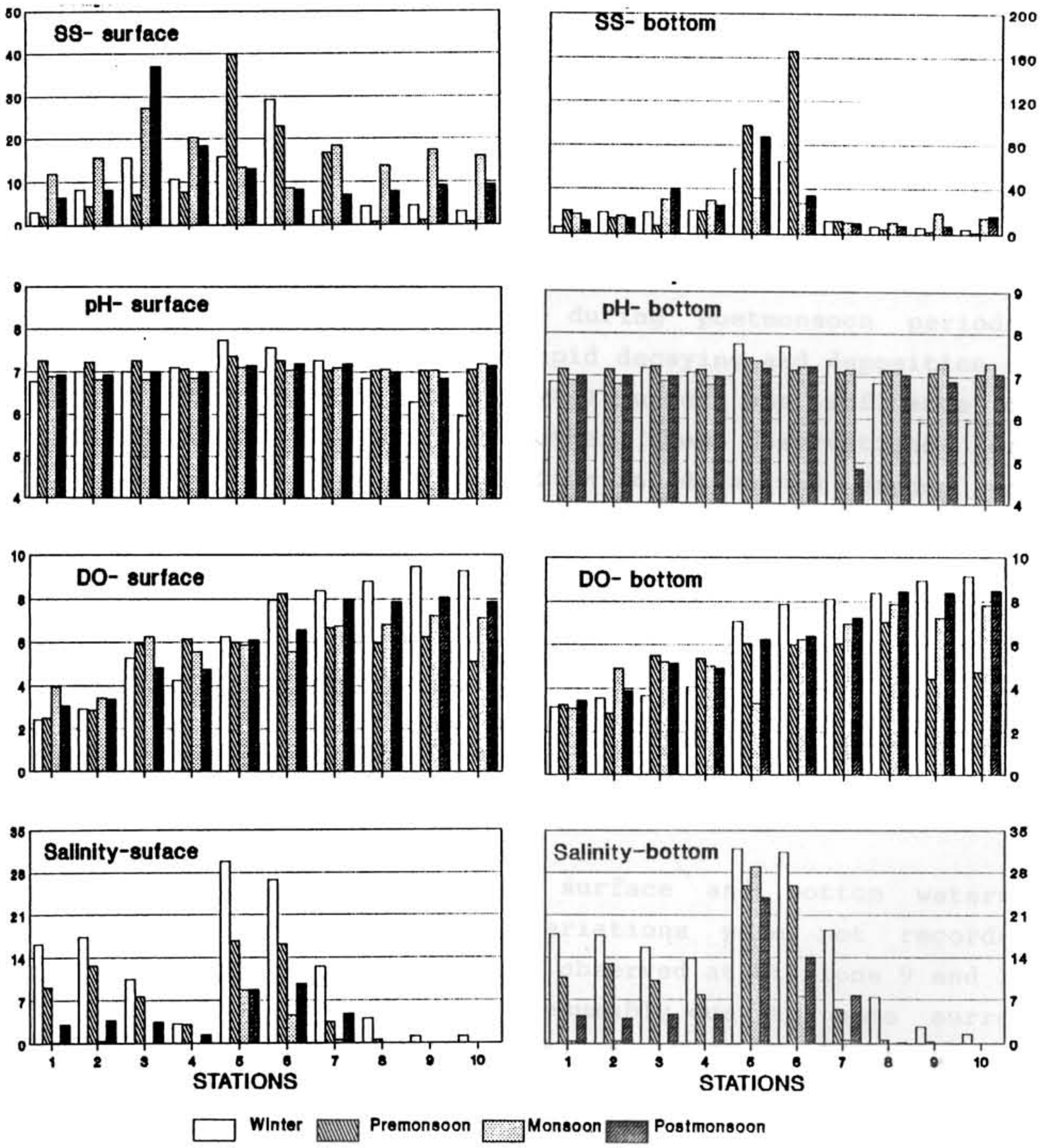

Fig. 3.1 Seasonal mean values of hydrographical parameters
(SS = suspended solids (mg/l); DO = dissolved oxygen (ml/l))

conformity with observations recorded by earlier workers (Vijayan et al. 1976; Sarala Devi et al. 1979; Anirudhan, 1988). Except for the Stations 5 and 6 in the lower reaches of the northern arm of the estuary, the surface waters recorded the lowest values of dissolved oxygen during the premonsoon months. This may be due to the high temperature prevailing during this period. Dissolved oxygen values were relatively lower in the southern part of the estuary, especially during the postmonsoon and the winter periods. Nair et al. (1990) observed comparatively high content of dissolved organic matter in this part of the estuary during postmonsoon periods. Gopalan et al. (1987) reported rapid decaying and deposition of salvinia (a freshwater macrophyte) under the influence of intruding saline waters. Put together, these observations lead to the conclusion that the depletion in dissolved oxygen was due to the rapid decomposition of organic matter. The lowest value for dissolved oxygen was recorded at Stations 3 and 4 on the southern arm, during the winter season. The variations between the surface and bottom waters were insignificant. In the riverine reaches of the estuary the dissolved oxygen content was comparatively higher during the monsoon season and it could be attributed to the high turbulence in river flow during this rainy period.

With regard to the pH of surface and bottom waters, significant seasonal or spatial variations were not recorded except for the high acidic waters observed at Stations 9 and 10 during December 1988; this was presumably due to some surreptitious discharge of acid containing industrial effluents. There was a steady increase of pH from 6.8 to 7.4 as the river water mixed with saline waters in the northern arm, but in the southern arm such a variation was not noted.

The highest concentration of suspended matter in the water column corresponded with periods of maximum river discharge in the upstream stations (Fig. 3.1) and with the period of maximum primary productivity in the lower reaches of the estuary. Suspended matter concentrations in the surface waters of the estuary were, thus, controlled by seasonal fluctuations of river runoff and biological productivity, with river runoff being predominant during the monsoon months and biological productivity being predominant during the premonsoon months. In near bottom waters, suspended matter concentrations were 3-4 times higher than surface water values and showed no obvious seasonal variability. The near bottom concentration increases were related to local resuspension events which were effected by tides and the input of fresh water from rivers.

3.3.2 SEDIMENT CHARACTERISTICS

The sediment-associated parameters considered in the present study were moisture content, grain size distribution, organic carbon content, exchangeable calcium, exchangeable mangnesium, total phosphorus and total iron. The twelve monthly mean and standard deviation determined for these parameters at the ten stations surveyed are presented in Table 3.3 to 3.6 · Fig. 3.2 depicts the seasonal mean values. Lower values were observed for the sediments of Segment III, whereas higher values were recorded for the sediments of Segment II. Seasonally (Fig. 3.2), the monsoonal values were lower except for Stations 1 and 2 in Segment I. The premonsoonal values were generally higher than those of other seasons. The variation in water content could be attributed to the variations in organic matter and clay content.

Natural sediments consist of particles of varying sizes and for deciding the size groups, several class intervals based on average diameter have been suggested. One such system includes the grading of particles into sand (>63μm) silt (4-63μm) and clay (<4μm) sizes (Krumbein and Pettijohn, 1938).

Table 3.3 Stationwise summary statistics on sediment parameters (moisture, sand and silt)

Station	Mean	SD	C.V.%	Min.	Max.
			Moisture %		
1	26.76	10.21	38.17	18.50	49.30
2	25.16	2.58	10.25	20.60	31.20
3	31.70	10.31	32.51	23.20	58.90
4	31.07	10.14	32.65	20.20	55.50
5	44.50	8.31	18.68	28.60	56.40
6	51.15	3.17	6.20	47.00	57.80
7	37.80	8.15	21.57	27.80	52.30
8	20.31	2.27	11.17	16.80	24.30
9	21.13	3.75	17.73	16.80	32.60
10	19.56	2.68	13.71	14.30	25.00
			Sand %		
1	82.37	12.08	14.66	62.31	97.12
2	83.88	7.37	8.78	67.26	90.37
3	75.93	20.36	26.81	25.41	91.34
4	78.05	18.04	23.11	33.88	91.69
5	39.97	23.72	59.34	10.79	83.99
6	15.65	10.07	64.34	4.00	35.88
7	63.53	21.72	34.19	26.83	89.39
8	97.04	1.93	1.99	93.03	99.26
9	96.14	2.80	2.91	90.07	99.50
10	93.76	4.52	4.82	82.46	98.17
			Silt %		
1	7.94	5.90	74.21	1.05	18.37
2	9.20	5.67	61.70	2.88	20.64
3	11.81	10.18	86.26	3.31	36.26
4	13.67	13.04	95.35	2.58	44.93
5	36.25	16.74	46.18	5.89	52.90
6	46.69	8.77	18.78	32.55	57.45
7	17.82	10.64	59.73	4.13	39.62
8	1.01	0.79	78.18	0.25	2.72
9	1.99	1.31	66.07	0.12	4.25
10	3.10	2.84	91.64	0.49	9.24

Table 3.4 Stationwise summary statistics on sediment parameters (clay, < 16 µm fraction and organic carbon)

Station	Mean	SD	C.V.%	Min.	Max.
			Clay %		
1	9.68	6.26	64.64	1.83	19.32
2	6.92	2.22	32.01	4.10	12.10
3	12.26	10.35	84.37	3.85	38.33
4	11.60	9.01	77.65	4.78	33.90
5	22.13	10.00	45.17	10.12	46.20
6	37.66	3.18	8.44	31.55	43.14
7	18.65	11.37	60.96	6.48	36.80
8	1.95	1.31	67.29	0.23	4.25
9	1.88	1.58	84.35	0.25	5.68
10	3.14	1.84	58.62	0.75	8.30
			<16 µm size fraction %		
1	12.51	7.98	63.78	2.15	27.34
2	9.79	3.09	31.59	6.00	16.35
3	18.24	17.98	98.57	5.79	61.95
4	16.01	12.89	80.52	6.25	48.50
5	35.41	18.10	51.13	13.12	67.02
6	62.21	7.65	12.30	49.85	70.90
7	28.48	16.95	59.49	9.75	54.55
8	2.55	1.65	64.72	0.38	5.20
9	2.88	2.04	70.66	0.44	7.35
10	4.17	2.69	64.53	0.98	11.33
			Organic carbon (mg/g)		
1	7.72	5.58	72.24	1.70	19.35
2	5.12	2.20	43.05	3.00	10.35
3	9.04	6.31	69.87	3.72	23.32
4	8.68	6.40	73.70	1.62	26.46
5	21.42	7.16	33.43	6.90	28.74
6	29.76	3.54	11.89	22.32	33.54
7	21.89	9.26	42.32	7.77	34.98
8	1.59	1.20	75.86	0.36	4.68
9	2.60	3.88	149.22	0.18	14.08
10	1.66	1.28	76.73	0.30	4.53

Table 3.5 Stationwise summary statistics on sediment parameters (exchangeable Ca, Mg and Ca+Mg).

Station	Mean	SD	C.V.%	Min.	Max.
		Exchangeable Ca (meq/100g)			
1	1.88	0.75	39.76	0.96	3.64
2	2.33	1.16	49.88	1.37	5.41
3	5.60	2.61	46.58	0.41	11.19
4	4.99	1.69	33.87	2.53	8.34
5	16.52	3.17	19.22	11.90	22.36
6	14.73	3.71	25.17	7.79	21.41
7	3.53	2.12	59.90	0.90	8.28
8	0.74	0.83	113.02	0.06	3.20
9	0.43	0.50	115.12	0.03	1.56
10	0.37	0.30	80.53	0.04	0.90
		Exchangeable Mg (meq/100g)			
1	2.85	1.10	38.67	1.72	5.46
2	2.50	1.11	44.54	0.77	4.95
3	4.45	3.82	85.80	0.49	15.36
4	3.10	2.61	84.24	0.45	7.50
5	11.33	2.85	25.13	5.40	14.42
6	16.59	5.36	32.31	7.63	30.92
7	4.22	4.00	94.87	0.92	14.40
8	0.87	1.29	148.77	0.06	4.60
9	1.76	4.20	238.52	0.03	15.23
10	0.56	0.79	141.24	0.03	2.80
		Exchangeable Ca + Mg (meq/100g)			
1	4.73	1.34	28.40	3.02	7.34
2	4.84	1.33	27.47	2.51	6.73
3	10.05	5.92	58.96	3.21	26.55
4	8.09	3.02	37.28	3.83	12.60
5	27.85	4.70	16.86	17.62	35.33
6	31.32	5.72	18.25	21.19	43.03
7	7.75	4.69	60.49	2.00	17.05
8	1.60	2.09	130.72	0.12	7.80
9	2.19	4.62	210.50	0.06	16.79
10	0.93	0.98	106.07	0.07	3.70

Table 3.6 Stationwise summary statistics on total phosphorus and iron.

Station	Mean (mg/kg)	SD	Min. (mg/kg)	Max. (mg/kg)
		Phosphorus		
1	472.2	280.7	218.9	1336.7
2	431.0	101.5	313.7	651.0
3	1100.0	993.6	456.8	3526.2
4	750.8	125.3	549.5	940.2
5	1620.4	458.1	1067.2	2597.5
6	2185.0	340.8	1675.6	3003.5
7	1995.5	660.5	1255.9	3241.2
8	406.0	180.9	144.1	677.4
9	325.5	157.8	96.2	606.6
10	318.4	165.4	122.8	669.6
		Iron		
1	7898.6	1665.8	5515.7	10636.8
2	8302.1	851.1	7126.6	9972.2
3	6585.2	931.1	4998.2	8500.6
4	6928.6	953.8	5551.8	8780.4
5	14543.1	2173.6	11655.1	18886.2
6	15982.3	2437.6	12554.4	20182.8
7	7700.7	1083.7	5593.3	9502.3
8	5007.0	817.4	4021.0	6941.7
9	4655.8	1460.8	2810.9	7918.0
10	5642.2	1164.3	3863.3	7326.9

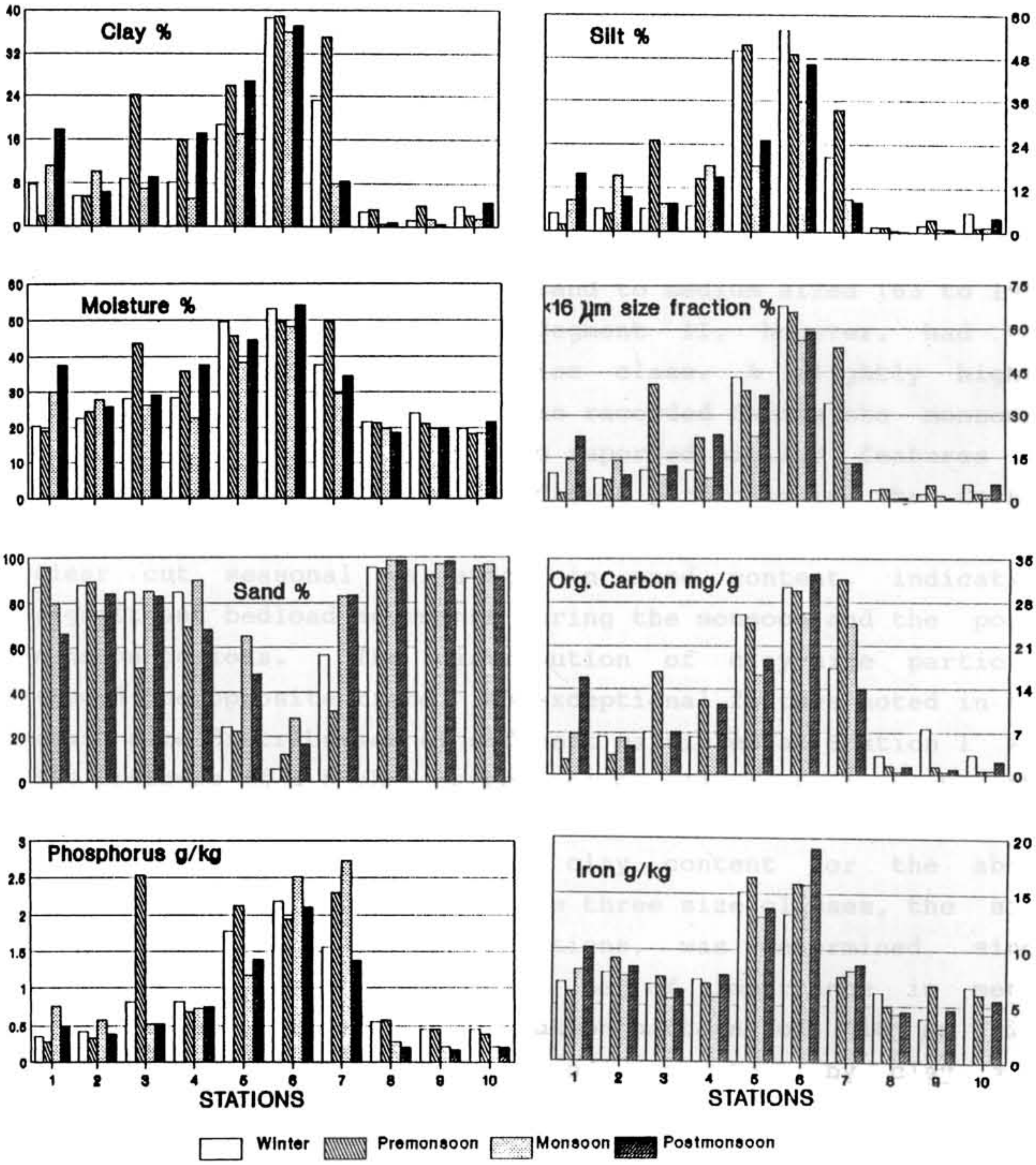

Fig. 3.2 Seasonal mean values of sediment characteristics

The Shepard (1954) diagram is utilised to describe the composition of grain sizes. The relative abundance of the various grain-size groups in the surficial sediments are presented in Tables 3.3 and 3.4. The seasonal variations are presented in Fig. 3.2. The sediments of Segment III were mainly composed of sand particles. Cobbles and gravel also constituted a major fraction of the sediments, especially in the samples collected during the monsoon period. In the sediments of Segment I also (Stations 1 to 4) sand size particles constituted the bulk of the sediment, but the size of the particles varied from fine sand to medium sized (63 to 1000 μm) grains. The sediments of Segment II, however, had the lowest contribution from this size class. A slightly higher sand percentage, neverthless, was recorded during the monsoon. Recently, Sundaresan (1991) also reported similar features in the seasonal distribution of sediment particles in the Cochin harbour area. Sediments of Station 7 in Segment II showed a clear cut seasonal variation in sand content, indicating significant bedload movements during the monsoon and the post-monsoon periods. The distribution of clay-size particles showed the opposite trend. An exceptional feature noted in the grain size distribution of sediment particles at Station 1 was the presence of a higher percentage of clay content during the monsoon and the postmonsoon seasons at Station 1, whereas the general trend was a depletion in clay content for the above periods. In addition to the above three size classes, the size group consisting of <16 μm fractions, was determined, since this fraction was considered to be of importance in metal transport in estuaries. Distribution pattern of <16 μm size fraction followed the same trends as shown by clay size particles.

The sediment distribution pattern in an estuary depends on several factors such as sediment sources, the texture of the sedimentary material supplied, the bottom topography of the basin and general hydrographic features (Seralathan, 1986). In the Cochin estuary, the bulk of the sedimentary material is being supplied by the two rivers, the Periyar on the north and the Muvattupuzha on the south, mainly during the rainy months (i.e. from June to September). The sediments are transported as bedload as well as suspended load (Veerayya and Murty, 1974). The percentage distributions of different size fractions of sediments broadly indicated the existence of a partition between the coarser and finer components of the sediments. Coarse sand dominated in the upper reaches (Segment III) of the northern arm, whereas medium to fine sand and silt dominated the southern parts (Segment I). Major part of Segment II was underlain with sediments of fine size. Further, it was indicated that in the estuarine region, the settling of finer fractions of the sediments took place preferentially during the winter and pre-monsoon season. The decreased percentage of the silt and other finer particles during the monsoon periods could be attributed to flushing of finer materials from the estuarine region to the sea. Likewise, the increase noted in the case of finer fractions during the winter and premonsoonal period could be attributed to the low fluvial discharge and a better mixing of saline and freshwater that facilitated flocculation and settling of suspended particles.

The distribution pattern of organic carbon content also exhibited distinct spatial and seasonal trends (Fig. 3.2). Relatively higher values were recorded for the sediments of Segment II. The coarse sandy sediments of Segment III were associated with the minimum content of organic carbon. Seasonal maximum was recorded during the pre-monsoon period and minimum during the monsoon period. A comparison of data on grain size distribution and organic carbon distribution revealed that the organic carbon distribution in estuarine sediments followed broadly the sediment distribution pattern, in that, finer the sediment, higher was the organic carbon content. Both were high in sediments of mid-estuarine reaches in the north. From this relation it could be inferred that the adsorption of organic compounds onto clay minerals was promoted under saline conditions; organic coating on clay minerals affected the size distribution and settling rates of inorganic particles and thus contributed to the increase in both clay-size particles and organic matter.

The present study was confined to the 0-5cm layer of surface sediments, which was usually influenced by the varying inputs into the estuary. Qasim and Sankaranarayanan (1972) studied the seasonal variations in the quantity and composition of detritus which settled to the bottom and reported that the bottom sediment was chemically similar to the detritus. These authors had also noted that the quantity of settled detritus was minimum during the monsoon and postmonsoon periods when the turbidity in the estuary was maximum; they attributed it to the stratification which developed in the estuary from June to October as a result of discontinuity in the vertical profiles of temperature and salinity, which probably reduced substantially the settling rates of detritus. The rate of detritus settlement showed a sharp increase as the estuary returned to a well-mixed condition. The seasonal variations observed in fine particle composition and organic carbon content, during the present study, also indicated that surficial sediments were quite sensitive to the periodic addition of detritus, mainly composed of inorganic matter (fine silt and sand) to which organic matter adhered and formed aggregates.

Calcium and magnesium ions determined in neutral, normal ammonium acetate was designated as `exchangeable' and expressed as milliequivalents per 100g of sediment. The content of these in the surficial sediments seemed to be regulated by both salinity of ambient water and particle size distribution in sediments. It is interesting to note that magnesium and calcium shared the available sorption sites almost equally in both riverine and estuarine sediments.

Total phosphorus determined in the sediments after digestion with nitric-perchloric acid mixture exhibited significant seasonal and spatial variations. The highest value was recorded in the sediments of Segment II and the spatial distribution pattern followed the texture in the sense that higher the percentage of finer particles, higher was the phosphorus content. This dependency of phosphorus content on particle size is in agreement with an earlier report by Murty and Veerayya (1972) from the southern parts of the estuary. The post-monsoonal values were high except at Stations 1, 2, 6 and 7 where the maximum was recorded during the monsoon. Seasonal fluctuations and range of values recorded during the current investigations were in unison with the observations of Sankaranarayanan and Punampunnayil (1979).

Total iron values in the estuarine sediments varied from 2811 to 20183 mg/kg (Table 3.6). The highest value was observed at Station 6 (Segment II) during the postmonsoon season (Fig. 3.2). Stations 2, 3 and 4 of Segment I, 5 of Segment II and 8, 9 and 10 of Segment III, recorded the minimum iron concentrations during the monsoon season. The winteral/premonsoonal values were generally higher at these Stations. For the remaining Stations (Stations 1 of Segment I, 6 and 7 of Segment II) the minimum value for total iron was recorded during winter with values increasing slightly through monsoon and post monsoon. The variation in seasonal distribution followed the trends observed in the case of total phosphorus and a close association of these two elements was indicated. It was concluded from the above relation that the iron supply to the estuary mainly depended on land drainage and erosion of agricultural soils of this tropical region, where iron phosphate formation was the rule rather than a mere probability as judged from chemistry of tropical soils (Juo, 1981).

3.3.3 TRACE METALS

The summary statistics giving the minimum and maximum values, mean, standard deviation and percentage coefficient variation of the total content of iron, manganese, zinc, copper, cadmium, lead, cobalt, nickel and chromium in sediments of the Cochin estuary are furnished in Table 3.7. The concentration of these metals varied over a wide interval; the minimum variation (%CV= 47.41) was recorded in the case of iron and maximum (%CV = 113.32) for cadmium. The percentage coefficient variation had a bearing on the abundance of metals: iron was the most abundant (mean = 8325 mg/kg) and cadmium, the least abundant (mean = 1.66 mg/kg) metal in this system. The observed order of abundance of other metals was, zinc> manganese > chromium > nickel > lead > copper > cobalt.

The ranges, mean and the 95% confidence intervals for the mean of the total concentrations of the nine metals studied are presented stationwise in Fig. 3.3. The data revealed the following salient features with regard to the spatial distribution of trace metals in the sediments of the Cochin estuary.

(i) The highest values, for all the nine metals studied were recorded in the sediments of Segment II (Stations 5 to 7)

(ii) The contents of iron, manganese, cobalt, nickel, chromium and copper were higher in the sediments of Segment I (Stations 1 to 4) in comparison to that of Segment III (Stations 8 to 10)

(iii) The content of zinc was slightly higher in sediments of Segment III than that of Segment I.

Table 3.7 Summary statistics on total metal distribution (n = 120)

Metal	Mean (mg/kg)	SD	CV%	Min. (mg/kg)	Max. (mg/kg)
Iron	8325	3947	47	2811	20183
Manganese	66.03	48.32	73.18	7.00	169.60
Zinc	70.40	67.22	95.48	13.53	258.89
Copper	12.20	11.43	93.70	1.33	50.19
Cadmium	1.66	1.88	113.22	0.34	8.44
Lead	14.86	10.99	73.95	3.49	49.85
Cobalt	9.23	6.89	74.57	1.29	24.92
Nickel	21.15	17.74	83.88	1.86	70.63
Chromium	29.99	24.80	82.70	4.13	99.73

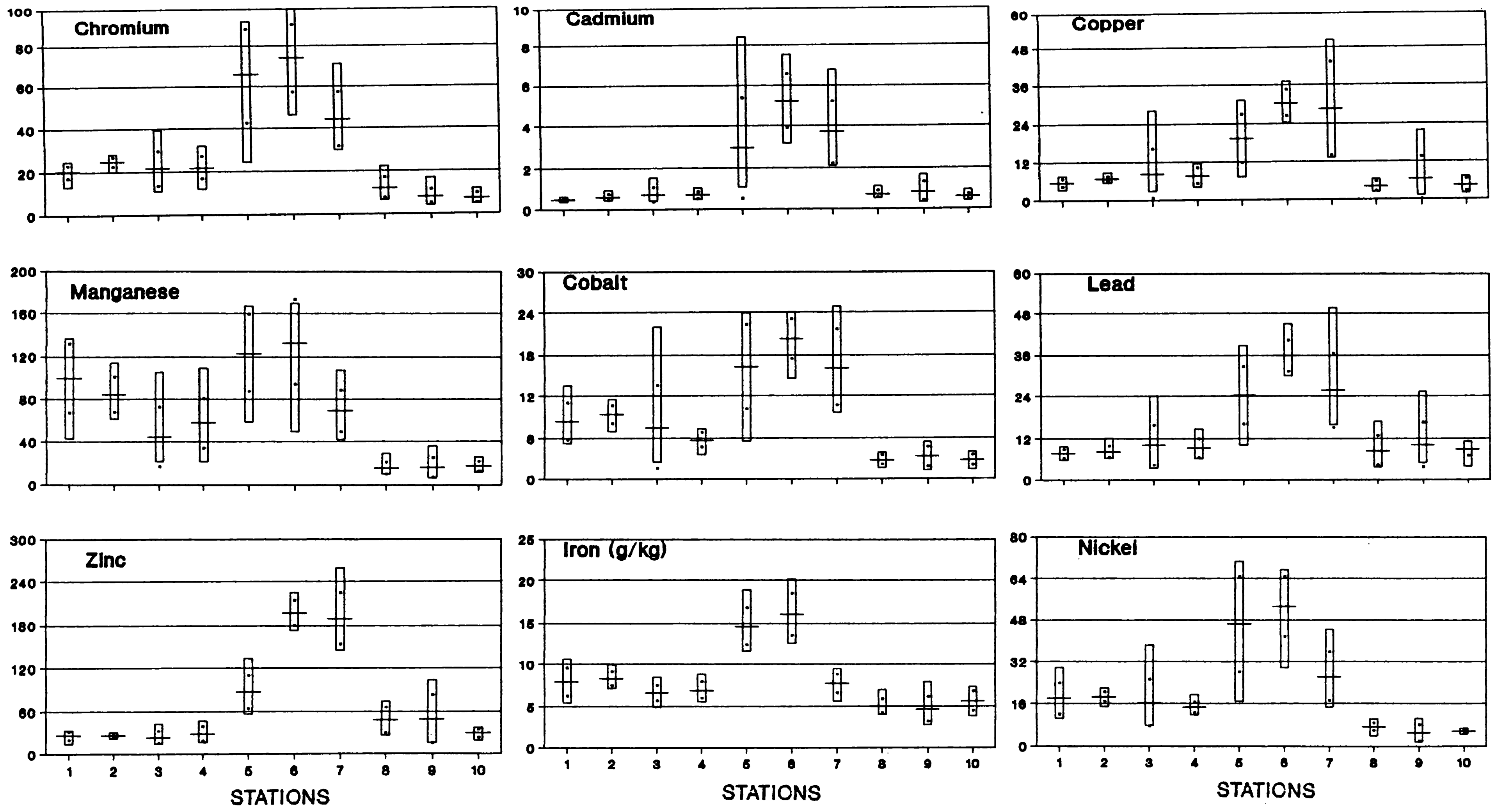

Fig. 3.3 Spatial distribution of total trace metals in sediments of the Cochin estuary; Range (bar ends), Mean (cross line) and Standard deviation (points). All values in mg/kg dryweight except iron which is in g/kg.

(iv) Total lead and cadmium were distributed more or less in equal levels in Segments I and III.

(v) Within Segment I, the concentration of manganese, iron, chromium, nickel and cobalt exibited a slight decreasing trend towards the marine side.

The above observations demonstrated that the total concentration of metals in sediments was biased towards particle size distribution in sediments which in turn was controlled by the fluvial processes that operated at each Station. Thus in Segment II, the zone of accumulation where the fine suspended particles got deposited at a faster rate, the total metal concentrations were relatively high. The stations of Segment III located on the northern arm of the estuary, which was erosional in character, as revealed by the coarse texture of the sediments, contained low levels of metals. Sediments of Segment I, in the southern arm of the estuary which was transportational in character, had intermediate metal values. However, an exemption to the above generalisation was noted in the case of zinc as the values were higher in Segment III than in Segment I, and this exceptional behaviour could be attributed to anthropogenic inputs from the chemical industries operating on the banks of Periyar river as have been well documented (Venugopal et al. 1982; Paul and Pillai, 1983; Nair et al. 1990)

In order to reduce the bias due to the textural class differences, metal data were normalised to the iron values and the seasonal mean values were computed. Iron was selected primarily because of its abundance and also because of its well established estuarine behaviour. The data presented in Fig. 3.4 brought out some additional information on the distribution pattern of trace metals. One striking observation was that the spatial distribution pattern of the trace metals cadmium,

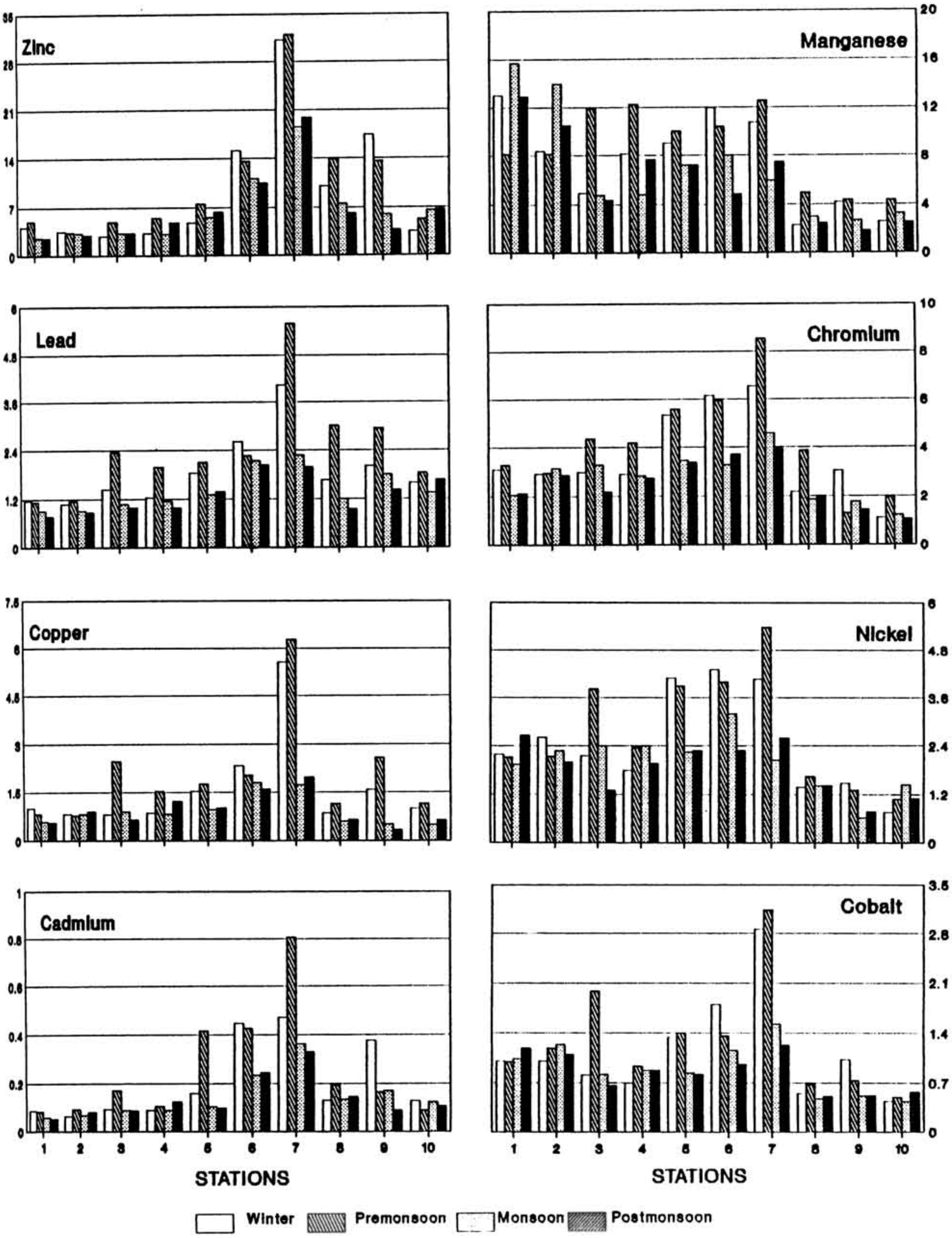

Fig. 3.4 Seasonal mean values of total trace metals expressed in mg/g of iron in sediments

copper, lead and zinc were quite similar. In the northern arm of the estuary these metals exhibited a gradual increase from upstream upto the middle estuary (Station 7) and then a sharp decrease towards the marine regions. In the southern arm of the estuary also these metals exhibited a slight increasing trend towards the marine side. The uniform distribution pattern suggested similar transportation and mixing behaviour for these metals in this estuary. A decrease in the content of copper, lead and cadmium in the estuarine sediments under the marine influence was recently reported by Forstner et al. (1990) for the Elbe estuary and they observed that the same corresponded with an increase in marine borne sediments which diluted the contaminated sediments. Similar conclusions were made by Nolting et al. (1990) from studies in the Rhine and Meuse estuaries. Several other workers attributed this reduction in trace metal content of sediments to desorption reactions as the particulates interacted with saline waters of high ionic strengths (Aston, 1978; Keeny-Kennicutt and Presley, 1986). For the Cochin estuary also, it was reported that the sediments of the harbour area was comprised of both riverine and marine inputs (Gopinathan and Qasim, 1971; Pillai, 1989) and that the sediments from inshore region were transported into the estuary (Gole and Tarapore, 1966) under the influence of tidal action. Hence the reduction in metal values could be ascribed to both the events: dilution by marine-borne particles and desorption under the influence of saline waters.

The metals nickel, chromium and cobalt also exhibited a decreasing trend towards the marine side in Segment II, especially during the periods of increased salinities, but the decrease was not as sharp as was noted for zinc, lead, copper and cadmium. However, the behaviour of manganese was exceptional and the values did not exhibit any variation between the Stations in Segment II (Fig. 3.4). This exceptional behaviour of manganese was reported from other estuaries as well (Wollast et al. 1979; Trefry and Presley, 1982; Wilke and Dayal, 1982). This was attributed to the fact that the manganese was not readily susceptible to impoverishment in nearshore marine sediments. However within Segment I, manganese values decreased sharply from riverside to marine side. Higher manganese content in low-saline and freshwater sediments was reported also from the Hudson estuary (Williams et al. 1978). A decreasing trend from head to mouth was observed in the case of cobalt and nickel also, in Segment I.

The increasing trend in the total content of cadmium, copper, lead and zinc within Segment I and III towards the marine side was attributed to the increasing influence of salinity during flocculation, precipitation and settling of fine colloidal and suspended particles. Manganese requires a higher salinity (Fukai and Huynh-Ngoc, 1968) for precipitation and therefore may move unchanged within this estuary. However, the sharp downstream decrease noted in the case of manganese, cobalt and nickel in Segment I could not be explained on the basis of these chemical factors, and this aspect would be considered in greater detail while discussing seasonal variations.

The seasonal variations in total trace metal content are also depicted in Fig. 3.4. The salient results that could be summarised from the data are as follows.

i) All metals exhibited significant seasonal variations with lower values during the monsoon and postmonsoon periods (corresponding to high discharges through the river), and higher values during the winter and premonsoon. For all the metals, the highest seasonal value was recorded during the premonsoon period almost at all stations.

ii) Seasonal variations were not very conspicuous for Stations located in the southern part of the estuary (Segment I), as it was for Stations on the northern arm of the estuary (Segment II and III)

iii) Sediments from Stations 1 and 2 located on the southern most part in Segment I, exhibited an exceptional behaviour in the seasonal distribution of trace metals. A well defined seasonal pattern, as observed at the other Stations was absent here, and most of the metal values were slightly higher during the monsoon in comparison to the premonsoon values.

When the data on seasonal distribution of total metals were further examined together with the data recorded by earlier workers (Nair et al. 1990) a sinusoidal type of variation in metal levels was indicated . This cyclical seasonal pattern with a minimum during monsoon and maximum during premonsoon was most pronounced for the stations located on the northern arm of the estuary. The premonsoonal maxima in trace metal content could be related to the biogeochemical changes occurring in the river itself and also to the hydrological and sedimentological character which vary along with reduced discharge rate conditions during these months. The premonsoon maxima coincided with a salinity maximum of the ambient water and also with an increase in sediment organic carbon. It is postulated that, during periods of low riverine flow, the longer residence times of water and suspended matter would result in an enhancement of metal scavenging, coagulation and settling, resulting in higher content of metals in sediments.

The seasonal enrichment factors on total trace metals, organic carbon and <16 μm size fractions are presented in Table 3.8. The values were obtained by dividing the mean seasonal value with the mean monsoonal value at each station. At a given Station, the seasonal enrichment factors for the different

Table 3.8 Seasonal enrichment of trace metals, organic carbon (O.C.) and <16 µm size fraction.

Station	Fe	Mn	Zn	Cu	Cd	Pb	Co	Ni	Cr	O.C.	<16 µm
	a) Winter/Monsoon										
1	0.9	0.7	1.4	1.5	1.3	1.1	0.8	1.0	1.3	0.8	0.7
2	1.0	0.6	1.1	1.0	1.0	1.2	0.8	1.2	1.0	1.0	0.6
3	1.2	1.2	1.0	1.1	1.3	1.6	1.2	1.1	1.1	1.4	1.2
4	1.3	2.1	1.3	1.3	1.3	1.4	1.0	0.9	1.3	1.3	1.3
5	1.2	1.5	1.0	1.9	1.9	1.7	1.9	2.2	1.8	1.6	1.9
6	0.8	1.3	1.1	1.1	1.6	1.0	1.3	1.2	1.6	1.2	1.2
7	0.8	1.4	1.3	2.5	1.0	1.4	1.5	1.6	1.1	0.7	2.6
8	1.4	1.1	1.9	1.9	1.4	1.9	1.6	1.4	1.6	7.0	4.5
9	1.3	1.9	3.7	3.9	2.9	1.4	2.6	3.0	2.2	20.3	1.4
10	1.5	1.2	0.8	3.0	1.6	1.8	1.5	0.8	1.4	5.3	2.6
	b) Premonsoon/Monsoon										
1	0.8	0.4	1.4	1.1	1.1	0.9	0.7	0.8	1.2	0.4	0.2
2	1.2	0.7	1.2	1.2	1.7	1.5	1.2	1.1	1.1	0.5	0.5
3	1.3	3.4	2.1	3.8	2.7	2.9	3.3	2.2	1.8	3.2	4.5
4	1.2	3.0	2.1	2.2	1.4	2.1	1.3	1.2	1.8	2.6	2.7
5	1.3	1.8	1.7	2.3	5.3	2.1	2.2	2.3	2.1	1.5	1.7
6	1.0	1.3	1.2	1.2	1.9	1.1	1.2	1.3	1.9	1.1	1.2
7	0.9	2.0	1.6	3.4	2.1	2.4	2.0	2.5	1.8	1.3	4.1
8	1.1	1.9	2.1	2.1	1.7	2.8	1.6	1.3	2.4	3.2	4.9
9	2.2	3.5	5.1	10.9	2.1	3.6	3.1	4.7	1.6	3.4	2.9
10	1.4	1.7	1.0	2.9	0.9	1.8	1.6	1.0	2.0	1.2	1.2
	c) Postmonsoon/Monsoon										
1	1.2	1.0	1.2	1.2	1.1	1.0	1.4	1.7	1.3	2.3	1.6
2	1.1	0.8	1.0	1.2	1.3	1.1	1.0	1.0	1.0	0.8	0.6
3	1.1	1.0	1.1	0.8	1.1	1.0	0.9	0.6	0.7	1.4	1.3
4	1.3	2.1	2.1	1.9	1.9	1.1	1.3	1.1	1.3	2.5	2.9
5	1.1	1.1	1.2	1.1	1.0	1.1	1.1	1.1	1.1	1.2	1.6
6	1.2	0.7	1.2	1.1	1.3	1.2	1.0	0.9	1.4	1.2	1.1
7	1.1	1.3	1.2	1.2	1.0	0.9	0.9	1.4	0.9	0.6	1.0
8	1.0	0.9	0.8	1.1	1.1	0.8	1.1	1.0	1.1	3.1	1.4
9	1.5	1.0	0.9	1.0	0.8	1.2	1.5	1.9	1.2	2.6	0.6
10	1.3	1.0	1.3	1.6	1.1	1.6	1.6	1.0	1.1	3.5	2.7

metals and other parameters varied within very narrow ranges and this suggested that the factors and processes responsible for the seasonal variation were more or less similar for all the metals. In other words, it is the physical and biological processes rather than the chemistry of individual metals which was more important in controlling the seasonal enrichment of total content of trace metals. However, the seasonal enrichment factors varied greatly between the stations, indicating that the physical processes acted with different intensities at different stations. Seasonal enrichment was much higher in the sediments sampled from the northern arm of the estuary than in those from the southern part. Sediments of Station 9, the industrial effluent receiving site, recorded the highest seasonal enrichment factor, for all the metals during the premonsoon period.

An exceptional feature noted in the seasonal enrichment pattern was the depletion of manganese and cobalt during winter and premonsoon periods at Station 1 and 2. Iron and nickel also recorded slight depletion at Station 1 during winter and premonsoon periods. With respect to the spatial distribution it was noted that these metals (iron, manganese, cobalt and nickel) exhibited a decreasing trend downstream in the southern part (Segment I). This indicated additional sources of metals at these two Stations on the southern end of the study area, during the monsoon and postmonsoon periods. This anomalous seasonal behaviour was noted also in the sediment parameters like water content, organic carbon content, and particle size distribution.

A possible reason for this unique behaviour of sediment based metal content at Station 1 and 2 could be the impounding of water beyond the Thanneermukkam bund for the winter and premonsoon periods (December- May) and the releasing of the same after the onset of monsoon (May- June). During the periods of impoundment the suspended matter with high content of organic matter and trace metals (Mallik and Suchindan, 1984) settled just inwards of the bund as unconsolidated mud. On opening the bund just after the onset of monsoon rains, the loose mud got eroded fast alongwith considerable amount of muddy turbid water discharging into the southern Cochin estuary; the southern end of the study area (Fig. 2.1) received these deposits in the shallower but broad estuarine regions around Station 1 and 2. Only after prolonged periods of high discharge, later during the monsoon months when all the fine sediment was transported, the system returned to normalcy.

3.3.4 CORRELATION BETWEEN VARIABLES

The relationship between the distribution pattern of various metals studied has been determined by finding out the Pearson coefficient `r'. The values for the various metal pairs are presented in Table 3.9. The table also provides the correlation coefficient of trace metals with some of the sediment and hydrographic parameters studied. Significant and positive correlation between sediment moisture content and metal contents indicated that both were closely related to the fine particle and organic matter content in sediments. The relation between salinity and metal content was also found to be positive and significant; the relationship observed for iron, chromium, manganese, nickel and cobalt was more strong than that observed for zinc, copper, cadmium and lead. These features again could not be attributed to any direct relationship between metals and salinity, but had to be traced to the hydrological conditions that controlled the transport of silt and suspended matter. The erosional and transportational zones in the upper estuary were conducive neither for fine particle settling nor for salt water intrusion; so also the high discharge rates during the monsoon periods encouraged transportation by resuspension as well as bedload

Table 3.9 Correlation r values between the pairs of parameters compared (n = 120; all values positive).

Parameter	Fe	Cr	Mn	Ni	Zn	Pb	Co	Cd	Cu
Moisture %	0.68	0.85	0.75	0.86	0.68	0.82	0.89	0.75	0.86
SS	0.55	0.58	0.50	0.58	0.32	0.40	0.44	0.50	0.33
Salinity	0.66	0.71	0.64	0.69	0.38	0.50	0.60	0.48	0.46
O.C. %	0.75	0.86	0.71	0.84	0.77	0.84	0.87	0.79	0.79
Phosphorus	0.65	0.76	0.57	0.73	0.75	0.81	0.82	0.74	0.79
<16 µm %	0.76	0.84	0.76	0.86	0.72	0.83	0.88	0.77	0.82
Cu	0.61	0.82	0.60	0.79	0.88	0.93	0.89	0.87	
Cd	0.66	0.87	0.62	0.82	0.88	0.89	0.84		
Co	0.75	0.91	0.83	0.92	0.76	0.86			
Pb	0.73	0.87	0.61	0.83	0.88				
Zn	0.57	0.74	0.46	0.66					
Ni	0.84	0.96	0.87						
Mn	0.76	0.81							
Cr	0.83								

SS = Suspended solids; O.C. = Organic carbon
<16 µm = percentage of <16 µm size fraction.

movement. However a depositional environment existed at the lower reaches of the estuary under the influence of tidal action. Lack of a highly significant relation between salinity and total content of zinc, copper, cadmium and lead suggests that there areother important factors, other than hydrualic processes described above which influenced the distribution of these trace metals in this estuary. As in the case of salinity, the suspended solid particles in bottom waters also exhibited strong and positive relationship with total iron, chromium, manganese and nickel, but weaker relationship with zinc, lead, cobalt and copper. Several workers (e.g., Jouanneau et al. 1983; Satyanarayana et al.1985b) have pointed out that the metals iron, chromium, nickel and manganese are mostly associated with fast settling denser suspended particles whereas zinc, copper, cobalt etc., are more often associated with lighter particles of biogenic origin. The significant relationship between the trace metals and organic matter in sediments was due to the simultaneous coagulation and settling of metals and organic matter derived from urban sewage or industrial effluents.

A high degree of correlation and the significant regression relation among the nine metals studied, thus, established identity in the sources, transport and deposition of these metals within the estuary. Among the metals compared, the weakest relationship with other metals was recorded for zinc, followed by copper, cadmium and lead. This pointed out additional sources for the group of metals zinc, copper, cadmium and lead, different from that for the group consisting of iron, manganese, nickel, chromium and cobalt. Spatial distribution studies had revealed that this second group of metals were distributed in comparatively higher levels in Segment I than in Segment III whereas the metals of the first group were found to be in higher (e.g.,zinc and cadmium) or in equal (e.g.,lead and copper) levels in the above segments. The results confirmed anthropogenic inputs of zinc and cadmium into the northern part of the estuary reported by earlier workers (Paul and Pillai, 1983a; Ouseph, 1987; Nair et al. 1990).

3.3.5 THE GEOCHEMICAL BACKGROUND

The ranges of metal values reported from the Cochin estuary by previous workers are shown in Table 3.10. A direct comparison of the data presented in the table was not possible as the earlier studies were confined to isolated parts of the estuary. Murty and Veerayya (1981) surveyed the southern parts of the estuary in 1969 and their survey extended beyond the present study area in the south and hence, part of the data related to the present study area only, was reproduced from their studies in the above Table. The study area of Venugopal et al. (1982) was confined to the northern part of the estuary. Paul and Pillai (1983a) conducted their studies in Periyar river covering a distance of about 50 kms upstream. Only the data related to the estuarine region was reproduced from their studies. The more recent studies (Ouseph, 1987; Nair et al. 1990) covered major parts of southern and northern parts of the estuary, but differed in the total number of samples and also in the location of sampling sites. In spite of these limitations, there is a striking similarity in the data reported by various workers on trace metal content of surficial sediments.

Major differences observed was in the case of iron and manganese. Earlier workers reported comparatively higher values. The major sources of iron and manganese to this estuary were river inputs. The Cochin estuary has undergone significant physical and biological changes during the last three decades (Gopalan et al. 1983). Water flow was diverted from Periyar for agricultural purposes. Marshes have been reclaimed to provide residential areas to the fast growing population. A lot of

Table 3.10 Range of trace metal concentrations reported in sediments of the Cochin estuary (mg/kg dry weight)

	Location	Fe	Mn	Zn	Cu	Cd	Pb	Co	Ni	Cr	Reference
i)	Southern part	2200-73700	120-600		3-100			30-82	10-60		Murty and Veerayya, 1981
ii)	Southern part	3100-90600	44-1439	10-417	8-63	0.1-6.5	3-46	2-42	14-85	5-96	Mallik and Suchindan, 1984
iii)	Northern part		73-318	103-664	17-71			10-43	22-82		Venugopal et al. 1982
iv)	Northern part	4400-29100	15-640	116-1385	5-61	0.8-18.0			3-45		Paul and Pillai, 1983a
v)	Entire estuary (1985/86)			35-780		0.5-8.4	10-90			7-130	Ouseph, 1987
vi)	Entire estuary (1987/88)			23-245	1-42	0.3-4.0	8-40	3-22	11-123	3-118	Nair et al. 1990
vii)	Entire estuary (1988/89)	2800-20200	7-170	14-259	1-50	0.3-8.4	3-50	1-25	2-71	4-100	PRESENT STUDY

Note: Southern part refers to South of Cochin barmouth; northern part is north of Cochin barmouth.

changes have been brought about in the hydrology and hydrography of the estuary by engineering works (e.g., commissioning of the Thanneermukkam bund; inter-basin transfer of Periyar water to Muvattupuzha to facilitate the Idukky hydro-electric project; impoundment of water in dam reservoirs etc.). All these changes were of significance to trace metal behaviour within the estuary, although the links between the specific changes and specific effects were only poorly understood. The construction of dams and impoundment of water reduced considerably the suspended load in river water and this might have had serious consequences in the transport of trace metals to the estuary.

The present data compared well with previous data not only in the ranges of metal values but also in certain spatial and seasonal trends reported. The accumulation of metals in the mid-estuarine region and their depletion towards the marine side were observed by Nair et al. (1990). Venugopal et al. (1982), Ouseph (1987) and Nair et al. (1990) observed monsoonal low values and postmonsoonal enrichment for all the metals they studied, as also recorded during the present study. The downstream depletion of manganese and cobalt in the southern arm of the estuary was previously reported by Murty and Veerayya (1981). Nair et al. (1990) observed comparatively higher levels of manganese, chromium, nickel, cobalt and iron in the southern part in comparison to the northern upper riverine parts. The results from the present study confirmed the above observations.

Table 3.11 compares the metal data from the Cochin estuary (present study) with that of the more recent data reported in sediments of various estuaries and rivers in India. Average value for riverine sediments and global average value for surface soils also have been furnished. In comparison to other major estuaries and harbours of India, the Cochin estuary was

Table 3.11 Mean trace metal values reported in sediments of Indian estuaries and rivers (mg/kg dry weight).

Location	Fe	Mn	Zn	Cu	Cd	Pb	Co	Ni	Cr	References
Ashtamudi, Kerala	1800		60	60		38		12		Nair et al. 1987
Bombay harbour	86000	1140	155	105	10	48	50	111	124	Patel et al. 1985
Cauvery estuary	34000	1310	75	33	1.8	38		379	229	Subramanian et al. 1989
Ganges estuary	42000	732	151	44		32		49	98	Subramanian et al. 1988
Godavary estuary	76000	1294		119		5		91	128	Biksham and Subramanian, 1988
Godavary river	57000	1070	54	82		11	47	51	126	Subramanian, 1987
Krishna estuary	100000	6978	1482	69		4		149	174	Subramanian et al. 1989
Krishna river	25000	906	26	35			32	32	82	Ramesh et al. 1990
Mindhola estuary		1109	157	113		19		92		Zingde et al. 1988
Narmada estuary	89000	1097	140	136				81		Borole et al. 1982
Tapti estuary	76000	1125	125	128				70		- do -
Thana creek	70000	867	146	115	2.3	52	32	117	51	Mahajan et al. 1987
Ulhas estuary	63600	230	149	97	2.3	37	44	93	86	- do -
Visakhapatnam - inner harbour	62600	454	7421	120	43	296	30	50		Satyanarayana et al. 1985b
- outer harbour	58000	490	4240	41	11	104	11	37		- do -
COCHIN ESTUARY	8300	66	70	12	1.7	15	9	21	30	PRESENT STUDY
Indian average (river sediment)	29000	605	16	28			31	37	87	Subramanian et al. 1985
World average (top soils)	40000	1000	90	30	0.4	35	8	50	70	Martin and Whitfield, 1983

less contaminated with trace metals in surficial sediments. However, the levels of zinc was much above the Indian average for riverine sediments. Cadmium levels were higher than that of surface soils. Nair et al. (1990) compared the trace metal content of sediments of the Cochin estuary with that reported in sediments from other geographical units world-wide, and concluded that the mean and ranges of values recorded in sediments of Cochin estuary was comparable with that reported from other regions. The comparatively lower content of trace metals in the surficial sediments of the Cochin estuary might be due to the fact that the rivers that drain into the estuary traverse highly weathered tropical lateritic surface caps.

The large variations in trace metal distribution observed were primarily due to the variations in particle size, organic matter content, net deposition rates and sediment mixing. The ability of fine particles and organic materials to scavenge trace metals effectively in estuaries has been discussed by several authors (de Groot et al. 1976; Williams et al.1978; Thorne and Nickless, 1981; Olsen et al. 1982; Brook and Moore, 1988). In environments where particle size distribution and mineralogy were heterogenous, substantial variability in trace metal concentration were recorded even in the absence of metal contamination. This variability was further modified in estuaries by the fact that fine particles were more easily re-suspended than coarser particles, retained in suspension for longer periods and were swept across wide areas before coming to rest in an environment that was topographically or dynamically suited for fine particles and associated trace metals to be accumulated. In the Cochin estuary, the mid-estuarine reaches in the northern arm provided such a dynamically suited niche, housing excessive trace metal burdens relative to coarser grained areas of the upper and lower estuary.

CHAPTER 4

TRACE METAL PARTITIONING IN SEDIMENTS

4.1 INTRODUCTION

4.2 MATERIALS AND METHODS

4.3 RESULTS AND DISCUSSION

- 4.3.1 IRON
- 4.3.2 MANGANESE
- 4.3.3 ZINC
- 4.3.4 COPPER
- 4.3.5 CADMIUM
- 4.3.6 LEAD
- 4.3.7 COBALT
- 4.3.8 NICKEL
- 4.3.9 CHROMIUM

4.1 INTRODUCTION

Sediments are heterogenous mixtures of dissimilar particles varying in size, composition and origin. Each particle is a complex assemblage of inorganic and organic components such as silicates, amorphous oxides, carbonates, organic matter etc. A quantitative knowledge on the selective distribution of trace metals among the specific components of the sediments is of great practical significance as it serves to evaluate their fate in the environment. However, direct methods are not presently available to quantify these metal distributions. Techniques available for the characterisation of metal binding in well defined media to specific well defined surfaces such as, oxides and organic materials (James and Healy, 1972; Hohl and Stumm, 1976; Davis and Leckie, 1978a), have only limited applications for the aggregated, multiligand, multicomponent surfaces that occur in natural sediments (Luoma and Davis, 1983). Empirical methods suggested for quantifying the various metal associations in sediments include sequential chemical extractions (Engler et al. 1977; Tessier et al. 1979) and statistical correlations (Luoma and Bryan, 1981 & 1982; Luoma and Davis, 1983). Models describing partitioning in sediments have also been developed (Oakley et al. 1981; Davies- Colley et al. 1984; Nyffeler et al.1984: Tessier et al. 1985; Luoma, 1986; Reuber et al. 1987; Hirose, 1990). Historically, efforts to describe quantitatively metal partitioning in natural sediments have involved a search for extractants which selectively remove specific forms of metals from sediments. Their usefulness have been proved by actual usage rather than by theoretical discussion (Forstner, 1982; de Mora and Harrison, 1984; Tessier and Campbell, 1991). The study reported herein was aimed at demonstrating the usefulness of the chemical partitioning in delineating the accumulative phases of trace metals in surficial sediments of the Cochin estuary, distributed in space and in time. The trace metals studied were iron, manganese, zinc, copper, cadmium, lead, cobalt, nickel and chromium. Although iron and manganese are not generally referred to as trace metals in the literature, they have been so designated and included in the studies to simplify the presentation of results and to amplify the scope of discussion.

4.2 MATERIALS AND METHODS

The details on site selection, sampling and chemical analysis of the samples are furnished in Chapter 2. For partitioning of trace metals into the various accumulative phases, the sequential extraction scheme proposed by Tessier et al. (1979) was used with slight modifications (Nair et al. 1991). There were five steps in the extraction procedure and the metal phase extracted at each stage was defined by the extractant used. Because of this operational definition, the fractions extracted have been referred to (in the text and figures) as fractions 1 to 5 along with the chemical symbol of the element under discussion. The numbers representing the fractions are 1. Exchangeable 2. Carbonate bound 3. Fe-Mn oxide bound 4. Organic/ sulphide bound and 5. Residual. The total metal concentration has been indicated by adding the subscript `T' to the chemical symbol of the metal. Thus, for iron, the various fractions have been described as Fe1, Fe2, Fe3, Fe4 and Fe5 and the total iron as FeT. Several research workers have utilised sodium dithionite as the extractant to extract the moderately reducible phases, and this fraction has been assigned the number 6 in the Tables.

4.3 RESULTS AND DISCUSSION

The summary statistics, indicating the mean, standard deviation, percentage coefficient of variation and range of values for each of the five fractions of the nine metals studied are furnished in Table 4.1. The Table depicts information also on the ratio of the relative contribution of each fraction to the total concentration of the metal concerned. The data showed wide scatter as indicated by the percentage

Table 4.1 Summary statistics on distribution of different chemical fractions of trace metals.

Fraction	Concentration mg/kg					Percentage				
	Mean	SD	CV%	Min.	Max.	Mean	SD	CV%	Min.	Max.
Fe1	4.66	3.46	74.1	0.40	18.70	0.06	0.04	75.3	0.01	0.23
Fe2	6.60	10.60	160.6	0.30	54.00	0.07	0.07	107.7	0.00	0.33
Fe3	103	63	60.6	16	262	1.27	0.67	52.6	0.30	3.23
Fe4	108	99	92.3	12	389	1.16	0.75	64.2	0.21	3.30
Fe5	8103	3828	47.2	2768	19561	97.44	1.21	1.2	93.25	99.22
Mn1	4.79	6.34	132.4	0.30	33.50	7.52	5.05	67.2	0.90	27.06
Mn2	8.71	8.16	93.7	0.30	34.10	11.16	4.59	41.2	1.82	22.46
Mn3	5.86	5.33	91.1	0.10	21.10	8.91	4.67	52.4	1.41	25.71
Mn4	17.91	14.29	79.8	1.50	53.60	26.11	5.98	22.9	10.10	37.96
Mn5	28.77	20.19	70.2	2.60	81.70	46.30	9.10	19.7	27.84	82.15
Zn1	1.19	1.88	157.6	0.07	13.16	1.75	2.18	124.1	0.24	13.35
Zn2	6.82	9.97	146.2	0.20	37.42	6.43	5.35	83.3	0.38	19.70
Zn3	8.12	10.71	131.9	0.77	46.19	9.37	4.35	46.4	2.43	19.32
Zn4	20.71	23.87	115.3	1.15	81.40	24.28	10.01	41.2	6.71	43.38
Zn5	33.57	24.14	71.9	5.85	91.01	58.22	17.19	29.5	28.01	88.77
Cu1	0.17	0.13	76.7	0.02	1.12	2.08	1.32	63.3	0.37	6.67
Cu2	0.18	0.13	70.3	0.06	0.96	2.72	2.17	79.7	0.32	9.52
Cu3	0.04	0.04	89.9	0.00	0.19	0.74	0.91	124.1	0.00	4.44
Cu4	2.50	2.99	119.5	0.16	15.89	20.34	9.03	44.4	7.56	49.19
Cu5	9.31	8.96	96.3	0.94	34.46	74.21	9.66	13.0	46.57	89.80

Contd...

Table 4.1 contd.....

Fraction	Concentration mg/kg Mean	SD	CV%	Min.	Max.	Percentage Mean	SD	CV%	Min.	Max.
Cd1	0.07	0.05	72.8	0.01	0.24	5.76	3.07	53.3	1.40	18.89
Cd2	0.08	0.06	71.1	0.01	0.26	7.48	4.84	64.8	0.68	22.58
Cd3	0.11	0.12	112.3	0.02	0.86	8.13	4.45	54.7	1.72	26.09
Cd4	0.68	0.96	140.6	0.07	3.83	34.90	8.94	25.6	15.22	59.53
Cd5	0.73	0.85	116.1	0.14	4.55	43.73	9.13	20.9	23.33	69.35
Pb1	0.37	0.26	69.4	0.05	1.13	2.86	1.59	55.6	0.60	7.55
Pb2	0.55	0.42	75.6	0.04	2.13	4.32	2.57	59.5	0.94	15.47
Pb3	0.75	0.72	96.5	0.05	4.93	5.68	4.08	71.8	1.04	20.94
Pb4	1.16	0.65	56.2	0.26	3.20	10.37	6.58	63.5	1.39	28.63
Pb5	12.03	10.05	83.5	2.25	45.45	76.78	10.24	13.3	52.47	92.70
Co1	0.18	0.12	65.3	0.02	0.72	2.40	1.20	49.9	0.57	5.69
Co2	0.16	0.11	68.4	0.02	0.57	2.35	1.86	79.1	0.37	9.95
Co3	0.29	0.17	59.2	0.03	0.86	4.09	2.39	58.3	0.49	13.59
Co4	1.81	1.39	76.9	0.27	6.32	19.81	4.42	22.3	10.37	30.47
Co5	6.80	5.34	78.6	0.79	18.98	71.35	6.17	8.6	55.77	83.51
Ni1	0.23	0.15	65.0	0.04	0.89	1.45	0.68	46.8	0.34	3.57
Ni2	0.22	0.14	62.6	0.02	0.66	1.40	0.96	68.1	0.19	5.08
Ni3	0.35	0.24	69.5	0.02	1.12	1.98	0.97	49.0	0.42	4.99
Ni4	2.58	2.79	108.5	0.20	11.56	10.94	3.79	34.6	3.05	21.85
Ni5	17.77	14.70	82.7	1.52	58.91	84.23	4.25	5.0	71.39	92.04
Cr1	0.20	0.11	57.2	0.02	0.49	0.95	0.73	76.7	0.08	5.19
Cr2	0.12	0.06	50.3	0.02	0.27	0.64	0.53	83.5	0.08	3.28
Cr3	0.04	0.03	83.2	0.01	0.16	0.16	0.09	58.4	0.03	0.46
Cr4	4.30	5.48	127.5	0.12	22.57	11.01	6.64	60.3	2.24	27.63
Cr5	25.34	19.99	78.9	3.73	81.14	87.25	6.22	7.1	71.01	95.56

coefficient variation, as for example, a variation of 160.6 % from mean was indicated for Fe2 and 157.6 % for Zn1. The variability could be attributed to the total metal concentration, the site of sampling and time of sampling. To test this hypothesis the data was subjected to the analysis of variance. The technique used was the one usually adopted for analysis of data from experiments of asymmetric factorial designs. In this case three factors were considered, the fractions, the stations and seasons. The monthly data were considered as replicates, and were pooled into four seasons, namely, winter, premonsoon, monsoon and postmonsoon as detailed previously. For each metal, 600 cases were processed. The two way interactions between the factors considered were worked out. The results revealed highly significant variation due to fractions (total concentration), seasons (temporal) and stations (spatial) for all the nine metals studied. Interactions between the factors tested were also highly significant. Therefore a direct interpretation based on mean values was only of limited value (Snede~~k~~Ccar and ~~K~~Cochran, 1968). Hence, in the following pages the results obtained for each metal have been discussed season-wise and station-wise in the order of iron, manganese, zinc, copper, cadmium, lead, cobalt, nickel and chromium.

4.3.1 IRON

In estuarine studies iron has received more attention than any other transition metal (Aston, 1978) owing to the possibility of formation of new solid phases during estuarine mixing.Oxidation of iron(II) to oxides and hydroxides is one of the most likely reactions of this type to occur when the pH of the river water is raised by mixing with sea water (Boyle et al. 1977; Mayer, 1982). The formation of these oxides are considered to be very important in controlling the uptake of other metals from solution (Bowers and Huang, 1987). Gibbs (1973) observed that iron coatings which covered the suspended grains of Yukon and Amazon estuaries were important in the transport of manganese, nickel, cobalt, chromium and copper. This incorporation was attributed to co-precipitation during iron oxide formation. Published data (Coonley et al. 1971; Windom, 1975; Holliday and Liss, 1976; Boyle et al. 1977; Murray and Gill, 1978; Eaton, 1979a; Hart and Davies, 1981; Morgan, 1982; Sharp et al. 1984) indicate that estuaries are efficient traps for iron, implying that for iron the seaward losses are unlikely (Helz and Sinex, 1986). Iron gets flocculated in the early stages of estuarine mixing, but the eventual removal from the estuary may be by currents and accompanying turbulent processes.

The levels of total iron recorded in the sediments of the Cochin estuary during the present study ranged from 2811 to 20183 mg/kg (Table 3.7). 93 to 99 percent of the total iron was found to be in the Fe5 phase (Table 4.1) which was generally considered as environmentally inert. Though the relative contributions from other fractions of iron were quite small, their distributions in absolute terms were quite recognisable. The various forms of iron ranked in abundance in the order Fe5>>> Fe4 = Fe3>> Fe2 = Fe1. Figure 4.1 depicts the spatial and seasonal mean distribution pattern of the five fractions of iron in absolute concentrations as well as in relative terms (as pecentage of total).

The Fe1 values ranged from 0.40 to 18.7 mg/kg dry weight contributing only about 0.01 to 0.23 percent of the total iron present in sediments (Table 4.1). Maximum value was recorded in the silty clay sediments of Segment II and minimum in the coarse sandy sediments of Segment III (Fig. 4.1). The values decreased towards the marine side in Segment II and towards riverine side in Segment III. There was more or less equitable distribution of Fe1 among the four Stations in Segment I, but a significant seasonal pattern was evident with very high values being recorded during the postmonsoon season except at Station 1, where the highest value was recorded during the monsoon season. In Segment II, higher values were noted during the

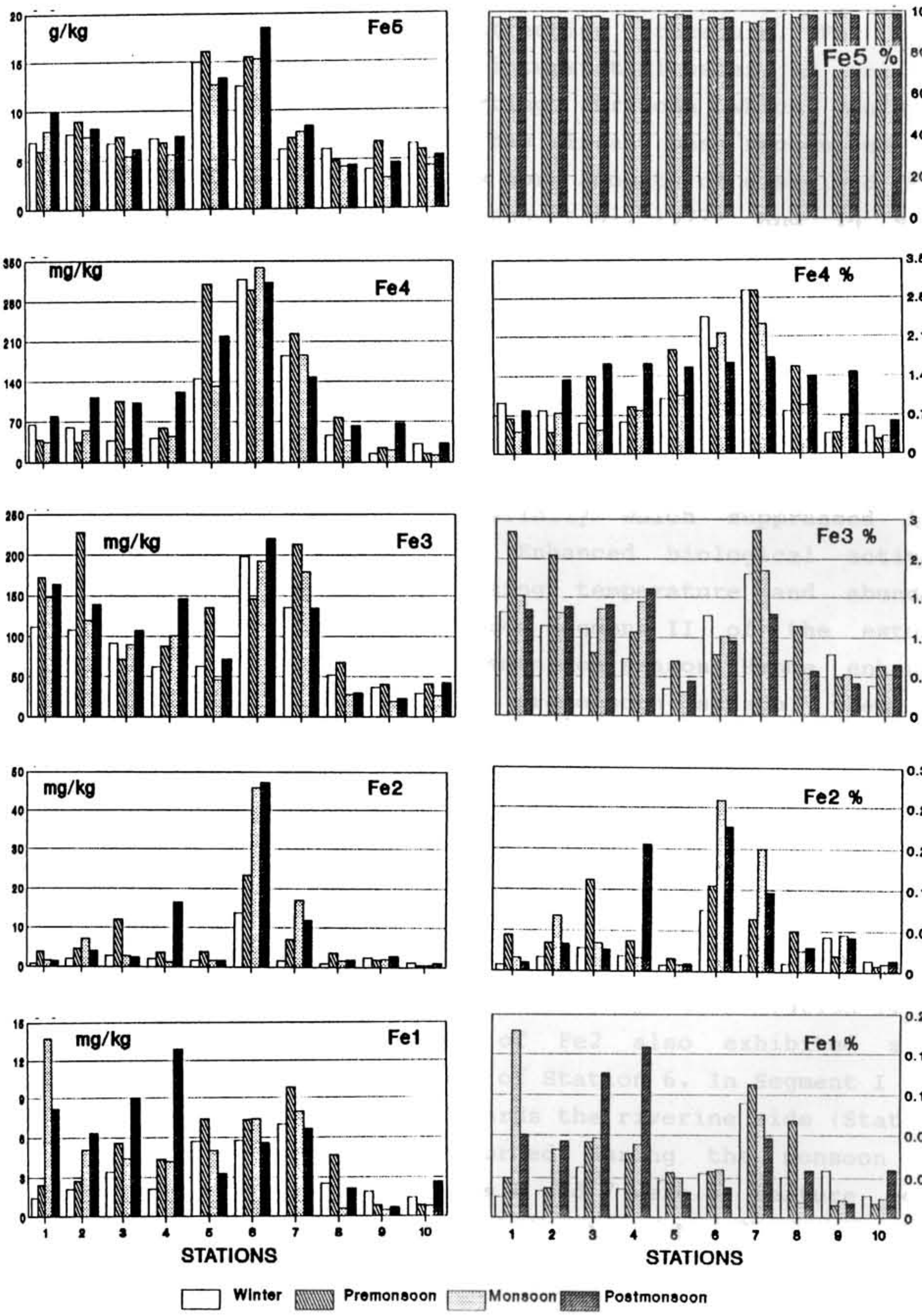

Fig. 4.1 Seasonal mean concentrations and percentages of iron fractions (concentrations in mg/kg dryweight except for Fe5)

premonsoon season. In the extraction procedure, Fe1 phase includes the iron dissolved in interstitial water as well as the iron loosely bound to adsorbing surfaces which could be replaced by ammonium ions. It has already been recognised that the interstitial water contains more amounts of dissolved iron than the overlying waters (Brannon et al. 1977) and in sandy sediments the exchange of metals between the interstitial water and overlying water will be more rapid than in clayey environments. This, together with the presence of high organic matter which mobilise iron under mildly reducing conditions explain the higher amount of Fe1 in the silty clay sediments of the mid-estuary. A diminishing trend towards the marine side within Stations of Segment II was noted. This might be due to the increasing effects of salinity which suppressed iron solubility (Sholkovitz, 1976). Enhanced biological activity under the influence of increasing temperature and abundant organic detritus was reported from Segment II of the estuary (Anirudhan, 1988) during the premonsoon season. Hence enhanced values for the Fe1 during the premonsoon season, when the salinity of water was maximum, were regarded as indicative of the profound influence of biological factors over the physical factors in controlling iron solubility.

The Fe2 values ranged from 0.30 to 54 mg/kg contributing a maximum of 0.33 percent of the total iron (Table 4.1). The highest value was recorded at Station 6 followed by Station 7, with values declining sharply on either sides of Station 6. The relative percentage abundance of Fe2 also exhibited sharp declining trend on either sides of Station 6. In Segment I the percentage values decreased towards the riverine side (Stations 4 to 1). The higher values recorded during the monsoon and postmonsoon seasons, at Stations 6 and 7 were a feature noted only in the case of Fe2 distribution. No distinguishable seasonal trends in Fe2 distribution could be observed at other Stations.

Very high amounts of Fe2, both in absolute and relative terms recorded during the monsoon and postmonsoon periods suggested that this fraction was associated with the suspended load derived from terrestrial sources under the influence of storm water and erosion. Further, Station 6 in the northern arm of the Cochin estuary was reported to be a sheltered sedimentary environment even during the monsoon periods (Pillai, 1989). In the highly acidic soils of the tropics, the fixation of phosphate as iron phosphates became a well established phenomenon (Le Mare, 1981). On the basis of all these observations, it was concluded that the abnormally high values of Fe2 recorded at Station 6 during the monsoon and postmonsoon might be due to the trapping of eroded soils rich in iron phosphates. However it was noted that the Fe2 fraction was subjected to rapid diagenetic changes after deposition as was evidenced by the decreasing percentage values after the monsoon season, most probably under the influence of saline water which could change the solubility of phosphates [as demonstrated by Bale and Morris (1981) in laboratory simulation studies] or unquantified biological activity [as shown by Hines et al. (1984) in the New Hampshire sediments] resulting in mineralisation of phosphates.

The Fe3 values ranged from 16 to 262 mg/kg contributing 0.30 to 3.23 percent of total iron (Table 4.1). Higher values were again recorded at Stations 6 and 7, with values declining on either sides of Station 6. Percentage wise, the maximum contribution was found to be in the sediments of Station 7 which received the sewage from the metropolitan city of Cochin. One characteristic feature noted in the distribution of Fe3 was the downstream declining trend both in absolute and relative values, in Segment I, but with significant seasonal trends. The Station 5 at barmouth recorded lower values than Station 6. Fletcher et al. (1983) also observed lower concentration of hydroxylamine hydrochloride extractable iron in the salt water intrusion zone in the Fraser estuary and they attributed this to iron desorption at intermediate salinities. However, a downstream increase was noted in Segment III, which was quite perceptible during the winter and premonsoon seasons when the river flow was low.

The extractant used for the extraction of Fe3 was acidified hydroxylamine hydrochloride (pH = 2.0) which could dissolve the oxides of iron and manganese that were relatively stable under oxidising conditions (Engler et al. 1977). Brannon et al. (1977) noted that the extractant dissolved approximately 85 percent of manganese oxides while dissolving only 5 percent of the total iron present in Mobile Bay sediments. Tessier et al. (1979) also observed that manganese oxides were more easily leached down than iron oxides. The iron oxides occur in estuarine sediments in a continuum of states ranging from a highly amorphous (or microcrystalline) oxyhydroxide which form upon precipitation to increasingly crystalline solids which form as the initial precipitate ages (Forstner, 1979c). The highly oxidised conditions and the turbulence restricted the amount of soluble iron reaching the system, and this explains the comparatively low values recorded for Fe3 in surficial sediments of the Cochin estuary. The enhancement of Fe3 downstream in Segment III, especially during the winter and premonsoon seasons could be attributed to the rapid precipitation under the influence of low salinities experienced at these stations under conditions of tidal incursions. The chemistry of Fe3 in Segments I and II appeared to be controlled by the presence of manganese oxides and organic matter. The influence of organic matter buried into the sediments might account for the high Fe3 values recorded at Stations 6 and 7 which received sewage effluents. In Segment I, a downstream decrease was noted for Mn3 also, as observed for Fe3 and both might be related to processes which resulted in the mobilisation of iron and manganese from sediments, as demonstrated by Fletcher et al. (1983) for the Fraser estuarine sediments.

The mean Fe4 values ranged from 12 to 389 mg/kg contributing 0.2 to 3.3 percent of total iron (Table 4.1). The range of values recorded was comparable with that of Fe3, but the spatial and seasonal distribution pattern was different for these two fractions of iron. Higher values were, again, recorded at Station 6 and the content of Fe4 decreased on either sides of this Station in the northern arm of the estuary. In Segment I all the four Stations recorded more or less similar content of Fe4. In percentage-wise distribution, the maximum contribution from this fraction of iron was recorded at Station 7, which was a noticeable sewage effluent receiving site. There was a decrease in relative values on either sides. Seasonwise, higher values were recorded during the postmonsoon season in most of Stations in Segments I and III, both in absolute and relative values. A distinct seasonal trend was not observed at Stations in Segment II.

The two important features noted in the distribution of Fe4 were the enhanced values in Stations of Segment II and the relative enrichment in sediments during the postmonsoon periods. The sewage effluent being received in Station 7 might be an important factor in controlling the iron fractionation in this phase. However, in other two Segments, seasonal importance of biological productivity reported by Joseph and Pillai (1975) and Joseph and Nair (1975) could be the controlling factor of iron fractionation as evidenced by enhanced values during the postmonsoon season.

The Fe5 values ranged from 2768 mg/kg to 19561 mg/kg, contributing 93 to 97 percent of the total iron. Its distribution pattern mimicked that of total iron and was greatly influenced by the sedimentary environment. Thus higher values were recorded in the accumulative environments of Segment II and lower values in the erosional environments of Segment III. As noted for total iron, the seasonal trends were subdued or indistinct.

The Fe5 fraction represented the metal associated with primary minerals, secondary minerals and refractory organic materials (Engler et al. 1977; Tessier et al. 1979). The major part of total iron was found in the Fe5 fraction which was regarded as chemically inert and biologically inactive and this explained the minimum seasonal variation observed in the case of total iron distribution in estuarine sediments.

Table 4.2 furnishes data on chemical partitioning of iron (reported in percentage) from other parts of the globe. It can be seen from the table that the range of values recorded for Fe1, Fe2, Fe3 and Fe4 during the present study in the Cochin estuary compared well with values reported from other parts of the world. The difference noted in the case of Fe5 fraction could be traced to the differentiation into moderately reducible and residual fractions, as done by some workers (Brannon et al. 1977; Patchineelam and Forstner, 1983).

4.3.2 MANGANESE

Manganese is an essential element in biological systems. Availability of manganese from soils to plants depends upon a number of factors, like, the concentration in soil solution, concentration on exchange sites, pH, Eh etc. Manganese contamination is relatively insignificant except for the common biological toxicity effects found in plants exposed to excess of natural manganese in the soil under some peculiar conditions, particularly flooding. In oxic environments, it is present mainly as manganese (IV) oxides and oxyhydroxides. Under anoxic conditions, as in flooded paddy-soils, manganese (IV) compounds are readily reduced to manganese (II) and the process is considered to be both chemical and biochemical (Ponnamperuma, 1972). The manganese (II) when diffused or advected into oxic environments gets oxidised to manganese (IV). Manganese (II) was found to react with carbonates and bicarbonates and the chemistry of manganese carbonate has an important role in controlling the dissolved manganese concentration in soil solution and interstitial waters of sediments (Smith, 1990).

Table 4.2 Percentage of iron fractions reported in sediments from different geographical locations

Location	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	FeT (mg/kg)	Reference
Yukon-SPM	0.01		40.60	11.00	48.20		63000	Gibbs, 1973
Mobile bay, Site 1	1.35		4.10	12.67	9.11	72.75	28000	Brannon et al. 1977
Site 2	0.97		2.28	19.41	8.79	68.54	30700	- do -
Yamaska river - SPM	0.01	2.10	32.00	4.80	61.00		43800	Tessier et al. 1980
St. Francois river - SPM	0.01	1.30	22.00	3.80	73.00		42700	- do -
Rhine river	0.10	2.00	0.10	47.10	50.80		23300	Forstner, 1982
Subae river-unpolluted			3.00		83.00	14.00	26161	Patchineelam and Forstner, 1983
-polluted			3.60	0.20	26.80	69.40	48540	- do -
Yellow river	0.10	1.00	1.00	7.00	65.00	26.00	14198	Hong and Forstner, 1983
Axios river	0.14	1.60	18.81	37.06	42.39		17370	Samanidou and Fytianos, 1987
Axios estuary	0.19	0.96	18.31	37.28	43.26		15640	- do -
Aliakmon river	0.14	0.65	26.82	46.39	25.90		70300	- do -
Aliakmon estuary	0.23	3.65	31.61	40.05	24.46		65900	- do -
COCHIN ESTUARY-MEAN	0.06	0.07	1.27	1.16	97.44		8323	PRESENT STUDY
-RANGE	0.01-0.23	0.01-0.33	0.30-3.23	0.21-3.30	93.25-99.22		2800-20200	- do -

Reactivity of manganese in estuarine systems has been widely studied. Manganese has been reported to exhibit a complex behaviour with removal, addition as well as conservative nature for different estuaries (Burton and Liss, 1976; Evans et al. 1977; Yeats et al. 1979; Morris and Bale, 1979; Wollast et al. 1979; Wilke and Dayal, 1982). Its mobilisation from sediments to overlying water has also been investigated (Graham et al. 1976; Lu and Chen, 1977; Lacerda et al. 1987). Manganese can occur in sediments as discrete oxide particles, coatings on particles and as manganese (II) adsorbed on organic materials (Graham et al. 1976; Feely et al. 1982). In estuaries organic matter accumulation may lead to the dissolution of manganese from sediments (Luoma, 1990). Since manganese can apparently be complexed by dissolved organic materials and can be retained in solution by the control of redox potential through oxidation of the more labile dissolved organics, the amount and kind of organic material present would determine the proportion of manganese exported from the estuary (Wangersky, 1986). Delfino and Otto (1986) observed that in the Chesapeake bay, the phase distribution patterns for manganese contrasted sharply with those of Fe. While iron was preferentially bound (89-99 percent) to the particulate phase, 75 percent of manganese was present in the soluble phase in Susquehanna river during fall, winter and the snowmelt runoff periods and about 50 percent was soluble in summer. It is difficult to understand the behaviour of manganese at the estuarine sediment/water interface because factors such as physical mixing, reactions between suspended loads and dissolved materials and input of pollutants complicate the interpretation of the data.

In the Cochin estuary the abundance of manganese on an average was only next to zinc. The values for total manganese in sediments varied from 7 to 170 mg/kg with a mean value of 66 mg/kg (Table 3.7). In contrast to the behaviour of iron, a considerable portion of manganese recorded in this estuary was found to be in the environmentally labile fractions (Table 4.1) leaving an average of only 46 per cent as the residual fraction. This was indicative of the high chemical reactivity of this transition element in this estuary, which was noted in other estuaries also (Evans et al. 1977; Wollast et al. 1979; Rosental et al. 1986; Prohic and Kniewald, 1987; Samanidou and Fytianos, 1987). The order of abundance of the various fractions of manganese was Mn1< Mn3< Mn2<< Mn4<<< Mn5. It was also noted that the percentage coefficient variations decrease from Mn1 to Mn5 indicating that the less firmly held fractions of Mn exhibited wider variability in distribution.

The spatial and seasonal mean distribution of the various fractions of manganese determined in the surficial sediments of the Cochin estuary are presented in Fig. 4.2. The values for Mn1 fraction ranged from 0.3 to 33.5 mg/kg, contributing 0.9 to 27.1 percent of total manganese (Table 4.1). Higher values were recorded (Fig. 4.2) at Station 1 during monsoon and postmonsoon periods with values decreasing sharply downstream. Very low values of Mn1 were recorded at the three Stations in Segment III, except for the premonsoon period. During winter and premonsoon periods more or less similar values were recorded for all the Stations in Segments I and II . An unique feature observed in the case of Mn1 distribution was the absence of a mid-estuarine maxima. Percentage-wise distribution of Mn1 showed gradually decreasing contributions in the seaward direction, throughout the year, on both the arms of the estuary, the Stations 5 and 6 nearer to barmouth recording the minimum contribution.

The more or less equitable distribution of Mn1 fraction between the sediments which differed greatly in their grain size could be explained on the basis of the estuarine reactivity of manganese. Though the hydrogenous precipitation of the oxides of iron and manganese and the co-precipitation of trace metals were regarded as means of removal of trace metals from river water in the early stages of estuarine mixing, many workers (Holliday and Liss, 1976; Aston, 1978; Duinker, 1980;

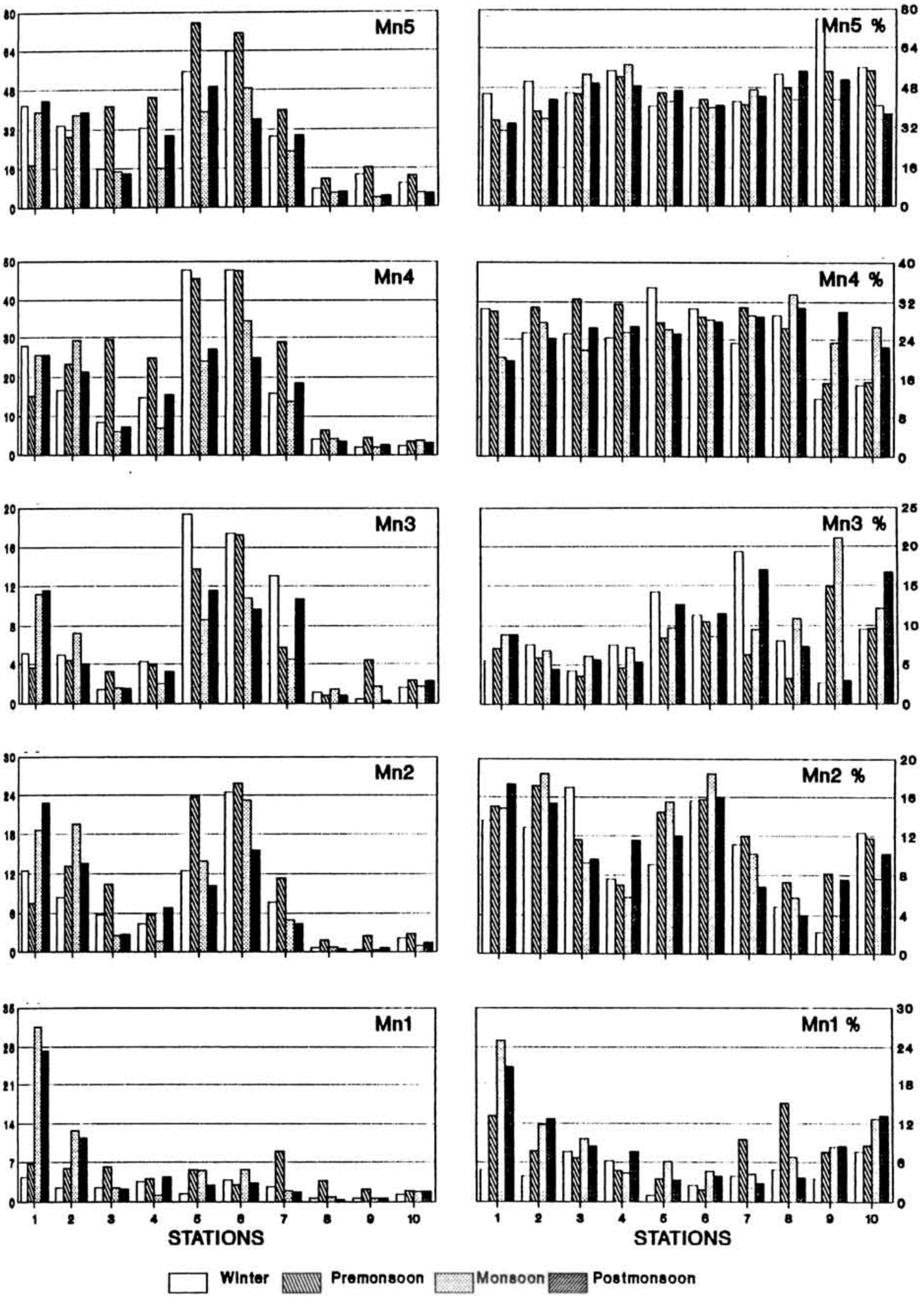

Fig. 4.2 Seasonal mean concentrations and percentages of manganese fractions (concentrations in mg/kg dryweight)

Duinker et al. 1982; Gibbs, 1986; Nolting et al. 1990; Windom et al. 1989) observed variations in the rate of removal of various metals. Although the removal of iron was quite rapid and complete, the removal of manganese was not so. Fukai and Huynh-Ngoc (1968) demonstrated that the manganese precipitation required conditions of higher pH than those normally encountered in estuaries. The preponderance of soluble species of manganese in riverine sections, especially during period of high runoff, also has been reported (Delfino and Otto, 1986). The increased amounts of soluble manganese present in the riverine parts of the estuary compensated for the decreased number of sites involved in cation exchange in the sandy sediments. On the other hand the limited solubility of manganese under saline conditions restricted the availability of manganese ions which might be involved in exchange reactions in the silty clay sediments of Segment II. The anomalous values of Mn1 recorded at Stations 1 and 2 during monsoon and post-monsoon could be attributed to the impounding of water beyond the Thanneermukkam bund (see, Fig. 2.1) and its release to the estuary with the commencement of monsoons. The effect of impoundment in enhancing the manganese solubility is well documented (Delfino and Lee, 1971; Eat~~e~~on, 1979b).

The Mn2 fraction in the sediments varied from 0.30 to 34.1 mg/kg contributing 1.8 to 22.5 percent of total manganese (Table 4.1). Higher values were recorded at Station 6 of Segment II, with values decreasing sharply on either side, in absolute as well as relative amounts (Fig. 4.2). Mn2 exhibited a downstream decrease in Segments I and III at all seasons, both in absolute and relative terms. Season-wise, higher values were recorded during the premonsoon period and lower during monsoon/ postmonsoon at Stations of Segment II and III, but significant interactions between Stations and Seasons were noted in the seasonal distribution of Mn2 in Segment I.

Ponnamperumai (1984) reported that there was a decrease in the water soluble manganese after an initial rise following flooding and this was attributed to the precipitation of manganese as manganese carbonates. Therefore the sediments of the impounded water which was released to the southern parts of the estuary with the commencement of monsoon might be a contributing factor for the high amounts of Mn2 detected in the sediments of southern parts. Within the estuary, this fraction of manganese was subjected to rapid conversion either under the influence of biological agencies (as evidenced by the increasing percentage of Mn4 fraction) or geochemical processes (as evidenced by increased percentages of Mn5 fraction). In Segment II, the enhanced values during the monsoon season might be, as explained for Fe2 fraction, due to the influence of terrestrial soil particles that contained manganese bound to phosphates and settled preferentially in these sheltered sedimentary environments. Once settled, these phosphates released manganese under diagenetic influences, thus showing the monsoonal peak and decreasing trend afterwards.

The content of Mn3 fraction in surficial sediments varied from 0.1 to 21.1 mg/kg contributing 1.41 to 25.71 percent of total manganese (Table 4.1). Sediments of Segment II recorded the maximum value and the values were significantly higher during the winter and premonsoon months (Fig. 4.2). As observed for Mn1 and Mn2 fractions, Station I in Segment I recorded relatively higher values during the monsoon and postmonsoon periods. In general, the values of Mn3 exhibited a down-river declining trend in Segments I and III. Percentage-wise, the maximum contribution from this fraction of manganese was recorded at Station 7 during the postmonsoon and winter periods. Sporadic high percentages were observed at Station 9 which received industrial effluents. Sediments of Segment I had the lowest contribution from this fraction of manganese. A downstream decrease in the relative contribution of Mn3 was observed during the premonsoon and monsoon in Segment I and during the winter, monsoon and postmonsoon in Segment II.

The distribution pattern of Mn3 in Segment I was similar to that of total manganese indicating that a definite portion of manganese delivered to this part of the estuary was in the Mn3 form. The sporadic high values recorded for Mn3 at Station 9 had to be attributed to industrial effluents which might cause rapid precipitation of manganese oxides or to the addition of sand sized particles coated with manganese oxides. The higher content of Mn3 recorded at Stations in Segment II during the winter and premonsoon periods was due to the prevailing saline conditions which might cause the dissolved manganese to precipitate and flocculate.

The values of Mn4 fraction were found to be in the range of 1.5 to 53.6 mg/kg contributing 10 to 38 percent of total manganese (Table 4.1). Higher values were recorded at Stations 5 and 6 of Segment II during the winter and post-monsoon periods (Fig. 4.2). The premonsoonal values were higher at all stations except at Stations 1 and 2 in Segment I. The sediments of Segment III had the lowest content of Mn4 at all seasons. A downstream decrease was noted in the content of Mn4, in Segment I during postmonsoon and winter periods. The highest relative contribution from this fraction was observed in Segment I during the premonsoon periods. For the Stations in Segment II also, the higher relative contribution was recorded during winter and premonsoon periods. One interesting feature noted was the minimum variation observed in percentage values between Stations in Segments I and II. However, wide seasonal variation was indicated in Segment III, the higher percentage values being recorded during monsoon and post-monsoon periods.

The enhanced values of Mn4 during the winter and pre-monsoon periods could be attributed to the enhanced biological activity which resulted in the seasonal accumulation of autochthonous organic residues. The minimum variation in relative values of Mn4 indicated that in sediments an equilibrium was attained between the precipitation and remobilization of this fraction of manganese. The influence of terrestrial inputs of organic bound manganese was indicated by the high relative values recorded at the riverine Stations of Segment III during the monsoon and postmonsoon periods. The organic matter status of sediments had a profound influence on the distribution of Mn4 fraction, as was indicated by the strong relation between sediment organic carbon and Mn4 fraction.

The content of Mn5 fraction varied from 2.6 to 81.7 mg/kg, contributing 29 to 82 percent of total manganese in surficial sediments. In absolute terms, higher values were recorded at Stations in Segment II; the values exhibited high seasonal variation with monsoonal low and premonsoonal high values (Fig. 4.2). During the premonsoonal period, the values increased down-stream in Segment I, but during the other seasons, a down-stream decrease was indicated. In percentage-wise distribution, a gradual increase was noted for this fraction in Segment I and no trends could be detected in Segment II. In Segment III, a declining trend down-river was indicated during the winter and premonsoon periods and an increasing trend was indicated during the other periods.

In Segment I, a down-stream increase was observed in the percentage distribution of Mn5, whereas, the total manganese content showed a decreasing trend. A logical conclusion from this observation was that the more labile and active forms of manganese underwent changes in the sediments yielding the more resistant forms. A simultaneous decrease observed in the relative distribution of Mn1, Mn2 and Mn3 fractions also substantiated this view. It had been pointed out by several workers that microorganisms in the sediment/water interface would play a pivotal role in the transformation of these fractions (Ehrlich, 1980). The dissolution and removal of labile phases of manganese might also cause a net reduction in the total manganese, at the same time enhancing the relative contribution of Mn5 phase. Manganese substitution in the two layered silicate minerals could be another factor in the enrichment of residual fractions in an estuarine environment. The decrease in the percentage contribution of Mn5 fraction in the sediments of Segment II was attributed to the precipitation of authigenic fractions (as indicated by the enhanced percentages for Mn2 and Mn3 fractions at these Stations) which enriched the total manganese load in sediments bringing down the percentage contribution of Mn5. The behaviour of manganese at Station 9 might be due to industrial effluents that influenced the fate of manganese.

Table 4.3 furnishes data on the chemical partitioning of manganese reported from other parts of the globe. All the values are given in percentages. The mean and range values of the data recorded during the present study are also furnished for comparison. It can be seen that the data recorded for the Cochin estuary, for the fractions Mn 1, Mn2, Mn3 and Mn4, are within the range reported from other centres. The difference in the values for Mn5 fraction was mainly due to the extraction of moderately reducible phase by some workers, and if the values for Mn5 and Mn6 were summed up, then the difference would be marginal.

A comparison of the selective chemical extraction data for manganese and iron showed that there were greater differences in fractional distribution of manganese than for iron. Appreciable and roughly equivalent quantities of manganese were found in Mnl, Mn2 and Mn3 fractions, in the sediments of the Cochin estuary, and this was in unison with the observations recorded by Tessier et al. (1980) in the sediments from Yamaska and St. Francois rivers. An appreciable quantity of manganese was found to be associated with the organic phase (Mn4). Similar features in Mn4 distribution were observed in the sediments of Mobile Bay (Brannon et al. 1977) and Axios and Aliakmon estuaries (Samanidou and Fytianos, 1987), as well. An equitable distribution of manganese in various accumulative phases was observed, also in sediments from Puget Sound,

Table 4.3 Percentage of manganese fractions reported in sediments from different geographical locations.

Location	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	MnT (mg/kg)	Reference
Yukon-SPM	0.50		45.70	6.60	37.10		1270	Gibbs, 1973
Mobile bay, Site 1	14.93		35.50	35.53	8.07	5.97	1069	Brannon et al. 1977
Site 2	7.88		14.92	44.36	22.12	10.74	638	- do -
Yamaska river-SPM	29	23	24	1.70	22		1250	Tessier et al. 1980
St. Francois river-SPM	26	20	28	1.4	25		1400	- do -
Rhine river	8.5		32.4	3.8	17.2	38.1	583	Forstner, 1982
Subae river-unpolluted			45.8		47.1	7.1		Patchineelam and Forstner, 1983
-polluted			58.8	0.38	3	34.40		- do -
Yellow river	6.5	31.0	8.0	17.0	27.0	11.0	283	Hong and Forstner, 1983
Keum estuary	3.8		72.4	5.3	18.5			Lee, 1985
Krka estuary - range	12-35	45-78	bdl-15	bdl-11	1-6		700-2400	Prohic and Kniewald, 1987
Axios river	7.24	19.64	27.36	22.44	23.32		984	Samanidou and Fytianos, 1987
Axios estuary	5.57	21.94	27.55	23.99	20.95		815	- do -
Aliakmon river	3.26	23.15	32.91	30.69	9.99		534	- do -
Aliakmon estuary	3.95	23.33	32.67	31.23	8.82		504	- do -
COCHIN ESTUARY-MEAN	7.52	11.16	8.91	26.11	46.30		66	PRESENT STUDY
-RANGE	0.90-27.06	1.82-22.46	1.41-25.71	10.10-37.96	27.84-32.15		7-170	- do -

bdl = Below detection limit

Washington (Feely et al. 1986) and Amazon river, Brazil (Lacerda et al. 1990). The appreciable contribution of Mn1 and Mn2 fractions revealed that, contrary to iron, an important proportion of manganese was present in reduced forms. This corroborated the observation that in most natural waters manganese(II) oxidation was a much slower process than iron(II) oxidation (Stumm and Morgan, 1970). Because of the large amount of exchangeable manganese, a significant percentage of sediment manganese would be solubilised following an increase in salinity. The spatial distribution trend in the percentage values of Mn1 recorded during the present study emphasised the importance of salinity in regulating the exchangeable fractions of manganese. A decrease in relative abundance with increase in salinity was observed also for Mn3 and Fe3 fractions. The relative high abundance of less firmly held fractions of manganese indicated that this metal was predominantly associated with the labile fractions.

4.3.3 ZINC

Zinc plays an important role in the metabolic cycles of humans, animals and plants as a catalytic and structural element in numerous enzymes involved in energy metabolism. However, in higher quantities zinc is potentially hazardous to biota. The main pollutant sources of zinc are metalliferous mining activities, ore-dressing and processing, agricultural use of sewage sludge and composted materials, and the use of agro-chemicals such as fertilizers and pesticides. Kiekens (1990) furnished an excellent summary of the environmental chemistry of this element.

A number of studies have been reported on the behaviour of zinc in estuaries; the behaviour of the metal has been regarded as conservative in large unpolluted estuaries (Holliday and Liss, 1976; Elderfield et al. 1979; Danielsson et al. 1983; Paulson et al. 1989) and nonconservative in polluted estuaries (Duinker and Nolting, 1982; Duinker et al. 1985; Campbell et al. 1988). Considerable anthropogenic input of zinc into the Cochin estuary was reported by earlier workers (Sankaranarayanan et al. 1978; Paul and Pillai, 1983a; Ouseph, 1987; Nair et al. 1990; Shibu et al. 1990). Speciation studies on zinc in estuarine waters (Shibu et al. 1990) have shown that the river Periyar received considerable quantities of labile zinc with high zinc-organic matter associations. In freshwater most of the zinc was found in the dissolved phase where as in estuarine waters, the relative amount was found reduced (Shibu et al. 1990). Nair et al. (1990) observed significant seasonal and spatial variation in the distribution of zinc in surficial sediments. Chemical partitioning of zinc in surficial sediments (Nair et al. 1991) revealed that the various fractions of zinc were widely distributed in the Cochin estuary.

In estuarine sediments of the Cochin estuary, zinc ranks in abundance next only to iron. Total zinc (ZnT) varied from 14 to 259 mg/kg (Table 3.7). The high reactivity of zinc in the estuary was indicated by the high variability recorded for all fractions of zinc determined (Table 4.1). As noted for manganese the percentage variability recorded was in good agreement with the relative bonding energy of the different fractions; the percentage variability decreasing with increasing bonding energy. The order of abundance of the five fractions determined was, Zn1= Zn2< Zn3< Zn4<< Zn5. High seasonal and spatial variability was recorded for all forms of zinc determined. The spatial and seasonal variations are depicted in Fig. 4.3.

Large percentages of zinc were found in Zn4 and Zn5 fractions: other fractions also contributed significantly to the total pool although to a less extent. The Zn1 fractions varied from 0.07 to 13.2 mg/kg, contributing 0.2 to 13.4 percent of ZnT (Table 4.1). The content of Zn1 was very low in the sediments of Segment I in the southern arm of the estuary but abnormally high values were recorded in sediments from the northern arm of the estuary, especially at Station 9 which

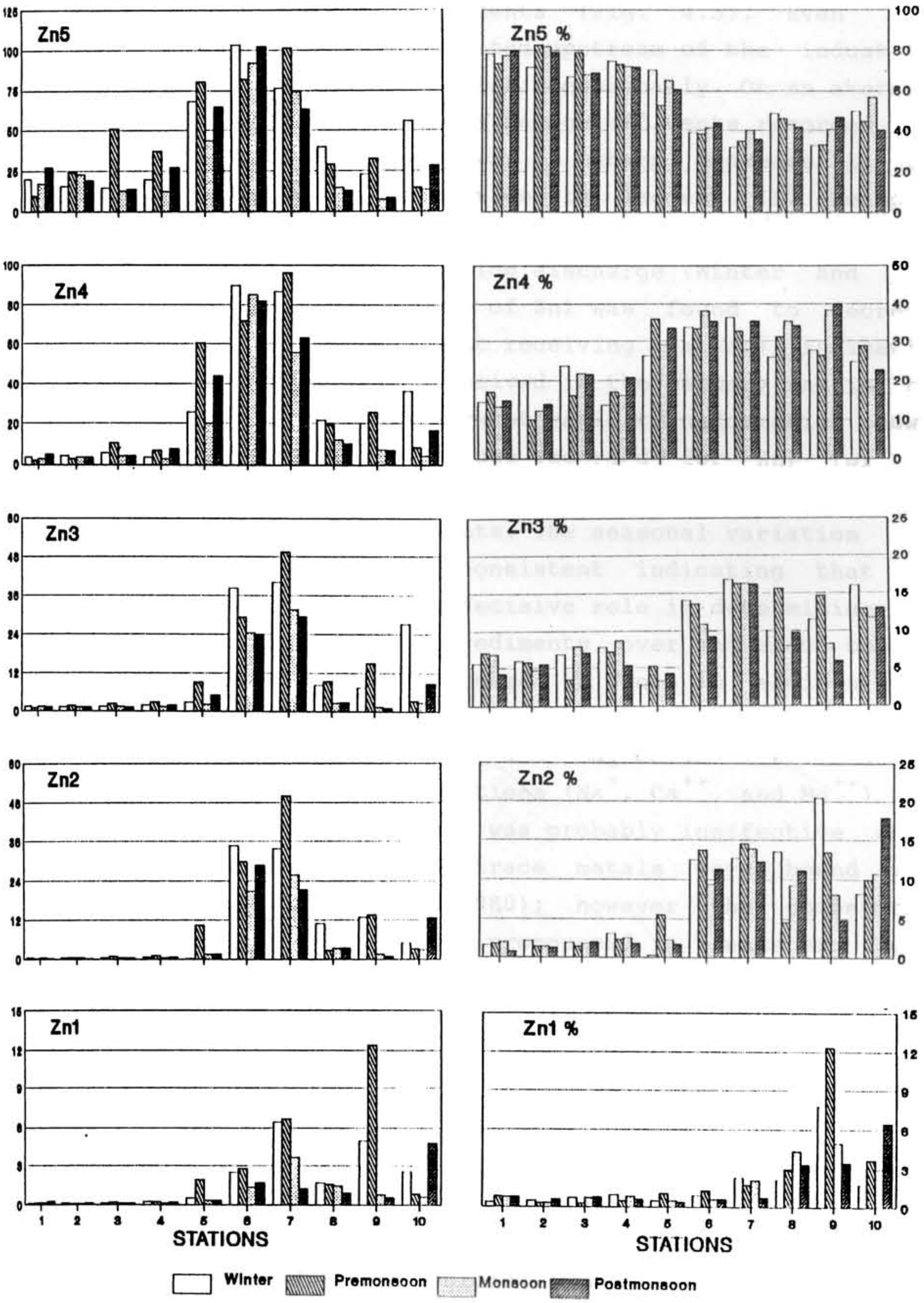

Fig. 4.3 Seasonal mean concentrations and percentages of zinc fractions (concentrations in mg/kg dryweight)

received the industrial effluents (Fig. 4.3). Even the sediments from Station 10, situated upstream of the industrial belt contained high content of Zn1 occasionally. On an average, the Station 7 which received the sewage effluents recorded the highest values of Zn1. There was a sharp decrease in Zn1 content towards the marine side in Segment II. Seasonal variations were quite prominent with the maximum values recorded during the periods of low discharge (Winter and pre-monsoon). The relative amount of Zn1 was found to decrease sharply from Station 9 (effluent receiving station) indicating that the major part of zinc received in the estuary was in the labile form, and the same underwent rapid transformation down-stream. The relatively low values recorded for Zn1 for the sediments in Stations 8 and 9 might be primarily due to the coarse sandy nature of sediments. The seasonal variation in percentage distribution was inconsistent indicating that the anthropogenic inputs played a decisive role in determining the partitioning of zinc metal in sediments, over and above to the seasonal influences. The decrease in Zn1 in sediments of Segment II might be due to the desorption of metal under the increasing influence of calcium and magnesium with seawater mixing. Competition of major cations (Na^+, Ca^{++}, and Mg^{++}) for surface sites on fine particles was probably ineffective under freshwater conditions, as the trace metals were bound very strongly (Dempsey and Singer, 1980); however the competition for surface sites could be more pronounced in seawater (Luoma and Davis, 1983). The premonsoonal increase in the absolute amounts of Zn1 at all stations could be attributed to the enhanced availability of exchange sites during the periods of low discharge because of the settling of finer suspended particles. The very low values on the southern part of the estuary established the absence of any anthropogenic zinc source in this part of the estuary.

Concentrations of Zn2 fractions ranged from 0.2 to 37.4 mg/kg contributing 0.4 to 19.7 percent of ZnT (Table 4.1). Higher concentrations were recorded at Stations 6 and 7 in

Segment II. Segment III had higher content of Zn2 than Segment I (Fig. 4.3), although the former had coarser sandy sediments. A unique characteristic feature observed in the seasonal distribution of Zn2 was the premonsoonal low values at majority of the Stations and abnormally high values in the winter. Very high amounts of Zn2 were found to be associated with sediments of Stations 6 and 7 during the monsoon and postmonsoon periods. The relative abundance of this fraction of Zn was significantly higher in all the Stations of Segment II and III (exception : Station 5 in Segment II). The seasonal variation pattern in the relative abundance was not distinguishable, again indicating the inconsistency caused by anthropogenic inputs.

As pointed out in the case of iron and manganese, phosphates might be playing an important role in controlling Zn2 distribution. The affinity of phosphates for zinc was well established (Burrow, 1987): an excess of phosphates in soil could cause zinc deficiency in crops (Kiekens, 1990). Thus the higher concentration of Zn2 recorded at Stations 6 and 7 during monsoon and postmonsoon periods could be attributed to eroded soils from uplands which might get trapped in these sheltered sedimentary environments (Pillai, 1989). Also, the contents of industrial effluents also might be influencing Zn2 form as was indicated by an exceptionally high percentage of this form for the winter and premonsoon seasons at Station 9.

The Zn3 fraction varied from 0.8 to 46.2 mg/kg in concentrations, and from 2.4 to 19.3 in percentagewise distribution (Table 4.1). Maximum values were recorded at Station 7, the sewage effluent receiving site in Segment III (Fig. 4.3), with values decreasing sharply towards the seaward direction. Seasonal higher values were recorded during the winter and postmonsoon periods and lower, during monsoons. Comparatively higher values were recorded in Segment III than in Segment I. Percentage wise also, the sediments in Segments II and III (with the exception of barmouth, Station 5) had significantly higher content of Zn3 than Stations in Segment I. No seasonal variation was observed at Station 7 in relative contribution but other Stations recorded slightly higher values during the premonsoon and winter periods.

The distribution pattern of Zn3 in sediments of northern arm of the estuary clearly demonstrated the influence of iron-manganese oxide precipitation in scavenging the metal under the influence of estuarine mixing. Thus at the low salinity regions of the estuary (Station 7) much of zinc was fluxed into the sediments in the easily reducible phases. Increase in hydroxylamine leachable zinc was also observed in suspended particles of the Fraser estuary as the freshwater changed into brackish waters (Grieve and Fletcher, 1977). The depletion of this form of zinc towards the more marine regions of the estuary might be either due to the dissolution [as pointed out by Hart and Davis, (1981) in Yarra river estuary] or dilution of sedimentary zinc with particles containing very low values of zinc as evidenced by the decreasing values for zinc down-estuary. Otherwise it might be due to diagenetic changes influenced by decomposing organic matter leading to further reduction of easily reducible fractions (as also indicated by a decrease in the abundance of Mn3 and Fe3 fractions). The enhancement of Zn3 at the upper riverine Stations during the periods of low river discharge indicated a change in the location of mixing zone as also indicated by the enhanced values for Fe3 during the corresponding periods.

The Zn4 values ranged from 1.2 to 81.4 mg/kg contributing 6.7 to 43.4 percent of ZnT (Table 4.1). Higher values were recorded at Stations 6 and 7 (Fig. 4.3). Sediments of Segment III had higher levels of Zn4 than that of Segment I. The minimum was recorded during the monsoons and maximum during the winter and premonsoon periods. Percentagewise, all the Stations in Segment II and III had higher content of Zn4 than the Stations of Segment I. Seasonal trends in percentagewise distribution was not quite distinct, although the monsoonal and postmonsoonal values were higher in most of the Stations.

One distinguishing feature noted in the distribution of Zn4 fraction was the minimum variability observed among the Stations within a Segment. The percentage values also showed less variation among the Stations in the northern arm, although the values were always higher than that of the southern parts. It indicated the influence of organic sources of both detrital and autochthonous nature in influencing the Zn4 fraction which was considered to be associated mostly with organic phases, in this estuary. In terrestrial soils it had been recorded that nearly 60-75 percent of soluble zinc was present in chelated zinc form (Hodgson et al., 1966 , Geering and Hodgson, 1969) and rain water draining the soil might contain appreciable amounts of zinc in this form. The high content of organic zinc in river waters would get flocculated and sedimented at the early stages of mixing, thus contributing an appreciable percentage to ZnT as evidenced by the higher percentage of this fraction during the monsoon and postmonsoon periods. However, the higher content of Zn4 recorded during winter and premonsoon had to be attributed to the autochthonous production of organic materials under the influence of enhanced productivity during these periods, and also to the coagulation and sedimentation of these products in a comparatively quiescent aquatic environment. Obviously, organic matter was an important factor affecting the behaviour of zinc in sediments. A high content of organically bound zinc was reported in the waters of this estuary (Shibu et al. 1990). Due to their colloidal nature, zinc humates could be considered as an organic storage pool of sedimented zinc.

The content of Zn5 fractions varied from 6 to 91 mg/kg contributing 28 to 89 percent of ZnT. In absolute values, the sediments of Segment II had the highest content of Zn5 (Fig. 4.3). Stations in Segment I had slightly higher content of Zn5 than Stations in Segment III. A monsoonal minimum and premonsoonal maximum were also observed at most of the Stations. Seasonal variations were not distinguishable in the percentage-wise distribution, but the Stations in the northern arm of the estuary had relatively low contribution (less than 50 percent) from this fraction than the Stations in the southern arm of the estuary, where the percentage wise distribution was above 70 percent.

The Zn5 fraction was generally considered as an inert fraction being detrital and lattice origin (Salomons and Forstner, 1980) and was usually taken as a measure of the geochemical contamination of the sediment sample. The slightly higher values of this fraction recorded for the sediments in southern part of the estuary were in agreement with the distribution of other residual metals, and therefore could be attributed to the particle size distribution of sediment particles. However, the consistent lower percentage contribution recorded for Zn5 fractions at all Stations of the northern estuary, at all seasons clearly demonstrated the effect of anthropogenic activities on metal partitioning. The distribution pattern of the various forms of zinc in Muvattupuzha (unaffected by anthropogenic inputs) and Periyar (severely contaminated by man's activities) rivers clearly demonstrated that the anthropogenic inputs were usually present in relatively loosely bound fractions as also recorded in various other locations (Tessier et al. 1980; Forstner, 1982; Calmano and Forstner, 1983; Samanidou and Fytianos, 1987; Pardo et al. 1990). This form might undergo rapid biogeochemical changes in the dynamic environments of estuaries giving rise to other forms of the metal.

In Table 4.4 percentage of zinc fractions reported in surficial sediments of different geographical locations are shown, along with the data from the present study. The trends in partitioning of zinc recorded during the present study agree well with the trend recorded from other centres. One major difference is the comparatively low values recorded for Zn3 fractions, although the ability of iron-manganese oxides to scavenge zinc from solutions is well established (Morgan and Stumm, 1964; Jenne, 1968) and this could be attributed to the low manganese values reported from this estuary, as it has been shown (Liang et al. 1990) that the manganese oxide fraction is more important than iron oxide fractions in the chemistry of zinc.

4.3.4 COPPER

Flemming and Trevors (1989) reviewed the available scientific literature on copper toxicity and chemistry in the environment and concluded that the chemical form of copper was important in controlling its geochemical and biological behaviour. Baker (1990) summarised the chemistry of copper in soils and pointed out that the plant availability depended on a number of soil factors which controlled its chemical speciation. Under natural conditions, copper forms sulphides, sulphates, carbonates and other compounds. Also, this metal is associated with organic matter, oxides of iron and manganese, silicate clays and other minerals. Copper in aqueous systems received attention mostly because of its toxic effects on biota.

Interestingly, the estuarine behaviour of copper differs markedly from that of iron - iron is removed almost totally from solutions in estuaries but copper behaves the other way (Wangersky, 1986). The free ion certainly interacts with the organic matter present but the result is usually an increase in solubility, rather than sedimentation (Nelson and Lund, 1982; Windom et al. 1983). The behaviour of copper in rivers was predicted to be similar to zinc based on the multi-river associations summarized by Martin and Meybeck (1979). They suggested that 10-50 percent of the total copper would be in the dissolved phase. The strong tendency of copper to remain in solution suggests that complexing agents, for example, organic matter from the decay of vegetative matter may stabilise copper in the soluble form. Very recently Paulson et al. (1991) demonstrated that the behaviour of copper in estuaries was linked to that of organic matter mineralisation.

Table 4.4 Percentage of zinc fractions reported in sediments from different geographical locations.

Location	Zn1	Zn2	Zn3	Zn4	Zn5	Zn6	ZnT (mg/kg)	Reference
Mobile bay, Site 1			4.15	52.04	43.79		257	Brannon et al. 1977
Site 2			2.25	58.97	38.76		177	- do -
Yamaska river-SPM	0.9	21	41	5	33		301	Tessier et al. 1980
St. Francois river-SPM	2.2	24	39	6	29		335	- do -
Rhine river	10.3		35.4	8.3	12.7	33.7	921	Forstner, 1982
Weser estuary	4		45	2	12	38	350	Calmano and Forstner, 1983
Rotterdam harbour	1		59	1	3	37	1130	- do -
Neckar river	3		48	2	13	34	610	- do -
Subae river-unpolluted			9.6	17.3	73.1		31	Patchineelam and Forstner, 1983
-polluted			34	6.2	17	42.4	1117	- do -
Yellow river	0.3	1	3	24	52	19	40	Hong and Forstner, 1983
Keum estuary			24.5	1.5	74		897	Lee, 1985
Krka estuary-range	9-33	27-43	1-4	9-15	20-37		32-72	Prohic and Kniewald, 1987
Axois river	0.76	8.36	28.41	32.03	30.44		249	Samanidou and Fytianos, 1987
Axios estuary	0.99	9.08	27.08	29.12	33.71		220	- do -
Aliakmon river	1.75	3.80	13.37	52.06	29.02		78	- do -
Aliakmon estuary	1.76	4.21	13.65	50.36	30.02		81	- do -
Pennsylvania (sludge)	0.5	17		6	42	34	527	Elliot et al. 1990
Pisuerga river	1.06	13.55	33.75	41.31	10.32		246	Pardo et al. 1990
COCHIN ESTUARY-MEAN	1.75	6.43	9.37	24.28	58.22		70	PRESENT STUDY
-RANGE	0.24-13.35	0.38-19.70	2.43-19.32	6.71-43.38	28.01-88.77		14-259	- do -

Shibu et al. (1990) observed that the copper in the fresh and estuarine waters of the Cochin estuary was extensively associated with organic colloidal matter. Fresh water contained 69 percent copper in dissolved fraction, but in estuarine water it was reduced to 21 percent. These authors observed an increase in exchangeable and total particulate copper from freshwater region to estuarine region, in the Cochin estuary. Distribution of copper in the surficial sediments exhibited wide spatial and seasonal variability (Nair et al. 1990).

Adediran and Kramer (1987) observed variations in copper adsorption on clay, iron and manganese oxides and organic fractions along a salinity gradient. Luoma (1986) from both theoretical modelling and laboratory studies showed that copper was not partitioned exclusively to a single component of estuarine sediment and that copper distribution among components might change from sediment to sediment. Luoma and Bryan (1981) also concluded similarly from statistical assessment of copper distributions. Thus all available approaches suggest that copper competitively partitions among a variety of components in oxidised estuarine sediments and that partitioning is driven by the highly variable chemical characteristics of those sediments. Preliminary studies on chemical partitioning of copper in sediments of the Cochin estuary (Nair et al. 1991) showed that partitioning pattern varied widely with the sites sampled.

Total copper values in the sediments of the Cochin estuary determined during the present study varied from 1.3 to 50.0 mg/kg with a mean value of 212.2 mg/kg (Table 3.7). A very high percentage of copper (47 to 90 percent) was found to be in the Cu5 fraction (Table 4.1); the fraction next in abundance was Cu4 (8 to 49 percent). The least abundant fraction was Cu3 (<1 percent on an average). Cu1 and Cu2 fractions were distributed more or less in equal amounts constituting about 2 percent of total copper.

The stationwise seasonal mean values of the five fractions of copper determined by chemical extractions are depicted in Fig. 4.4. The values are shown in absolute as well as percentage values. The Cu1 values ranged from 0.02 to 1.12 mg/kg with an average of 0.17 mg/kg (Table 4.1). Relatively higher values were recorded in sediments of Segment II, followed by Segment I (Fig. 4.4). The values at Segment III were, generally lower, but for an anomalously higher value recorded at Station 9, (industrial effluent outfall) and this might be due to some surreptitious local discharge of copper containing effluents. Seasonal variations in the distribution of Cu1 were not quite evident, probably due to the low amounts detected. In relative amounts, the riverine Stations on either arms of the estuary had higher percentages of Cu1 than the saline Stations of Segment II. Higher percentages were observed during the monsoon period.

The percentage distribution pattern of Cu1 indicated that copper in sediments was released as the sediment particles entered the saline water region from freshwater regions. Salomons and Bril (1990) demonstrated from laboratory studies, simulating changing estuarine conditions, that copper contaminated sediments from Fly river were able to release copper. Salomons and Eagle (1990) confirmed release of copper in Fly river sediments, from field studies. These reports are in agreement with the results of this study. A simple explanation that can be given for the copper release from sediments is linked to ion-exchange process. In fresh water, the trace metals like copper were more competitive in getting adsorbed to the exchange sites available on particulates, as the competition from alkaline earth metal ions was minimum. However, in the low salinity regions of upper estuary, calcium and more effectively magnesium exchanged with copper (and other divalent trace metals) thus impoverishing the particles in trace metals. Apart from desorption processes which occurred when sediments were subjected to an increase in chlorinity, the reverse process, i.e. adsorption might also occur. Adsorption

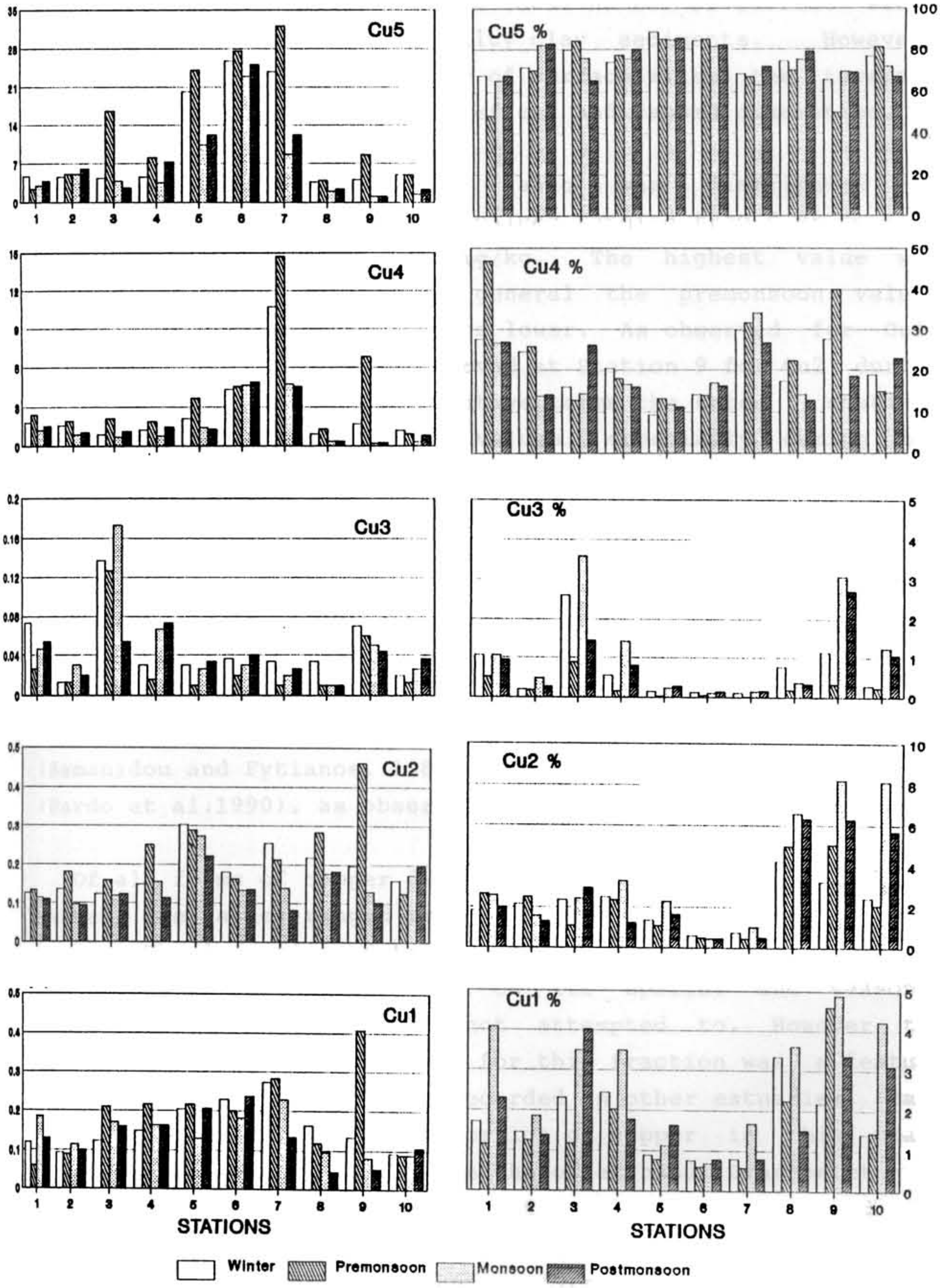

Fig. 4.4 Seasonal mean concentrations and percentages of copper fractions (concentrations in mg/kg dryweight)

processes were possible when the total number of surface sites in sediments increased as in silty clay sediments. However, even with an increase in number of surface sites, the increase in chlorinity counteracted the effect and caused desorption.

As observed for Cu1, Cu2 also was distributed in comparatively low amounts, the values ranging from 0.06 to 0.96 mg/kg with an average of 0.18 mg/kg. The highest value was recorded at Station 5 and in general the premonsoon values were higher and monsoonal values lower. As observed for Cu1, anomalous high value was observed at Station 9 for Cu2 during the premonsoon period. In relative terms the three stations in Segment III had higher values, especially during the monsoon and postmonsoon periods. The percentage value of this fraction was minimum at Stations 6 and 7 and the highest was recorded at the Station 10, located upstream of the industrial belt especially during the monsoon period. This indicated the terrestrial input of this form of copper probably associated with phosphates of agricultural soils eroded during monsoon rains. A low percentage contribution of this fraction of copper was reported from the Axios and Aliakmon river (Samanidou and Fytianos, 1987) and also from the Pisuerga river (Pardo et al.1990), as observed here in the Cochin estuary.

Of all forms of copper determined, Cu3 recorded the minimum values, the values ranged from below detection limits to 0.2 mg/kg. The low values detected in most of the samples placed restrains on any discussion on its spatial and seasonal distribution and hence it was not attempted to. However the consistent low values recorded for this fraction was a feature different from what had been recorded in other estuaries. Many workers detected significant portion of copper in this phase (e.g.,Tessier et al. 1980). On the other hand, Brannon et al. (1977) detected only very little copper extracted by hydroxylamine hydrochloride or dithionite reagents, in Mobile Bay sediments. Also they found no correlation between copper and manganese or iron extracted in these fractions. Moreover they observed that dithionite could extract more of copper than the hydroxylamine hydrochloride and this they attributed to the greater association of copper with iron oxides than with manganese oxides. Data from the Rhine (Forstner 1982), the Neckar (Calmano and Forstner, 1983), the Axios and Aliakmon (Samanidou and Fytianos, 1987) and the Pisuerga (Pardo et al. 1990) rivers all recorded very low percentage of copper in Cu3 fraction. In the Cochin estuary, it is surmised that the amorphous iron reaching the estuary readily undergoes transformation to crystalline forms with poor ability for co-precipitation, under the influence of the tropical climate.

The Cu4 fraction varied from 0.16 to 15.9 mg/kg and the average detected was 2.5 mg/kg (Table 4.1). The maximum value detected (Fig. 4.4) was at Station 7, the sewage effluent receiving station, with very high premonsoonal enrichment. Very high value was detected also at Station 9, during the pre-monsoon period. All the four Stations in Segment I had more or less similar values of Cu4, with significant premonsoonal enrichment. The relative value of Cu4 exhibited a sharp decrease down the estuary in Segment I and II. In Segment III the maximum percentage was recorded at Station 9, the industrial effluent receiving station. Seasonal trends were indistinct in percentage wise distributions.

Feely et al. (1983) showed that the sewage effluent receiving stations had very high amounts of trace metals in organic bound form and therefore, the high values of organic bound copper in Station 7 could directly be attributed to the city sewage discharged into this region. Tessier et al. (1980) also observed higher percentage of total copper bound to organic matter for the particulate matter of Yamaska and St. Francois rivers. This result was partly explained by the fact that for most ligands copper exhibited the highest stability constants of all the metals considered (Smith and Martell, 1976; Stumm and Morgan, 1970). Copper-organic matter association in sediments was reported by other researchers also

(Samanidou and Fytianos, 1987; Pardo et al. 1990). The reduction in percentage values indicated partial reduction of organic rich sediments which served to free copper into water column, thus reducing the CuT concentration in sediments. The enhancement of Cu4 values during the premonsoon periods indicated coagulation of organic matter rich in trace metals and their deposition during the more quiescent periods.

The values for Cu5 fractions ranged from 0.9 - 34.5 mg/kg with an average of 9.3 mg/kg (Table 4.1). The highest seasonal mean value (Fig. 4.4) was recorded at Station 7 with values decreasing sharply on either sides. The sediments of Segment III recorded relatively lower values for this fraction of copper. Seasonal higher values were recorded during the premonsoon and winter periods. The percentage-wise distribution showed the highest value in sediments of Stations 5 and 6 in Segment II and the seasonal variation was minimum. In segment I, the values increased downstream. No spatial or seasonal pattern in percentage wise distribution could be observed in riverine stations in the north, although the percentage values were lower than that recorded in lower saline Stations.

Forstner (1982), Calmano and Forstner (1983) and Hong and Forstner (1983) observed that a significant portion of CuT is associated with the moderately reducible phases of iron oxides in sediments. In the present study, this fraction was not separately estimated, and therefore the Cu5 fraction determined included this phase along with the residuals in the lattice minerals. This explains the high percentages recorded for this fraction of copper. Gibbs (1977) also reported high percentages (74-84%) of residual copper from the particulate matter of Amazon and Yukon rivers. The decreasing trend in CuT values (Chapter 3) together with an increasing trend in percentage Cu5 values suggested that the decrease was taking place at the expense of less firmly bound and organic bound fractions, and this hypothesis was further supported by the significant reduction observed for Cu1, Cu2, Cu3 and Cu4 fractions in

Segment II. The spatial distribution pattern of Cu5 followed the same pattern followed by other metals and was thus controlled by the geochemical and hydrological processes. It is known that the smectite type of clays in sediments could preferentially take up copper ions in their lattice structure, and in the marine environments these types of clays would be found in abundance. Therefore, the transformation of labile copper into less mobile Cu5 fraction by lattice substitution also could be expected; thus enhancing the percentage Cu5 values.

In Table 4.5 data reported on chemical partitioning of copper from other parts of the globe are presented, along with the data resulted from the present study. The range of values reported from the Cochin estuary is quite comparable with the global values for all the fractions of copper studied.

4.3.5 CADMIUM

Among the trace metals considered in this study, cadmium is of particular interest because of its high mobility in the environment and its long biological half-life in man (WHO, 1982). Pollution of the environment has been rapidly increasing in recent years as a result of rising consumption of cadmium by industry. Estimates of global emissions (Nriagu and Pacyna, 1988) relative to primary production of the metals showed that cadmium had the highest rate of emissions amongst all metals. Even before cadmium was used commercially, contamination with cadmium was reported as occurring from a wide range of materials containing cadmium as an impurity (Alloway, 1990); zinc minerals, lead minerals and phosphatic fertilizers contain cadmium as impurity.

Cadmium has no known essential biological function and as such is highly toxic to plants and animals (Craig, 1986). The concentrations normally encountered in the environment do not

Table 4.5 Percentage of copper fractions reported in sediments from different geographical locations.

Location	Cu1	Cu2	Cu3	Cu4	Cu5	Cu6	CuT (mg/kg)	Reference
Yukon-SPM	2.3		3.8	3.3	87.3		416	Gibbs, 1973
Mobile bay, Site 1			0.24	32.63	61.02	6.11	38	Brannon et al. 1977
Site 2			0.05	41.71	51.41	13.83	43	- do -
Yamaska river-SPM	1	8	20	31	41		64	Tessier et al. 1980
St. Francois river-SPM	1.2	14	12	52	22		165	- do -
Rhine river	2.7		0.2	14.5	34.2	48.4	202	Forstner, 1982
Weser estuary	1		<1	1	41	57	27	Calmano and Forstner, 1983
Rotterdam harbour	9		47	4	3	37	1062	- do -
Neckar river	3		<1	9	16	72	242	- do -
Yellow river	1.3	4	6	27	24	37	9	Hong and Forstner, 1983
Keum estuary	1.2		47.7	11.9	39.2		283	Lee, 1985
Krka estuary (range)	8-78	9-48	2-35	4-29	6-16		10-95	Prohic and Kniewald, 1987
Axios river	0.80	1.47	3.08	44.65	49.69		47	Samanidou and Fytianos, 1987
Axios estuary	0.98	2.19	6.01	42.98	47.84		46	- do -
Aliakmon river	1.15	2.25	4.97	70.85	20.78		43	- do -
Aliakmon estuary	0.96	2.11	4.67	73.98	18.28		37	- do -
Pennsylvania (sludge)	1	5.8		6.3	55	32	50	Elliot et al. 1990
Pisuerga river	0.31	3.31	0.05	64.2	32.12		67	Pardo et al. 1990
COCHIN ESTUARY-MEAN	2.08	2.72	0.74	20.34	74.21		12	PRESENT STUDY
-RANGE	0.37-6.67	0.32-9.52	<0.01-4.44	7.56-49.19	46.57-89.80		1.0-50	- do -

cause acute toxicity. However, in view of the chronic accumulation of cadmium in the human body, the factors influencing its bio-magnification through the foodweb are of great importance. Therefore, strict control of the agricultural use of dredged materials, restrictions on the non-essential uses of cadmium, stringent regulation of its emissions etc. are recommended (WHO, 1982).

Studies on the behaviour of cadmium in estuaries received attention along with the studies on copper, zinc and lead. Duinker (1985) reported extensive removal of cadmium, copper and zinc in the Rhine estuary. Elbaz-Poulichet et al. (1987) reported high concentration of cadmium in the Rhone river due to intensive use of phosphatic fertilizers in the catchment. Huynh-Ngoc et al. (1988) observed that hydrographical conditions greatly influenced the partitioning of cadmium between dissolved and particulate phases. Zwolsman and van Eck (1990) who studied the Scheldt estuary observed that the content of cadmium, copper and zinc were high in fresh water, that there was a rapid decrease in the low salinity region and that the distribution of these metals was greatly controlled by biological processes. Forstner et al. (1990) reviewed metal pollution in the Elbe river and observed that cadmium enrichment was relatively small in the dissolved phase even in strongly polluted section on the river. Jouanneau et al. (1990), demonstrated with the data from the Gironde estuary, the existence of an estuarine particulate stock with a long residence time during which the contaminated particulates originating upstream released a large proportion of their cadmium in the dissolved form. Evaluation of available data from the Cochin estuary indicated that the estuary received anthropogenic inputs of cadmium (Paul and Pillai, 1983a; Nair et al. 1990; Shibu et al. 1990; Nair et al. 1991). Bio-accumulation of cadmium in the native flora and fauna also have been reported (Paul and Pillai, 1983b) although the levels recorded were quite below the permissible levels. Analysis of surficial sediments (Nair et al. 1990) revealed accumulation arising out of anthropogenic inputs especially in the northern parts. The chemical partitioning of this element in surficial sediments revealed high spatial variability (Nair et al. 1991). Shibu et al. (1990) observed gradual decrease of dissolved cadmium as the river water entered the estuarine regions. About 15-25 percent of cadmium in water was found to be associated with organic compounds. It was also observed that the increased suspended solids concentration at the barmouth region did not contribute to the progressive increase of cadmium associated with particulates and it was explained that the increasing salinity inhibited the association of cadmium into the particulate phase.

Cadmium was the least abundant of the trace metals determined in the sediments during the present study. The CdT values ranged from 0.34 to 8.44 mg/kg (Table 3.7) with a mean value of 1.66 mg/kg. The order of abundance in the distribution of various fractions of cadmium was Cd5> Cd4>> Cd3> Cd2> Cd1. The stationwise seasonal mean values for the various fractions of cadmium are depicted in Fig. 4.5.

The values of Cd1 ranged from 0.01 to 0.24 mg/kg contributing 1.4 to 18.9 percent of CdT (Table 4.1). All the three Stations in Segment II had comparatively higher content of Cd1 values showing pronounced enhancement during the winter and premonsoon periods. Sediments of Station 9, which received the industrial effluents, also recorded higher Cd1 values during the winter and premonsoon periods. All the four Stations in Segment I (southern parts) had more or less similar content of Cd1. The percentagewise distribution pattern exhibited, an entirely different trend. The three Stations in Segment II had the lowest percentage contribution from this fraction of cadmium, and the percentage values showed an increasing trend towards the riverine end members. Moreover, relatively higher percentages of this fraction were noted during the monsoon in most of the Stations. Station 9 was an exceptional case in the sense that Cd1 was much higher in this Station both in

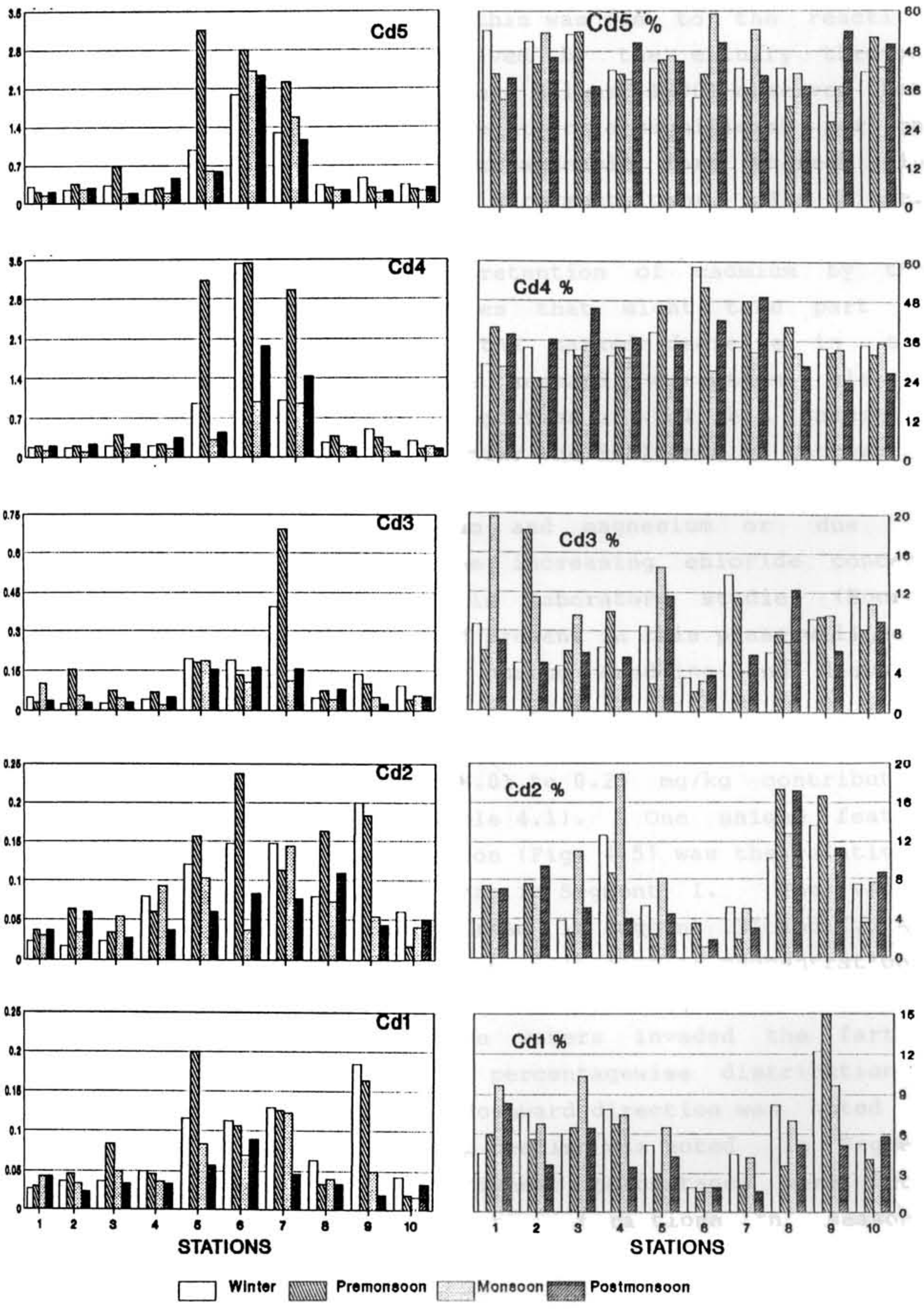

Fig. 4.5 Seasonal mean concentrations and percentages of cadmium fractions (concentrations in mg/kg dryweight)

absolute and relative terms and this was due to the reactive nature of cadmium being received by the estuary through industrial effluents. Elsokkary and Muller (1990) observed that in polluted sediments of the Nile river, a significant portion of cadmium existed in the exchangeable form whereas in unpolluted sediments, the values were much lower. The higher values recorded at the Stations in Segment II might be due to the sewage discharges and the retention of cadmium by the increased number of surface sites that might take part in exchange reactions. However, the marked decrease in the percentage values towards the seaward direction clearly demonstrated that a significant portion of Cd1 had undergone transformation to other forms under the influence of increasing salinity. Cadmium removal from exchange sites could be either due to exchange with calcium and magnesium or due to complexation of cadmium by the increasing chloride concentrations as had been observed in laboratory studies (Bourg, 1983). High concentration of Cd present in this phase will have adverse impact on water quality during dredging and disposal operations.

The Cd2 values ranged from 0.01 to 0.26 mg/kg contributing 0.7 to 22.6 percent of CdT (Table 4.1). One unique feature noted in its spatial distribution (Fig. 4.5) was the relatively higher values in Segment III than in Segment I. The values showed gradual increase downstream in Segment III and I. All Stations in Segment II had more or less similar concentrations. Seasonally, the highest values were observed during the pre-monsoon and winter as the saline waters invaded the farther regions of the estuary. In percentagewise distribution a distinct increase towards the downward direction was noted in Segments I and III, but a sharp decline was noted in Segment II. In the southern part, highest percentages were noted during the monsoon. Significant interactions in seasonal distribution between the Stations also were noted.

Both riverine inputs and estuarine processes had control over the distribution of Cd2 fractions. This fraction of cadmium was expected to be associated with carbonates and phosphates in the sediments. The higher percentages recorded during the monsoon could be attributed to terrestrial sources probably associated with the phosphates. Most of the phosphatic fertilizers contain cadmium as an impurity and thus, this association could be explained. The significantly higher content of Cd observed in the northern part of the estuary was identified as due to industrial discharges and sewage effluents. The increasing trends recorded downstream spatially and towards premonsoon season seasonally indicated that the gradually increasing salinities influenced precipitation of this form of cadmium. However, under higher salinity conditions, this fraction appeared to be unstable and underwent rapid remobilization as indicated by the sharp decline in percentage values. The distribution pattern of Cd1 and Cd2 fractions revealed that an appreciable percentage of sediment cadmium would be solubilized and become readily mobile following an increase in salinity and/or a slight lowering of pH. That, substantial percentages of particulate cadmium would be readily desorbed from suspended sediments in contact with seawater was shown by Van der Weijden et al. (1977), for the Rhine river sediments.

The Cd3 fractions exhibited wider variability (C.V.= 112.3 percent) than the other two fractions (C.V.= 72.8 percent and 71.1 percent) described above. Values ranged from 0.02 to 0.86 mg/kg, contributing 1.7 to 26.1 percent of CdT (Table 4.1). Higher values were recorded at Segment II (Fig. 4.5). Sediments of Segment I and III had more or less similar values. Pronounced premonsoonal hike was recorded at Station 7. Premonsoonal hike was recorded at Stations 2, 3 and 4 of Segment I also. Significant seasonal variation was not observed at the barmouth (Station 5). In percentagewise distribution a gradual decreasing trend was observed from the riverine end members towards the marine regions, the minimum percentage contribution being recorded at Station 6 of Segment II. Percentage values were higher during the monsoon season in many of the stations.

In comparison to the values reported by Forstner (1982), Calmano and Forstner (1983), Hong and Forstner (1983), Samanidou and Fytianos (1987) and Pardo et al. (1990), very low percentage values had been recorded for Cd3 fraction in the Cochin estuary. However, the trends in spatial distribution paralleled that of Mn3 and Fe3 fractions determined in the estuarine sediments. Therefore, the lower percentages recorded for Cd3 fractions could be due to the lower abundance of Mn3 and Fe3 fractions in the sediments.

An unique feature in the partitioning of cadmium fractions was the preponderance of Cd4 fraction over the other three fractions discussed. Of all the metals studied in the estuary, cadmium showed the highest relative abundance in this phase. The Cd4 values ranged from 0.07 to 3.83 mg/kg contributing 15 to 60 percent of CdT. The highest value was recorded in Segment II. Very high enrichment was observed during the premonsoon season (Fig. 4.5). Contents of Cd4 in other Stations were more or less equal, with slightly higher values during the premonsoon period. Percentagewise also, the sediments of Segment II had higher values and the values exhibited premonsoonal enrichment. However, at the four Stations in Segment I, the percentage values were higher during the postmonsoonal period, indicating strong interaction between sites and seasons in the distribution of Cd4 forms.

The distribution pattern of Cd4 fraction in the Cochin estuary was quite different from what had been reported from other estuaries by Tessier et al. (1980) and Calmano and Forstner (1983), that, a higher portion of CdT was found as Cd4 fraction in the Cochin estuary. The percentage distribution pattern suggested that this form of cadmium had undergone minimum transformation during the estuarine mixing processes (as was evidenced by minimum variation between the Stations during a particular season). However, seasonal variability in the biological processes had an effective control on the distribution of this fraction of cadmium as indicated by enhanced values for the premonsoon period. Corroborative observations to the influence of biological activity in controlling the estuarine behaviour of cadmium were reported from other estuaries, as well (Noriki et al. 1985; Kuwabara et al. 1989; Zwolsman and van Eck, 1990; Slauenwhite and Wangersky, 1991). During the winter and premonsoon periods, cadmium desorbed from the Cd1, Cd2 and Cd3 fractions appeared to be counteracted by their subsequent removal in the lower estuary which was most likely caused by phytoplankton bloom occurring in this region. Direct uptake of cadmium might be involved similar to the findings in the Delaware estuary (Sharp et al. 1984). The phytoplankton bloom might also affect the behaviour of cadmium by causing a sudden pH increase in the lower estuary, which strongly favoured adsorption of these metals by suspended matter (Bourg, 1983). Increased content of Cd2, especially during the winter and pre-monsoon seasons was noted during this study. The behaviour of Cd4 is much similar to that of Zn4 in Segment II, but contrasted that of Cu4. This could be explained on the basis of stability of organic complexes of these metals. Organic complexation of dissolved cadmium and zinc was less significant because the stability constants of their respective humic acid- metal complexes are four orders of magnitude lower (Turner et al. 1981). On the other hand, the strong association between copper and humics not only prevented uptake by phytoplankton but also suppressed adsorption onto suspended matter at high pH values.

The Cd5 content varied from 0.1 to 4.6 mg/kg, contributing 23 to 69 percent of CdT (Table 4.1). As observed for this fraction of other metals, higher values were recorded at Station 6 and the values decreased sharply on either side (Fig. 4.5). Cd5 fraction was more or less, equitably distributed in the sediments of other Segments. Generally, the premonsoon values were higher and monsoonal values lower. The highest relative contribution from this fraction was recorded at Stations 6 and 7 during the monsoon period. At other Stations, the seasonal trend was varying. The effluent receiving station had the lowest relative contribution from this fraction.

The lowest percentages of Cd5 in the sediments of Stations 8 and 9 pointed out anthropogenic input of this metal in more mobile forms. This was confirmed by the increasing percentages of Cd1 and Cd2 forms recorded in these Stations. The comparatively lower percentages of this fraction of cadmium (Cd5) indicated that cadmium was highly reactive in this estuary, and equally higher percentages in the Cd4 fraction suggested that the phytoplankton in the estuary were essentially involved in the biogeochemical cycling of this toxic trace metal.

Table 4.6 presents the percentages of cadmium fractions reported from surficial sediments of different geographical locations, along with data recorded during current investigation. Except for the values of Cd3 and Cd5 fractions, the data recorded agree well with the range reported from other centres. The lower values noted for Cd3 have already been explained on the basis of relative low abundance of freshly precipitated manganese and iron oxides in this tropical environment. Higher percentage of Cd5 fractions indicated that the magnitude of anthropogenic inputs over the natural inputs was comparatively low. However, the sequential chemical extraction technique employed was efficient enough to bring out the reactive nature of anthropogenic inputs. The sedimentary environments in Segment II housed large amounts of Cd4 and Cd5 fractions which would get released into the estuarine water, should the environmental conditions change. The contribution of Cd4 fraction was highest during the winter and premonsoon periods signifying the high biological productivity during this relatively warmer season. These studies revealed that an important sink for cadmium in sediments of the Cochin estuary

Table 4.6 Percentage of cadmium fractions reported in sediments from different geographical locations.

Location	Cd1	Cd2	Cd3	Cd4	Cd5	Cd6	CdT (mg/kg)	Reference
Los Angels harbour	1	5	9	38	14	34	2.2	Gupta and Chen, 1975
Yamaska river-SPM	26	49	12	<1	12		59.8	Tessier et al. 1980
St. Francois river-SPM	28	31	13	<1	27		4	- do -
Rhine river	26.7		42.3	16.8	12.3	1.9	9	Forstner, 1982
Weser estuary	18		47	9	2	24	2.6	Calmano and Forstner, 1983
Rotterdam harbour	16		60	6	2	16	7.9	- do -
Neckar river	13	64	12	1	10		33.6	- do -
Subae river-unpolluted			82.6	10.8	6.6		0.1	Patchineelam and Forstner, 1983
-polluted			78	18.2	1.4	2.4	27.6	- do -
Yellow river	12.9	22	3	2	18	43	0.1	Hong and Forstner, 1983
Axios river	10.79	24.89	29.60	19.05	15.67	1	17.6	Samanidou and Fytianos, 1987
Axios estuary	9.59	35.53	22.16	10.77	22.13		13.5	- do -
Aliakmon river	1.22	13.54	42.82	24.10	18.32		2.0	- do -
Aliakmon estuary	1.03	15.25	41.43	24.80	17.49		1.7	- do -
Pennsylvania (sludge)	5.8	19		38	38		1.6	Elliot et al. 1990
Pisuerga river	3.85	13.56	46.76	23.77	13.14		1.1	Pardo et al. 1990
Nile river - range	1.8-43.8	7.3-50.4	9.1-23.6	6.2-22.7	1.4-9.1	4.8-36.4	0.1-1.1	Elsokkary and Muller, 1990
COCHIN ESTUARY-MEAN	5.76	7.48	8.13	34.90	43.73		1.7	PRESENT STUDY
-RANGE	1.40-18.89	0.68-22.58	1.72-26.09	15.22-59.53	23.33-69.35		0.3-8.4	- do -

was the non-residual fraction, especially the one associated with organic matter.

4.3.6 LEAD

Lead is an environmental contaminant in all habitats, except those remote areas far away from populous regions or where human settlement is very recent. It enters the environment from several sources, the main inputs being the lead alkyls used in petroleum byproducts. Lead has a relatively long residence time in comparison with most other pollutants. As a result, lead and its compounds tend to get accumulated in soils and sediments. There are fears that body burdens below those at which clinical symptoms of lead toxicity would appear may cause mental impairment in children. Plants take up this metal from contaminated soils but there are no significant evidences as to the essentiality of this metal in biota (Prosi, 1989; Davies, 1990).

There are only few studies reported on lead from aquatic systems, mainly because of the associated analytical problems (Elbaz- Poulichet et al. 1984; Windom and Smith, 1985). The available reports deal mainly with the distribution of total lead in dissolved and suspended phases which have importance in identifying areas of contamination and also in elucidating the estuarine behaviour of the metal. Available evidences suggest that in estuaries, lead is readily removed from solutions and remains bound to particulates.

Considerable seasonal and spatial variation in the distribution of lead in sediments of the Cochin estuary was reported by Nair et al. (1990). Sewage discharges were considered to be an important anthropogenic source. Higher values were recorded during the premonsoon and postmonsoon periods. Lead content was reported to be lower during monsoon probably due to bedload movement downstream as a result of higher river discharge and the sedimentation of fresh riverine particles. Nair et al. (1991) reported significant spatial variation in the distribution of different forms of lead determined chemically in the sediments of the estuary. The investigations reported herein, were aimed at improving the database.

The total lead content of the estuarine sediments varied from 3.5 to 49.9 mg/kg (Table 3.7). These values were quite low in comparison with values reported from other estuaries of India (Table 3.11), but the values closely agree with the values reported earlier from the Cochin estuary (Nair et al. 1990; Nair et al. 1991). The abundance of various forms of lead ranked in the order of Pb1 < Pb2< Pb3< Pb4 <<<Pb5. In the distribution behaviour, different forms of lead were found to behave similar to the corresponding form of copper except in details.

The seasonal mean values of various fractions of lead determined in sediments sampled from various sites, together with their percentage values are depicted in Fig. 4.6. Values of Pb1 ranged from 0.05 to 1.13 mg/kg contributing 0.6 to 7.6 percent of PbT (Table 4.1). Highest value in absolute terms was recorded at Station 6 during all the seasons, and the values decreased on either side. Stations in Segment I had slightly higher values than Stations in Segment III. The values recorded at Station 9 exhibited significant seasonal variations. Premonsoonal values were generally high and monsoonal values were low. Higher percentagewise distribution was noted in the Stations in Segment I, as also noted for the sediments at Station 9, in Segment III. The percentage contribution of Pb1 to PbT was low in the sediments of Segment II. Seasonal variations in percentagewise distribution did not show any clear cut trends.

The enhanced values in Segment II were ascribed to the silty clay nature of sediments which had high adsorption sites to

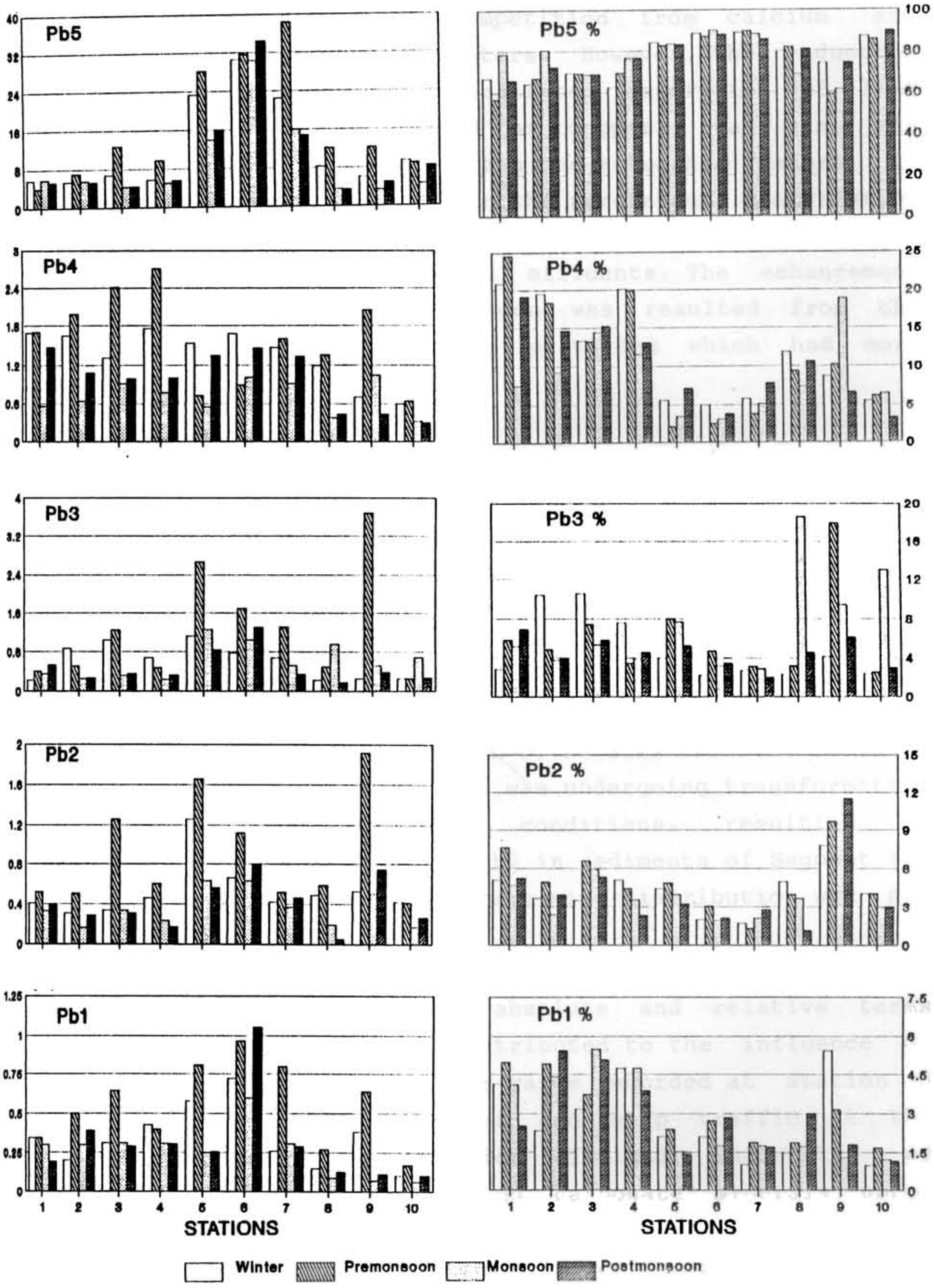

Fig. 4.6 Seasonal mean concentrations and percentages of lead fractions (concentrations in mg/kg dryweight)

hold lead ions amidst the competition from calcium and magnesium ions in high saline waters. However, the reduction in percentage values clearly demonstrated desorption of lead under these conditions. As noted for copper, lead also was more soluble in riverine waters than the estuarine waters, as indicated by a gradual decrease in the percentage contribution of Pb1 downstream. The seasonally higher values recorded at Station 9 was due to the industrial effluents. The enhancement in absolute values during pre-monsoon was resulted from the coagulation and settling of fine particles which had more exchange sites.

The Pb2 values ranged from 0.04 to 2.13 mg/kg and contributed 0.9 to 15.5 percent of PbT (Table 4.1). The highest value was recorded at Station 9, followed by the barmouth (Station 5) during the premonsoon period (Fig.4.6). Premonsoon values were higher at all Stations and the monsoonal values were minimum . In percentage-wise distribution, sediments of Station 9 had the highest contribution from this fraction of lead at all seasons. Percentage values decreased sharply towards the marine side on both arms of the estuary indicating that this form of lead was undergoing transformation under the changing salinity conditions, resulting in comparatively low percentage of Pb2 in sediments of Segment II. Seasonal influence in the percentage-wise distribution was not distinguishable.

The high Pb2 values both in absolute and relative terms recorded at Station 9 could be attributed to the influence of industrial effluents. The higher value recorded at Station 5 reflected the influence of boat and ship traffic at the barmouth Station. Precipitation of lead carbonates or occlusion of lead into hydrogenous carbonate minerals under saline influence was indicated by the pronounced enhancement in Pb2 fraction during winter and premonsoon seasons. However, reduction in the percentage values towards the marine side indicated remobilization of Pb2 under the influence of increased salinities, either due to competition from calcium and magnesium ions for exchange sites or due to formation of chloride complexes of lead.

The content of Pb3 in sediments ranged from 0.05 to 4.93 mg/kg contributing 1.0 to 20.9 percentage of PbT. During the monsoon and postmonsoon seasons, Pb3 was found to be distributed more or less equally at all Stations, irrespective of the texture of the sediments. However, higher values were recorded during the premonsoon and winter periods, with peak values appearing at Station 5 and Station 9 as observed for Pb2 fractions. Percentage-wise distributions exhibited a declining trend towards the marine side on either arms of the estuary with very high percentages recorded at Station 9 during the premonsoon and at Station 8 during the monsoon.

This fraction of lead was considered to be associated with the freshly precipitated oxides and hydroxides of iron and manganese. These oxides would remain as coating on both fine and coarse particles and hence could get more or less equally distributed throughout the estuary during the monsoon and postmonsoon periods. However, as the season proceeded from postmonsoon to premonsoon through winter,the rate of formation of authigenic hydroxide precipitates changed under the influence of varying salinities (as observed for Fe3 and Mn3 fractions), and this change was reflected in the distribution of Pb3 also during these seasons. The anomalous values recorded at Station 9 both in absolute and relative terms indicated contamination through industrial effluents.

Pb4 content in sediments ranged from 0.26 to 3.2 mg/kg contributing 1.4 to 28.6 percent of PbT. During the monsoon, postmonsoon and winter seasons, the values exhibited little variations in absolute amounts between sites, but seasonal variations were significant. The values increased from the monsoonal low values gradually to winteral high values. In Segments I and III, the premonsoonal deposition of this fraction was highest among the seasons, but in Segment II, the values showed a decrease during premonsoon. Higher contribution from this fraction of lead was indicated in the riverine sediments of southern parts especially during the winter and pre-monsoon periods. The sediments in Segment III also had elevated percentages than the saline Stations in Segment II. .

The distribution pattern of the relative amounts of Pb4 followed closely that of Cu4, except that Cu4 values were much higher than that of Pb4 values. The high percentage values in the riverine end members suggested proportionally large river input of this fraction, which would undergo transformation to more stable forms towards the lower parts of the estuary. Large scale remobilization of Pb1, Pb2, Pb3 and Pb4 fractions was indicated by the sharp decrease noted in the percentage values of these fractions in the lower parts of the estuary.

Pb5 was the most abundant of the lead fractions determined in sediments, and the values ranged from 2.3 to 45.5 mg/kg, contributing 52.5 to 92.7 percent of PbT (Table 4.1). Stations 5, 6 and 7 in Segment II recorded higher values, both in absolute and relative terms (Fig. 4.6). Sediments of Segments I and III had comparatively low values, but the premonsoonal enrichment was quite significant at these Stations. No trends could be distinguished in seasonal variations of the percentage values.

An unique feature noted was the increased percentages of Pb5 at the Stations of Segment II, whereas, a reduction was noted in the PbT values (Fig. 3.4). This suggested that the other forms of lead recorded in the sediments were quite unstable and were susceptible to transformation at the high saline conditions of the lower estuary. It was demonstrated in nearshore environments (Murty and Veerayya, 1981 and Satyanarayana et al. 1985) that the metals like copper and lead were associated with the smallest size particles of the sediment. ~~particles.~~ These particles flocculated only when subjected to rapid environmental changes as experienced in an estuarine situation. In Segment II more and more finer particles which were relatively rich in lead got flocculated and sedimented. The lower percentage contribution of Pb5 in Station 9 indicated anthropogenic input of lead in less tightly bound fractions which got converted rapidly to other forms when the sediments were transported downstream under conditions of bedload movement.

Table 4.7 compares the data resulted from the present study on chemical partitioning of lead with that reported from other parts of the globe. The range of values recorded from this study is in unison with values reported from other centres. The high percentages of Pb3 reported from other centres were different from the values reported here, and as explained for copper, might be due to the lower abundance of freshly precipitated iron and manganese oxides. Compared to zinc and copper a higher proportion of lead was found to be associated with residual fraction indicating low geochemical mobility and negligible biological availability of lead in this tropical estuary.

4.3.7 COBALT

Cobalt is an essential micronutrient for plants and animals. Its requirement especially by ruminants and N-fixing organisms has stimulated a great deal of research into the forms, quantities and chemical behaviour of this element in soils (Smith, 1990). Although the presence of cobalamine, a cobalt containing vitamin was detected in seawater, published work on the behaviour of cobalt in aquatic systems, especially under the estuarine systems, is scanty. In oceanographic considerations, behaviour of cobalt is usually related to that of manganese (Murray, 1975b; Amdurer et al. 1983; Li et al. 1984) in the sense that both these metals `recycle' within the system. Though they get removed from solution phase during estuarine mixing their removal mechanisms differ since

Table 4.7 Percentage of lead fractions reported in sediments from different geographical locations.

Location	Pb1	Pb2	Pb3	Pb4	Pb5	Pb6	PbT	Reference
Yamaska river-SPM	bdl	18	46	19	17		173	Tessier et al. 1980
St. Francois river-SPM	bdl	18	49	20	13		111	- do -
Rhine river	1.5		0.6	5.2	54.1	38.6	118	Forstner, 1982
Weser estuary	2		2	2	53	41	69	Calmano and Forstner, 1983
Rotterdam harbour	<1		66	1	15	18	256	- do -
Neckar river	<1		2	28	48	22	150	- do -
Subae river-unpolluted					100		25	Patchineelam and Forstner, 1983
-polluted			17.8	30.1	8.1	44	1775	- do -
Yellow river	0.3	16	4	<1	30	51	7	Hong and Forstner, 1983
Keum estuary			31.4		68.6		58	Lee, 1985
Krka estuary-range	9-58	11-66	10-49	bdl-4	2-21		23-67	Prohic and Kniewald, 1987
Axios river	0.96	15.54	25.50	29.80	28.20		217	Samanidou and Fytianos, 1987
Axios estuary	1.16	13.26	23.82	33.13	28.63		154	- do -
Aliakmon river	0.21	24.68	16.09	35.40	23.62		95	- do -
Aliakmon estuary	0.23	24.65	19.72	29.55	25.85		156	- do -
Pennsylvania (sludge)	4.20	2.60		13.0	72.0	8.4	204	Elliot et al. 1990
Pisuerga river	1.70	15.53	33.67	12.81	36.29		19	Pardo et al. 1990
Nile river - range	bdl-2.1	bdl-9.6	bdl-0.6	26.7-70	7.6-36.7	12.8-33.3	15-184	Elsokkary and Muller, 1990
COCHIN ESTUARY-MEAN	2.86	4.32	5.68	10.37	76.78		15	PRESENT STUDY
-RANGE	0.60-7.55	0.94-15.47	1.04-20.94	1.39-28.63	52.47-92.70		3.5-49.9	- do -

manganese and cobalt are far less `particle reactive'. Only very small percentages of cobalt and manganese were associated with particles in the water column; equally smaller percentages occurred in colloidal fractions (Amdurer et al. 1983). Environmental pollution problems are relatively insignificant for this trace metal.

Murty and Veerayya (1981) observed that in the Cochin estuary there was a decrease in manganese and cobalt content in the estuarine sediments in comparison with river sediments of similar texture and attributed this behaviour to the desorption of these elements from the river-borne detritus on coming in contact with saline waters and/ or to the mixing with marine sediments containing low concentrations of manganese and cobalt. Venugopal et al. (1982) while working on sediments from the northern parts of the estuary observed that the cobalt content of sediments was relatively low in monsoon periods than in other seasons. Nair et al. (1990) also reported higher rate of incorporation of this metal into sediments during post-monsoon and premonssoon seasons.

Results from the present investigations confirmed the relatively low levels of cobalt reported by earlier workers in sediments of the Cochin estuary. The range of values for total cobalt was 1.3 to 24.99 mg/kg with a mean of 9.2 mg/kg (Table 3.7). The abundance of different forms determined was in the order Co5 >> Co4 > Co3 > Co2 =Co1 (Table 4.1). The seasonal mean values of the different fractions of cobalt determined along with their relative abundant values are plotted in Fig. 4.7.

The Co1 values ranged from 0.02 to 0.72 mg/kg contributing 0.6 to 5.7 percent of CoT (Table 4.1). A unique feature noted in the distribution of Co1 fraction was the gradual increase downstream in Segments I and II both in absolute and relative values (Fig. 4.7). The downstream increase in percentage values was quite pronounced in these two Segments, but in

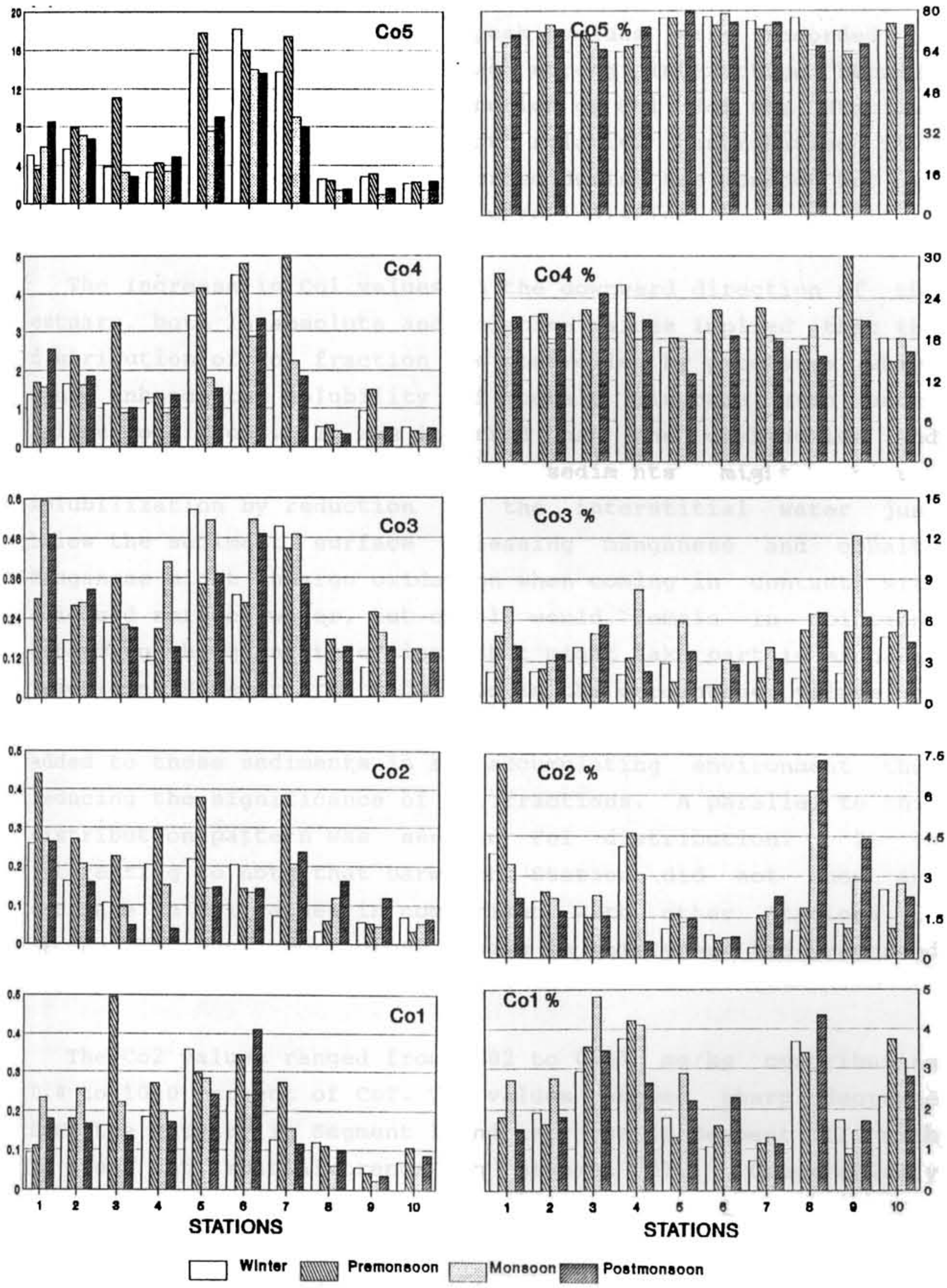

Fig. 4.7 Seasonal mean concentrations and percentages of cobalt fractions (concentrations in mg/kg dryweight)

Segment III, no spatial trend could be detected. In absolute terms the values were higher during the premonsoon at Stations 3, 4 and 8, but monsoonal peak values were recorded at Stations 1 and 2 thus indicating strong interaction between sites and seasons in the distribution of Co1. For the Stations in the southern part, the highest relative contribution from this fraction of cobalt was recorded during the monsoon but in other stations, seasonal trends were indistinct.

The increase in Co1 values in the downward direction of the estuary, both in absolute and relative values implied that the distribution of Co1 fraction was controlled by processes which could enhance the solubility of cobalt minerals even under saline conditions. It was inferred that the oxyhydoxide and carbonate phases of cobalt in sediments might undergo solubilization by reduction in the interstitial water just below the sediment surface releasing manganese and cobalt. Manganese might undergo oxidation when coming in contact with oxidised surface water, but cobalt would remain in solution, enhancing the quantity of ions that might take part in exchange reactions. However, the reduction in the percentage values of Co1 in Segment II hinted that other forms of cobalt were being added to these sediments in an accumulating environment thus reducing the significance of Co1 fractions. A parallel to this distribution pattern was seen in Fe1 distribution. It is interesting to note that barmouth Station did not show any decrease in Co1 values in comparison with other Stations in Segment II, but, most other metals in this phase had recorded depletion.

The Co2 values ranged from 0.02 to 0.57 mg/kg contributing 0.4 to 10.0 percent of CoT. The values showed sharp decrease down the estuary in Segment I and increase in Segment III, with no clear cut spatial trends in Segment II. Comparatively higher values were recorded at Stations 1 and 2 in spite of the sandy nature of the sediments. In percentage-wise distribution, the spatial trends were similar, but, the Stations in Segment

II recorded the lower percentages. Seasonally, the values were higher during the premonsoon period in all of the Stations of Segment I both in absolute and relative terms; but in Segment III relative values were higher during the postmonsoon period.

Downstream reduction in Segment I signified the dissolution of Co2 probably at subsurface layers in the sediments where organic matter decomposition would create reducing conditions. Premonsoonal enhancement in absolute values indicated the importance of increasing biological production and changing pH values that might influence cobalt precipitation in this phase, most probably, related to authigenic carbonates. Reduction in the percentage values down the estuary was paralleled by a gradual increase in percentage values of Co1 fractions, thus indicating that they were related events.

The Co3 values ranged from 0.03 to 0.86 mg/kg contributing 0.5 to 13.6 percent of CoT. Higher values were recorded at Stations of Segment II, and a noted feature was that the premonsoonal values were lower for this form of cobalt in Segment II. Stations of Segment I had comparatively higher values than those of Segment III. In Segment III, premonsoonal value was the highest; but in Segment I the seasonal pattern was indistinct. Percentage-wise distributions exhibited more or less equal values for all the Stations but seasonal differences were significant. Sediments had the highest contribution from this fraction of cobalt during the monsoon period.

The spatial distribution pattern of Co3 was similar to that of Fe3 and Mn3 fractions. Smith (1990) reported that there was a general tendency for total cobalt to increase with manganese, particularly with the easily reducible fraction, in the acidic grassland soils of England. In aquatic systems manganese and iron are probably removed from water column by oxyhydroxide precipitation and cobalt by co-precipitation. Their behaviour in the sediment is very sensitive to redox conditions (Amdurer et al. 1983). When mixed down into suboxic sediments (depending on the concentration of organic material in the sediments, temperature, bioturbation etc., this may be just below the sediment surface) manganese oxide is reduced releasing manganese and cobalt to the porewater. Since the kinetics of cobalt oxidation is relatively slow, and the pore water exchange in these sandy sediments is quite rapid, the cobalt released may get recycled rather than being `trapped' in the oxidised sediment layer as pointed out by McCaffrey et al. (1981) for Narragansett bay sediments.

The values of Co4 fractions ranged from 0.3 to 6.30 mg/kg contributing 10.4 to 30.5 percent of CoT. The highest value was recorded at Station 6 and the values decreased on either side. Sediments of Segment I had comparatively lower values than that of Segment III. Seasonal changes were characterized by monsoonal low and premonsoonal peak values. In percentage-wise distribution, the sediments of Segment I had relatively higher contribution from this fraction of cobalt than other Segments. Seasonal variations were not significant, although premonsoonal values were slightly higher.

The spatial distribution pattern of Co4 resembled that of Mn4 again indicating a similarity in the chemistry of these two elements in this estuarine environment. The enhanced values in the sediments of Segment II might be due to the high organic matter content in these sediments. The enrichment observed during premonsoon could be ascribed to the incorporation of cobalt into the authigenic organic materials and their subsequent deposition. The minimum variability in the percentage values suggested that the sediments attained certain equilibrium between the precipitation and remobilization of this fraction of cobalt. Though Co and Mn were similar in their oceanographic behaviour, Santchi (1988) has shown from microcosm experiments that in enclosures which received added nutrients, cycling of cobalt was completely decoupled from manganese, i.e., cobalt was removed more slowly than manganese. The differences noted in partitioning behaviour of cobalt and manganese could ,thus, be attributed to the difference in their chemical and biological behaviour.

The content of Co5 fractions varied from 0.8 to 19.0 mg/kg contributing 56 to 84 percentage of CoT. Its distribution pattern paralleled that of CoT (Fig. 4.1) suggesting that a definite portion of CoT was always found in this fractions. This observation was further supported by its relative distribution values which exhibited minimum variation within any segment. The seasonal variations in percentagewise distribution values were also insignificant. The absolute values of Co5 exhibited the same seasonal distribution trend, as exhibited by CoT, thus indicating that the cobalt loading in the sediments was controlled by natural processes and influence of anthropogenic inputs was minimum. Gilkes and McKenzie (1988) have shown that cobalt could replace manganese from manganese minerals under oxidizing conditions and under ideal conditions cobalt adsorbed on manganese hydroxides might become strongly bound to crystal lattices. The data on Co5 indicated that lattice substitution on manganese minerals could be an important process controlling the phase transformations.

Reports on chemical partitioning of cobalt in sediments are scanty. Available data is furnished in Table 4.8. The ranges reported from the present study agrees well with the values reported by Gibbs (1977) and Tessier et al. (1980) except for the Co3 fractions and that of Pardo et al. (1990), except for that of Co4 fractions. The lower abundance of freshly precipitated iron and manganese in the sediments of the Cochin estuary have already been stressed to explain the above feature.

4.3.8 NICKEL

Nickel and nickel compounds are used in a variety of industries such as stainless steel, alloys, electronic compounds, petroleum products and electroplating. Nickel is

Table 4.8 Percentage of cobalt fractions reported in sediments from different geographical locations.

Location	Co1	Co2	Co3	Co4	Co5	CoT (mg/kg)	Reference
Yukon-SPM	4.7		29.2	12.9	51.4	40	Gibbs, 1973
Yamaska river-SPM	bdl	bdl	31	12	51		Tessier et al. 1980
St. Francois river-SPM	bdl	bdl	47	13	35		- do -
Keum estuary	3.7		18.6	6.6	71.1	44	Lee, 1985
Krka estuary - range	2-18	14-23	20-32	21-34	13-26	3-10	Prohic and Kniewald, 1987
Pisuerga river	4.67	6.12	8.62	66.87	13.76	11	Pardo et al. 1990
COCHIN ESTUARY-MEAN	2.40	2.35	4.09	19.81	71.35	9	PRESENT STUDY
-RANGE	0.6-5.7	0.4-10	0.5-13.6	10.4-30.5	55.8-83.5	1.3-24.0	- do -

bdl = below detection limits
No data available on Co6

also used as a catalyst for hydrogenation of oils and also in domestic detergents. Thus the element reaches the environment from a number of point and non-point sources (Nriagu, 1980). Atmospheric inputs of nickel are also important (Nriagu and Pacyna, 1988) in many regions. Because of its widespread occurrence and known toxic effects at higher levels of contamination, several investigations on the environmental behaviour of this elemment have been taken up (McGrath and Smith, 1990). Anderson and Christensen (1983) observed that the most important factor determining the distribution of nickel between solid and solution phases was pH. The mobility of nickel in soils increased as the pH and cation exchange capacity decreased. Other factors which were reported to be influencing the mobility of nickel in soils were, the type and amount of clay present, amount of organic matter and presence of iron and manganese oxides. Lake et al. (1984) noted that there was an overall shift in the solid phase metal forms in sludge amended soils such that the residual forms decreased while that extracted with milder reagents increased. Waterbodies generally receive nickel from sewage discharges, oil spills and atmospheric outfalls (Nriagu and Pacyna, 1988). Though estuaries were likely to receive considerable supply of this metal much work has not been reported from estuaries (Campbell et al. 1988; Sadiq, 1989).

Murty and Veerayya (1981) reported total nickel values in the range of 10-60 mg/kg in sediments from the southern parts of the estuary. Venugopal et al. (1982) observed a downstream decrease in sediment nickel content on the northern parts of the estuary. Paul and Pillai (1983) reported monsoonal high values, in the sediments collected from Periyar river, nearer to the industrial belt. However, Nair et al. (1990) observed that the nickel distribution pattern was characterized by a preonsoonal mid-estuarine build-up following irregular post-monsoonal deposition. The total nickel (NiT) values determined in sediments during the present study varied from 1.9 to 70.6 mg/kg with an average value of 21 mg/kg (Table 3.7). Chemical partitioning (Table 4.1) revealed that 71 to 92 percent of the total nickel was present in the Ni5 fraction which was considered to be environmentally inert. The abundance of other forms of nickel was in the order Ni2< Ni1< Ni3 << Ni4. The seasonal and spatial distribution pattern of the various forms of nickel are depicted in Fig. 4.8. The data revealed significant spatial and seasonal variations. Significant interaction between the seasons and stations were also recorded.

The Ni1 values ranged from 0.04 to 0.89 mg/kg, contributing 0.3 to 3.6 percent of NiT. Highest value for Ni1 was recorded at Station 6 (except for the monsoon season) and the values decreased on either side. Comparatively higher values were recorded in the sediments in Segment I than that of Segment III. Seasonally higher values were recorded during premonsoon and winter. Percentagewise distribution indicated higher contribution of this fraction of nickel in the sediments of upper riverine regions of the estuary, whereas the percentages were very low in the saline regions. No seasonal trend was evident from the data available.

The very low percentages of Ni1 hinted that nickel was one of the least tenaciously sorbed of the transition metals so far discussed. On goethite surface, the sequence of adsorption was Zn> Cd> Ni (Breummer et al. 1988). The higher percentages of Ni1 recorded in riverine Stations indicated the higher solubility and mobility of nickel in the slightly acidic to neutral riverine waters in comparison to the more saline and alkaline waters of the lower estuary.

Ni2 values ranged from 0.02 to 0.66 mg/kg and contributed 0.2 to 5.1 percent of NiT. Comparatively higher values were recorded in Segment I and the values decreased sharply downstream. Seasonal variations were indistinct. The percentagewise distribution also exhibited down estuarine decrease in both the arms of the estuary at all seasons.

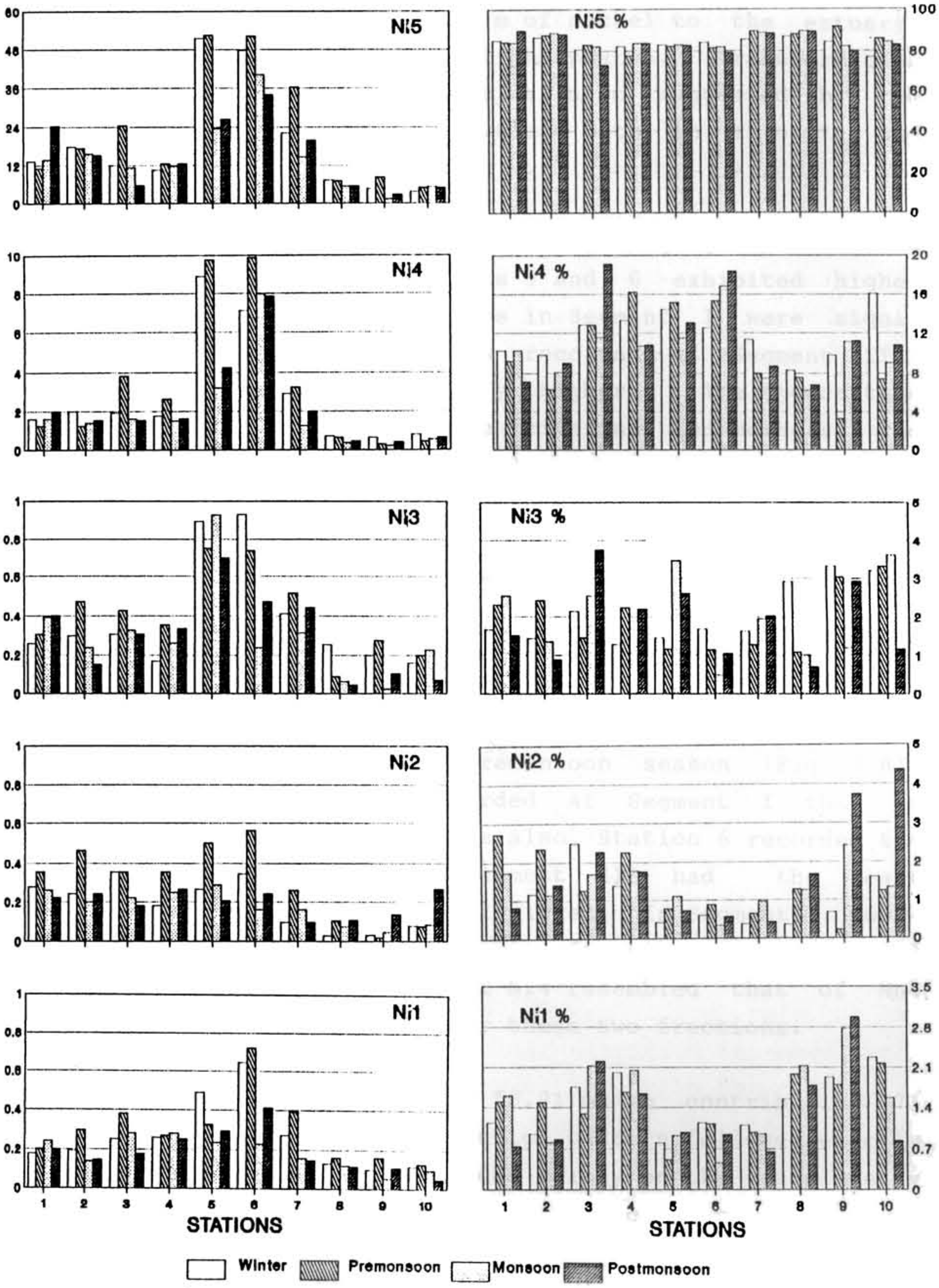

Fig. 4.8 Seasonal mean concentrations and percentages of nickel fractions (concentrations in mg/kg dryweight)

The distribution pattern suggested the influence of land drainage on the supply of this form of nickel to the estuary, most probably associated with soil phosphates. Transformation of this fraction into other forms was also suggested by the sharp decrease in down estuarine values both in absolute and relative terms.

The Ni3 values ranged from 0.02 to 1.12 mg/kg contributing 0.4 to 5.0 percent of NiT. Stations 5 and 6 exhibited higher values during all seasons. Values in Segment I were significantly higher than the values recorded at Segment III. Premonsoonal values were generally higher. The percentage values were slightly higher in the riverine end-members. The seasonal variations were irregular in percentage wise distribution. The very low percentages of nickel associated with this phase indicated the low mobility of nickel in these environments.

The Ni4 values ranged from 0.20 to 11.56 mg/kg contributing 3 to 22 percent of NiT (Table 4.1). The highest values were recorded at Station 6, and the values decreased sharply on either sides except for the premonsoon season (Fig 4.8). Slightly higher values were recorded at Segment I than at Segment III. In percentage values also, Station 6 recorded the highest value. Sediments of Segment III had the least contribution from this fraction of nickel. In Segment I, postmonsoonal values were higher for this fraction. The seasonal and spatial distribution trends of Ni4 resembled that of Mn4 signifying a similar behaviour for these two fractions.

Ni5 values ranged from 1.52 to 58.91 mg/kg contributing 71 to 92 percent of NiT. The distribution pattern followed exactly the distribution of NiT and depended mainly on the granulometry of sediments. Thus the silty clay sediments of the lower estuary (Segment II) had higher content of Ni5; and coarse sandy sediments of Segment III, lower values. Generally premonsoonal values were higher. Percentagewise distribution did not exhibit much variation except in Stations 3 and 9. The seasonal low percentages recorded for the postmonsoon period at these two Stations indicated occasional inputs of anthropogenic nickel, but there was no evidence of its spread to other sites.

The available data on chemical partitioning of nickel in sediments from other centres are furnished in Table 4.9 along with the data from the present study. Data from the Cochin estuary compared well with data from other centres. The tendency of nickel to remain in less mobile fractions was clearly evident from the data. The high percentage of nickel in Ni5 fraction, which was considered to be the geochemical contaminant suggested that input rates of anthropogenic nickel to this tropical estuary was much low.

4.3.9 CHROMIUM

Nowadays, environmental importance of chromium, its sources and hazards are receiving increased attention (Thessan et al. 1988). Chromium is found in varying concentrations in air, water, soil and essentially in all biological tissues. Chromium enrichment results from a number of anthropogenic sources including cement production kilns, smelting furnaces, tanning and pigment production etc. (McGrath and Smith, 1990). The burning of coal, oil and wood, and the incineration of municipal refuse and sewage sludge also contribute to atmospheric chromium concentrations. The presence of industries like tanneries and plating works help to trace the elevated levels of chromium in sewage sludges and water. Its role as an essential element in plant and animal nutrition has been well documented (Anderson, 1981); its essentiality in humans also is established. However, at elevated concentrations chromium is toxic. Chromium (III) compounds have no established toxicity but in the hexavalent state toxicity through skin ulcerations and nasal perforations as well as lung cancer have been reported (Bennet, 1982).

Table 4.9 Percentage of nickel fractions reported in sediments from different geographical locations.

Location	Ni1	Ni2	Ni3	Ni4	Ni5	Ni6	NiT (mg/kg)	Reference
Yukon-SPM	3.1		47.8	16	31.0		136	Gibbs, 1973
Mobile bay	1		2	7	90		127	Brannon et al. 1976
Ashtabula	1		2	10	65	23	185	- do -
Bridge port	1		2	26	69	3	182	- do -
Yamaska river-SPM	1.7	3.9	14	4.4	77			Tessier et al. 1980
St. Francois river-SPM	0.8	3.8	24	6.2	66			- do -
Keum estuary	0.9		18.9		80.2		40	Lee, 1985
Krka estuary - range	4-31	11-42	5-21	13-31	13-30		40-72	Prohic and Kniewald, 1987
Pennsylvania (sludge)	0.6	12		4.5	51	31.8	44	Elliot et al. 1990
Pisuerga river	4.34	16.34	14.06	53.66	12.31		47	Pardo et al. 1990
Nile river - range	0.2-3.7	1.8-7.8	1.0-3.3	34.5-41.7	43.2-49.4	8.3-14.9	74-98	Elsokkary and Muller, 1990
COCHIN ESTUARY-MEAN	1.45	1.40	1.98	10.94	84.23		21	PRESENT STUDY
-RANGE	0.34-3.57	0.19-5.08	0.42-4.99	3.05-21.85	71.39-92.04		2-73	- do -

Chromium exists in a number of oxidation states but the most stable and common forms are chromium(III) and chromium(VI). Chromium(VI) is an anion and is considered to be more toxic. Chromium(III) is much less mobile and adsorbs to particulates more strongly (McGrath and Smith 1990). The solubility of chromium(III) decreases above pH 4.0 and at about pH 5.5 complete precipitation occurs.

Most of the environmental studies reported on chromium were related to soil application of sewage sludges. In majority of soils the relatively insoluble and less mobile chromium forms predominated (Cary et al. 1977; Grove and Ellis, 1980). Cary et al. (1977) observed that addition of chromium either as chromium (III) or chromium (V1) to soils reverted to forms which were unavailable to plants. In sewage amended soils very stable organic complexes accounted for the extremely low availability of the element (Lake et al. 1989). However complexing chromium with soluble organic acids (for example, citric acid, fulvic acids and soil extracts of water-soluble organic matter) maintained chromium (III) in solution and was, therefore, a means of enhancing its mobility.

Reports on chromium content of sediments of the Cochin estuary are very few. Recently Nair et al. (1990) reported a chromium content of 3 to 118 mg/kg in the surficial sediments of the estuary. They observed that the southern part of the estuary was more contaminated with chromium than the northern part; seasonally, monsoonal values were low with gradual build up during postmonsoonal period, followed by a premonsoonal redistribution of sediment metals.

The total content of chromium determined in surficial sediments during the present study varied from 4 to 100 mg/kg, with an average value of 30 mg/kg (Table 3.7) and the values were in agreement with the earlier report (Nair et al. 1990). The summary statistics showing the maximum, minimum, mean and standard deviation in the values recorded for different fractions of chromium are presented in Table 4.1 along with percentage values. The abundance of the various forms of chromium was in the order, Cr5>>> Cr4>> Cr1> Cr2> Cr3. The seasonal mean values (both in absolute and relative terms) and spatial variations are depicted in Fig. 4.9.

The values for Cr1 fraction ranged from 0.02 to 0.49 mg/kg, and this fraction contributed 0.08 to 5.19 percent of the CrT. Higher values were recorded at Station 6, and values declined on either sides. Seasonal variations were characterized by higher values during premonsoon at most of the Stations. The percentagewise distribution did not show significant variations either in space or in time except at Station 9, the industrial effluent receiving Station. The very low percentage values (usually <1 percent) recorded is in agreement with the non-mobility generally assigned to this element in neutral to alkaline environments.

The values for Cr2 fraction ranged from 0.02 to 0.27 mg/kg, contributing 0.08 to 3.28 percent of CrT. Values were significantly higher in the southern part of the estuary, especially during the premonsoon period. The northern part exhibited low values in absolute terms, but the percentage values were higher in northern parts, especially in Segment III. Generally , the contribution of Cr2 fraction to CrT was quite insignificant evidencing the lack of affinity of chromium to carbonates and phosphates.

The Cr3 form was the least abundant of the chromium forms determined; the values ranged from below detection levels to 0.16 mg/kg contributing less than 0.4 percent of CrT. In absolute terms, higher values were detected at Station 5, the barmouth, with values decreasing slowly towards the riverine side.In the lower and middle estuarine regions, higher percentages were recorded during the monsoon and postmonsoon

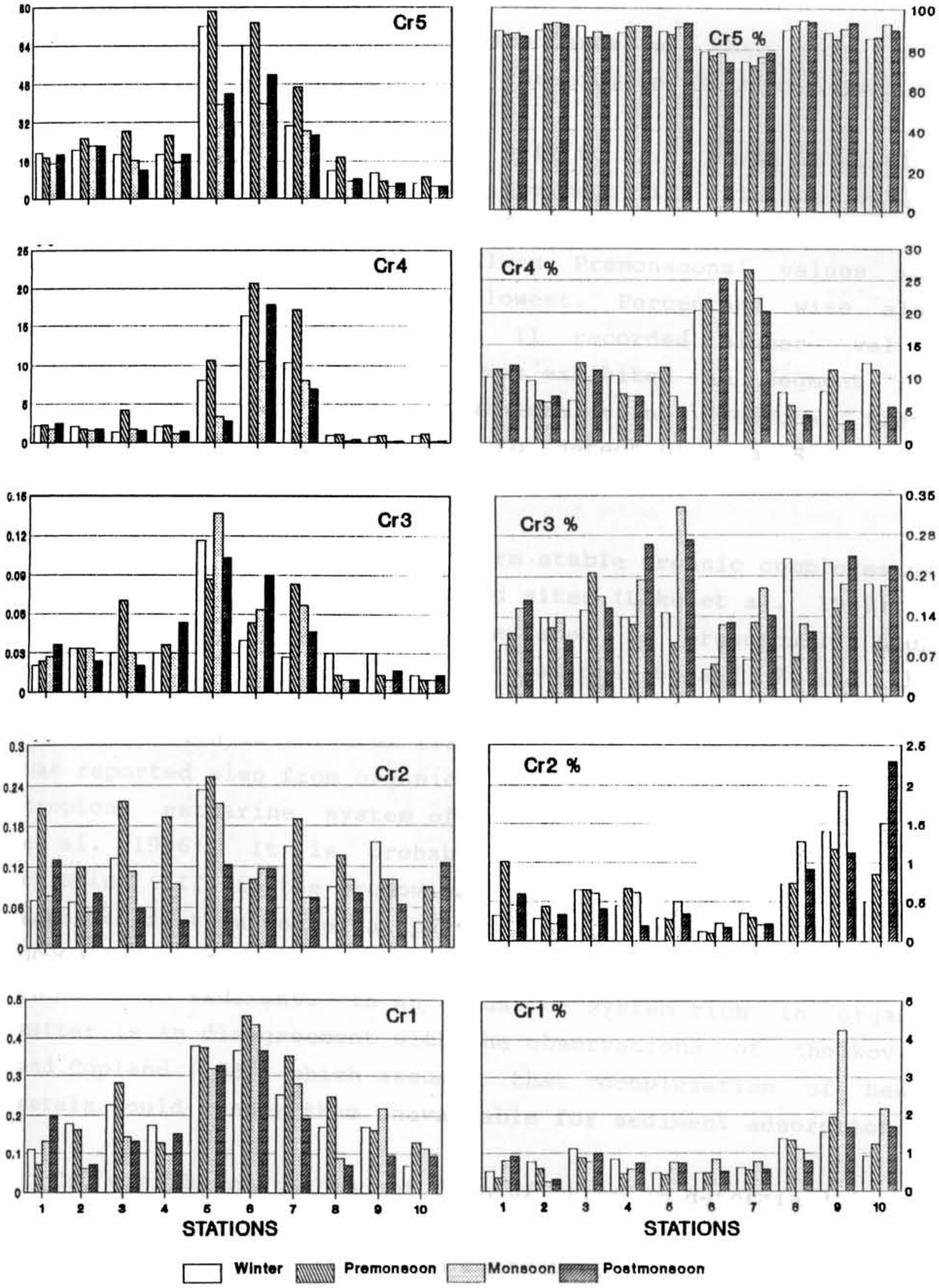

Fig. 4.9 Seasonal mean concentrations and percentages of chromium fractions (concentrations in mg/kg dryweight)

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seasons. The extremely low abundance of this form also signified the non-reactivity of chromium in the environment.

The Cr4 fraction varied from 0.12 to 22.57 mg/kg in absolute values, and from 2.24 to 27.63 percent in relative values. Maximum values were recorded at Station 6. Sediments of Segment I and III recorded very low values. Premonsoonal values were highest and monsoonal values lowest. Percentage wise also, Station 6 and 7 of Segment II recorded higher values. Significant seasonal variation was exhibited in Segment III, with higher premonsoonal and winteral values. Seasonal trends in percentage distribution were not detectable in Segments I and II.

The ability of chromium to form stable organic complexes has been reported from sewage amended sites (Lake et al. 1989). A significant portion of chromium existed in organically bound fractions in the sediments at Stations 6 and 7 and this evidenced the influences of sewage effluents in the transformation of chromium fractions. A high chromium content was reported also from organic rich regions of Guanabara, a tropical estuarine system of South America (De Luka Rebello et al. 1986). It is probable that under such situations chromium (III) is the predominant species and the same get adsorbed fast on colloidal particles which may eventually be deposited under estuarine influences. This fast removal of chromium to sediments in an estuarine system rich in organic matter is in disagreement with the observations of Sholkovitz and Copland (1981) which assumed that complexation of heavy metals would render them unavailable for sediment adsorption.

Cr5 was the most abundant form of chromium determined in the sediments of the Cochin estuary. The values of Cr5 ranged from 3.73 to 81.14 mg/kg; this form contributed 71 to 96 percent of CrT. The spatial distribution pattern was related to the granulometry of the sediments, the silty clay sediments in Segment II having the highest Cr5 value. The seasonal variation also was significant and was related to the depositional processes in the estuary; the highest values being recorded when the river flow was minimum during the premonsoon and winter periods. Lower values were recorded during monsoons. In percentagewise distribution a highly significant spatial pattern was exhibited. While the sediments in Segment I and III maintained very high proportions in the Cr5 fractions, the sewage effluent receiving Station and nearby Station in Segment II recorded relatively lower contribution from this fraction signifying the importance of other forms of chromium. The high values of chromium recorded at these stations together with the high percentages of organic bound fractions (Cr4) clearly demonstrated that the sewage effluents were an important source of chromium to this estuary.

Table 4.10 compares the data recorded during the present study with the data reported in estuarine sediments from other centres. The trends exhibited in distribution of chromium into various forms are similar for many cases. Most of the workers had observed the predominance of Cr5 (residual) fractions. Elsokkary and Muller (1990) attributed the higher percentages recorded in Cr4 fraction to anthropogenic reasons; in the Cochin estuary also, the higher percentages in Cr4 fraction could be traced to the sewage effluents.

Table 4.10 Percentage of chromium fractions reported in sediments from different geographical locations.

Location	Cr1	Cr2	Cr3	Cr4	Cr5	Cr6	CrT (mg/kg)	Reference
Yukon-SPM	2.3		7.2	13.2	64.5		115	Gibbs, 1973
Rhine river	0.1		0.4	6	7.1	86.3	338	Forstner, 1982
Yellow river	0.1	1	1	19	57	22	32	Hong and Forstner, 1983
Krka estuary - range	11-39	12-36	3-14	2-20	29-38		30-105	Prohic and Kniewald, 1987
Axios river	0.52	0.52	8.52	32.51	57.93		193	Samanidou and Fytianos, 1987
Axios estuary	0.19	0.63	9.69	30.70	58.79		167	- do -
Aliakmon river	0.23	0.69	3.54	66.90	28.64		212	- do -
Aliakmon estuary	0.22	0.65	2.87	69.88	26.38		179	- do -
Pennsylvania (sludge)	1	2.4		10	49	38	171	Elliot et al. 1990
Nile river - range	$<$0.1-0.1	0.2-1.9	bdl-0.8	29.9-53.2	12.2-62.5	8.3-31.9	174-940	Elsokkary and Muller, 1990
COCHIN ESTUARY-MEAN	0.95	0.64	0.16	11.01	87.25		30	PRESENT STUDY
-RANGE	0.08-5.19	0.08-3.28	0.03-0.46	2.24-27.63	71.01-95.56		4-105	- do -

CHAPTER 5

CHEMICAL PARTITIONING - IMPLICATIONS IN A TROPICAL ESTUARY

5.1 INTRODUCTION

5.2 TRACE METAL PHASES IN SEDIMENTS

- 5.2.1 EXCHANGEABLE PHASE
- 5.2.2 CARBONATE PHASE
- 5.2.3 EASILY REDUCIBLE PHASE
- 5.2.4 ORGANIC/SULFIDE PHASE
- 5.2.5 RESIDUAL PHASE

5.3 PHASE CONCENTRATION FACTOR

5.4 ESTUARINE ENRICHMENT

5.5 THE OUTLOOK

5.1 INTRODUCTION

The spatial and seasonal distribution pattern of the five chemical fractions of each of the trace metal was discussed in the previous Chapter, in relation to sedimentological and geochemical processes that are active in a typical tropical estuary. It was established that the estuarine processes had the potential to significantly alter the chemical partitioning of trace metals in the sediments. Since, in environmental studies, a better understanding of the processes and interactions involved is expected, when a group of constituents are considered, an attempt is made herein to rationalise the behaviour of trace metals in the estuarine environment with respect to a few parameters that reflect the geochemical/ oceanographical/ biological behaviour of the metals studied. The various accumulative phases have been characterised separately and their interactive processes compared and contrasted with variations in salinity.

5.2 TRACE METAL PHASES IN SEDIMENTS

The study quantified the trace metal phases in surficial sediments so as to assess the short term transformations that might affect the fate and transport of trace metals in toto and also to throw light on baneful ecological consequences. The average concentration of the different fractions of the nine metals studied and their average percentage distribution are presented in Figs. 5.1a and 5.1b. The observed order of abundance of the trace metals, was

$$\text{Fe} >>> \text{Zn} > \text{Mn} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Cu} > \text{Co} > \text{Cd},$$

which was the same as that reported in surface soils (Martin and Whitfield, 1983) except for the position of Zn, which is identified as a major contaminant in the northern parts of the estuary. A high variability was observed, in both

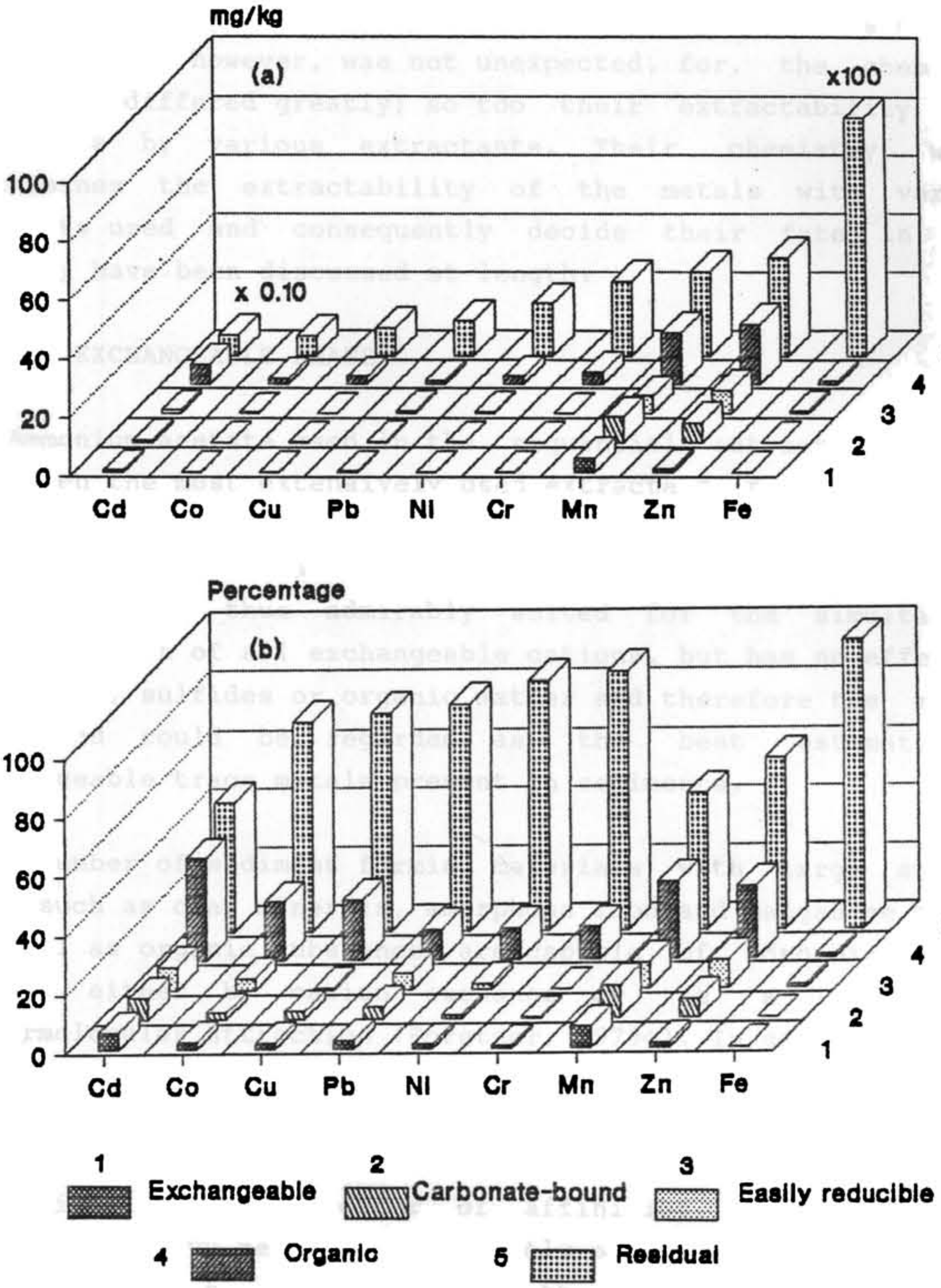


Fig. 5.1 Chemical partitioning of trace metals in sediments of the Cochin estuary. (a) concentration (mg/kg) (b) percentage

the absolute and relative amounts of various fractions of the metals. This, however, was not unexpected, for, the chemistry of metals differed greatly; so too their extractability from sediments by various extractants. Their chemistry which determines the extractability of the metals with various reagents used and consequently decide their fate in this estuary have been discussed at length.

5.2.1 EXCHANGEABLE PHASE

Ammonium acetate used in the sequential extraction scheme has been the most extensively used extractant to liberate the exchangeable metals from soils and sediments (Tessier et al. 1979). Ammonium acetate is strongly buffered around the neutral point and is thus admirably suited for the simultaneous determination of all exchangeable cations, but has no effect on silicates, sulfides or organic matter and therefore the metals extracted could be regarded as the best estimate of exchangeable trace metals present in sediments.

A number of sediment forming materials with large surface area such as clay minerals, amorphous iron and manganese oxides as well as organic substances are capable of adsorbing trace metals either by cation exchange or as a result of intermolecular attraction (Forstner, 1979c). In sediments these substrates for ion adsorption occur in the form of associations and the properties of such aggregates are quite different from that of the constituent particles. Thus it is impossible to establish a general order of affinities, applicable to individual heavy metals, based solely on ionic charge and ionic radii. Under estuarine conditions, the changing salinities and pH variations further complicate the problem~~s~~ (Bourg 1983; Bilinski et al. 1991).

The stationwise annual mean data for the exchangeable fraction of metals, is presented in Table 5.1 and the mean values for the percentages are furnished in Table 5.2. The

Table 5.1 Annual mean concentration (mg/kg) of the exchangeable fraction of trace metals in sediments of the Cochin estuary.

Station		Fe1	Mn1	Zn1	Cu1	Cd1	Pb1	Co1	Ni1	Cr1
1	Mean	6.69	17.46	0.15	0.12	0.04	0.30	0.15	0.20	0.13
	SD	5.56	12.14	0.02	0.05	0.01	0.08	0.07	0.04	0.05
2	Mean	4.01	8.08	0.10	0.10	0.04	0.35	0.19	0.19	0.12
	SD	1.79	4.41	0.03	0.02	0.01	0.15	0.05	0.08	0.07
3	Mean	5.57	3.34	0.12	0.17	0.05	0.39	0.26	0.27	0.20
	SD	2.26	1.71	0.02	0.05	0.02	0.17	0.19	0.08	0.07
4	Mean	5.85	3.29	0.17	0.17	0.04	0.36	0.21	0.27	0.14
	SD	4.39	1.46	0.03	0.05	0.01	0.13	0.04	0.06	0.04
5	Mean	5.33	3.85	0.82	0.19	0.11	0.47	0.30	0.34	0.35
	SD	1.63	1.82	0.86	0.06	0.06	0.25	0.07	0.10	0.06
6	Mean	6.52	3.91	1.94	0.21	0.10	0.83	0.31	0.50	0.41
	SD	1.42	1.38	0.95	0.04	0.02	0.21	0.08	0.23	0.05
7	Mean	7.85	3.78	2.59	0.23	0.11	0.41	0.17	0.24	0.27
	SD	1.70	3.01	0.55	0.07	0.04	0.25	0.07	0.11	0.06
8	Mean	2.45	1.40	1.28	0.11	0.04	0.16	0.10	0.13	0.14
	SD	1.51	1.38	0.32	0.05	0.01	0.07	0.02	0.02	0.07
9	Mean	0.98	1.06	3.82	0.27	0.10	0.30	0.04	0.11	0.16
	SD	0.55	0.73	4.34	0.33	0.07	0.24	0.02	0.04	0.05
10	Mean	1.40	1.72	0.92	0.10	0.03	0.11	0.08	0.10	0.10
	SD	0.95	0.36	0.50	0.02	0.01	0.05	0.03	0.03	0.03
General	Mean	4.66	4.79	1.19	0.17	0.07	0.37	0.18	0.23	0.20
	SD	3.46	6.34	1.88	0.13	0.05	0.26	0.12	0.15	0.11

Table 5.2 Annual mean percentages of the exchangeable fraction of trace metals in sediments of the Cochin estuary.

Station		Fe1	Mn1	Zn1	Cu1	Cd1	Pb1	Co1	Ni1	Cr1
1	Mean	0.08	15.96	0.60	2.31	7.11	3.93	1.85	1.24	0.64
	SD	0.07	7.89	0.21	1.15	2.04	0.97	0.64	0.43	0.25
2	Mean	0.05	8.96	0.38	1.48	5.90	4.25	2.03	1.02	0.48
	SD	0.02	3.73	0.12	0.43	1.83	1.80	0.57	0.37	0.28
3	Mean	0.09	8.03	0.59	2.75	7.30	4.35	3.69	1.84	0.94
	SD	0.03	1.53	0.18	1.21	1.96	1.32	1.04	0.46	0.22
4	Mean	0.08	5.70	0.64	2.43	6.40	4.06	3.68	1.84	0.65
	SD	0.05	1.84	0.16	0.85	1.99	1.40	0.85	0.37	0.20
5	Mean	0.04	3.46	0.81	1.11	4.73	1.85	2.04	0.80	0.59
	SD	0.01	1.89	0.64	0.45	1.47	0.44	0.64	0.26	0.18
6	Mean	0.04	3.18	0.97	0.72	1.85	2.35	1.57	0.91	0.58
	SD	0.01	1.23	0.43	0.18	0.32	0.67	0.50	0.33	0.17
7	Mean	0.10	5.01	1.39	0.97	3.10	1.58	1.07	0.91	0.63
	SD	0.03	2.60	0.31	0.45	1.35	0.50	0.28	0.28	0.11
8	Mean	0.05	7.55	2.95	2.67	6.01	2.02	3.59	1.85	1.15
	SD	0.03	4.56	0.84	1.16	2.14	0.64	0.66	0.49	0.32
9	Mean	0.02	6.90	6.16	3.82	10.54	2.91	1.45	2.37	2.33
	SD	0.01	2.28	3.66	1.34	4.02	1.72	0.97	0.61	1.27
10	Mean	0.02	10.46	3.03	2.55	4.61	1.26	3.02	1.70	1.49
	SD	0.02	2.84	1.56	1.22	1.33	0.41	0.80	0.67	0.51
General	Mean	0.06	7.52	1.75	2.08	5.76	2.86	2.40	1.45	0.95
	SD	0.04	5.05	2.18	1.32	3.07	1.59	1.20	0.68	0.73

order of abundance of the exchangeable fraction of the metal, in absolute quantities was,

Mn > Fe > Zn > Pb > Ni> Cr > Co > Cu > Cd

and the order roughly followed the abundance of total metals in the estuary, except for iron. However, when the percentage contributions were considered, the order of abundance was,

Mn > Cd > Pb > Co > Cu > Zn > Ni > Cr > Fe.

Van der Weijden et al. (1977) established an order

Cd > Zn > Mn > Ni > Co > Cu > Cr > Fe, Pb

for desorption of metals from suspended sediments of the Rhine river and the order observed for the sediments of the Cochin estuary agreed with the same except for Mn, Pb, Ni, and Zn. While the change in the order of Ni and Zn was not of much significance in the light of the low percentages of these metals found in this fraction and the wide dispersal of the data, the behaviour of Mn and Pb was quite significant. Higher percentages of exchangeable manganese was reported also from the sediments of the Mobile Bay (Brannon et al. 1977), Yamaska and St. Francois rivers (Tessier et al. 1980), Rhine river (Forstner, 1982), Axios river (Samanidou and Fytianos, 1987) and Krka river estuary (Prohic and Kniewald, 1987) - all pointing to a peculiar reactivity of manganese. Mitchell (1964) had established the following empirical affinity sequence of heavy metal towards clay minerals,

Pb > Ni > Cu > Zn .

Soong (1974), who studied the competitive sorption of heavy metals onto clay minerals established that lead was more competitive than copper and zinc. Forstner (1979c) quoted the following affinity series for cation exchange on organic and inorganic substrates,

Pb > Cu > Ni > Co > Zn.

Elliott et al. (1990) also reported the high affinity of Pb for adsorbing sites in soils. Recently Bilinski et al. (1991) reported high affinity of Pb to estuarine particles. All these studies clearly demonstrated that lead had a high affinity for clay minerals and organic substances. While its high affinity to clay minerals could be attributed to its ionic radii (Soong, 1974), its affinity to organic substances might be due to the high stability of lead-organic complexes (Irving and Williams, 1948). Thus the higher ranking obtained for exchangeable lead in the sediments of the Cochin estuary was justifiable in the light of the known adsorption behaviour of the element. Exchangeability of cations depends on their ionic radii, electronegativity, ionic potential etc. When the relative abundance of the trace metals in the exchangeable phase was compared with these parameters (all data from Krauskopf, 1967), it was found that the affinity series established for the exchangeable fraction of trace metals in the sediments of the Cochin estuary corresponded closely with the electronegativity (Fig. 5.2a), ionic potential (Fig. 5.2b), ionic radius (Fig. 5.3) and the negative logarithm of the solubility product of the respective metal hydroxide. Thus the data obtained from the ammonium acetate extractant was chemically explainable and the fraction extracted did have a separate chemical identity and meaning.

For all the metals studied, the percentage extractable fraction showed decreasing trends from the riverine regions to near marine regions, on both arms of the estuary. This observation was in agreement with the model presented by Bourg (1983) as well as with the experimental results of Duinker (1983) on particulates of the Rhine estuary. In both the studies, a decrease in the percentage of adsorbed fraction was indicated with an increase in salinity. It might be due to the competitive replacement of trace metals by the alkaline earth metals (calcium and magnesium) which are abundant in saline waters. Bourg (1983) demonstrated that although the increased pH in saline waters ought to have enhanced the adsorbed metals,

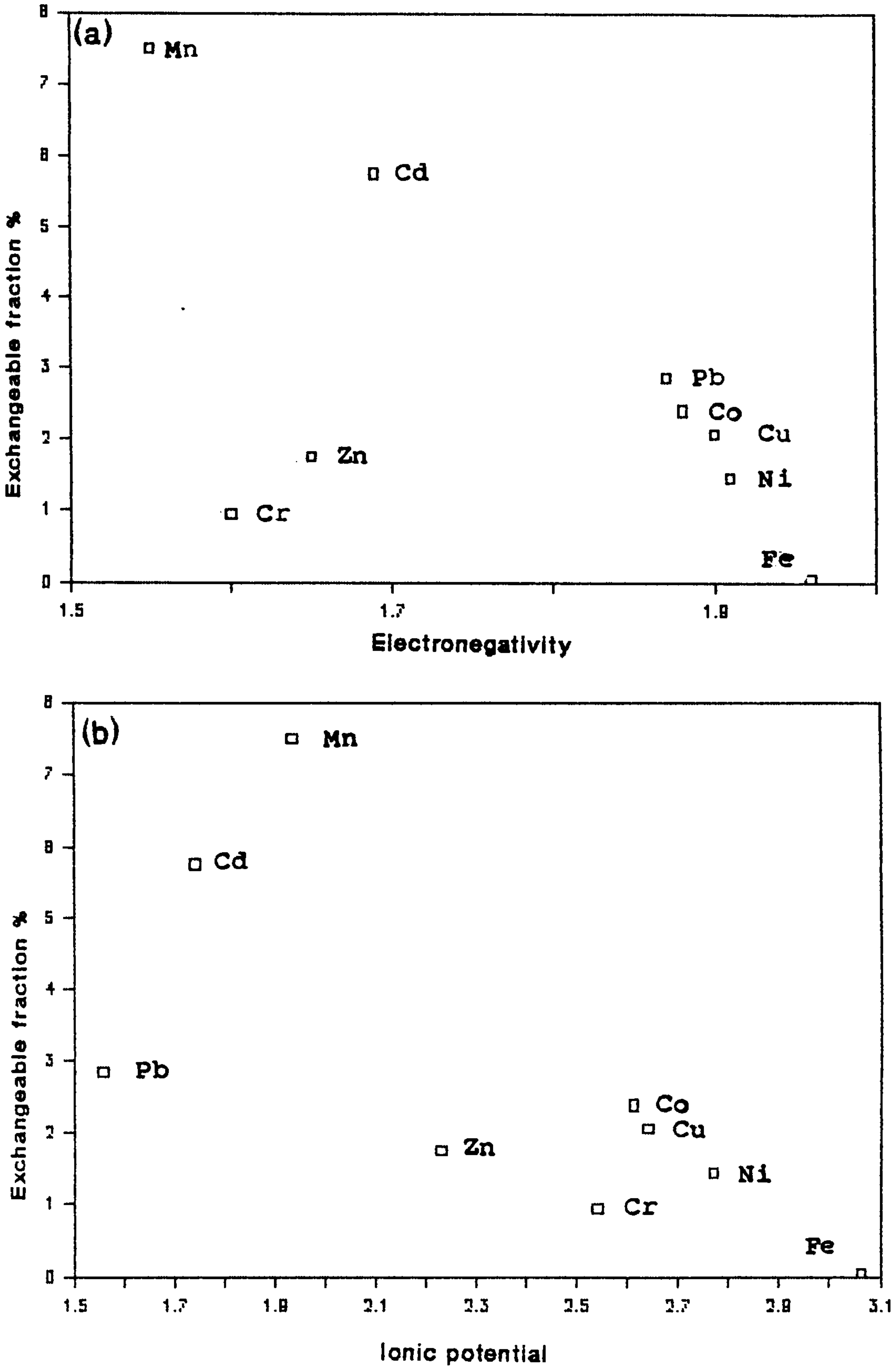


Fig. 5.2 Variations in percentage exchangeable fraction as related to (a) electronegativity and (b) ionic potential

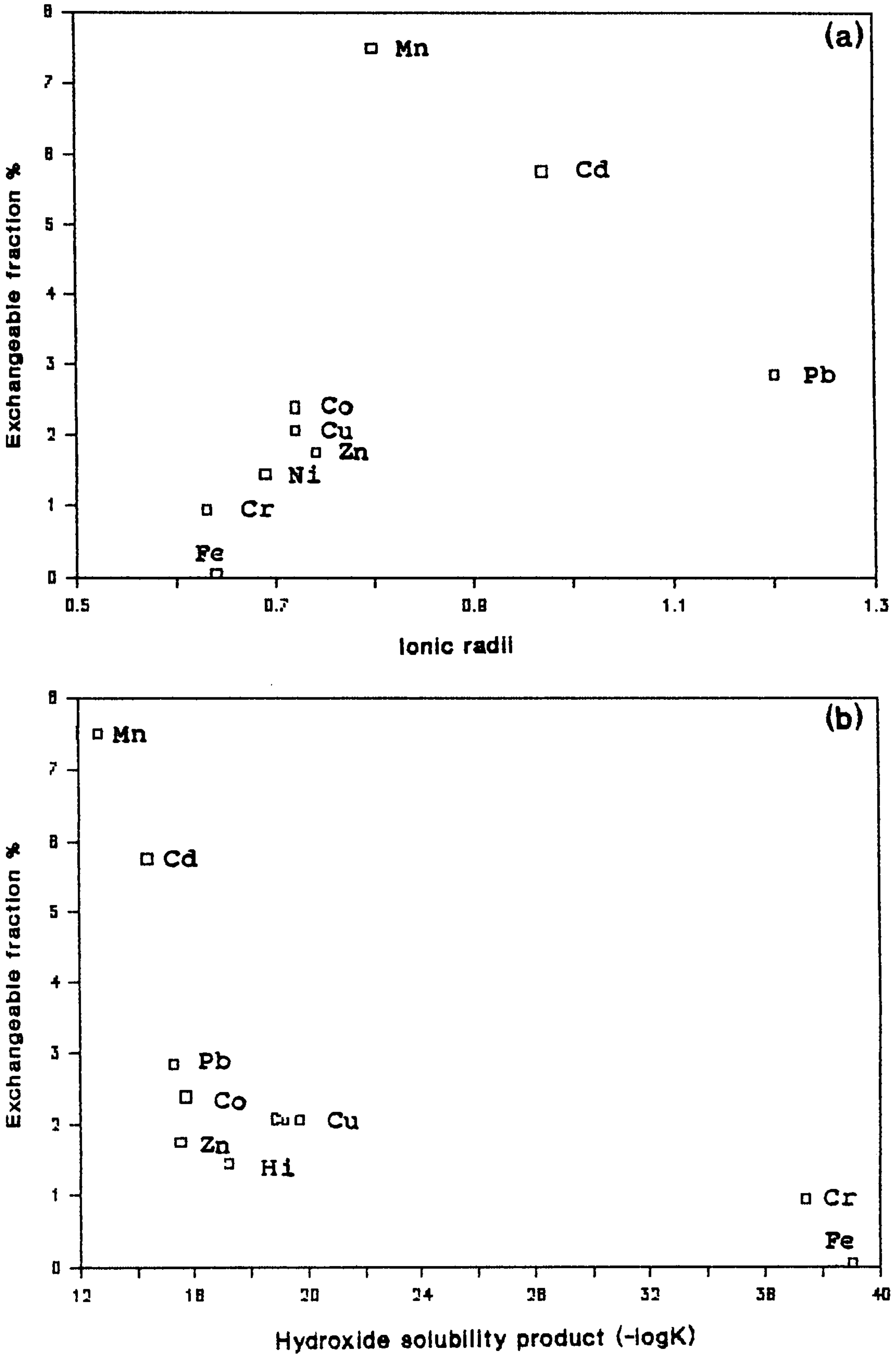


Fig. 6.3 Variations in percentage exchangeable fraction as related to (a) ionic radii and (b) negative logarithm of the solubility product of the corresponding metal hydroxide.

the effect of competing cations might have a stronger influence in the mixing zone of estuaries. In the Cochin estuary, the absolute values for exchangeable fractions of metals in sediments exhibited a down estuarine increase because of the fine grained nature of the sediments, but the percentage values for exchangeable trace metals were found to decrease. When the percentage values for exchangeable trace metals were compared with the amount of calcium and magnesium released by the ammonium acetate reagent, significant correlations were obtained for all the metals studied (Fig. 5.4), indicating the influence of calcium and magnesium (and thereby of salinity) in controlling the trace metal accumulation in this phase.

5.2.2. CARBONATE PHASE

Several workers (Chester and Hughes, 1967; Gupta and Chen, 1975) have shown that significant trace metal concentrations could be associated with sediment carbonates. This fraction would be highly susceptible to changes in pH. Sodium acetate, buffered at pH 5.0, was generally used for selectively extracting the carbonate fraction from the sediments (Table.1). With this reagent, dissolution of the sediment carbonate fraction was essentially complete (Tessier et al. 1979) and the attack on silicates and sulfides minerals was a minimum. The organic fraction remained unaffected. However, the specifically adsorbed trace metals, unaffected by the previous extractant (ammonium acetate, pH = 7.0) could also be extracted at this stage.

A clear cut spatial variation, related to the salinity gradient, as discussed in the case of exchangeable trace metals was not indicated in the case of the carbonate bound fractions (Tables 5.3 and 5.4). For Mn, Cd, Pb, Cu, Zn and Fe, the percentage of metals released with this reagent was higher than that released by ammonium acetate; the percentages of Cd, Cu, Zn, Pb and Cr liberated were found to be significantly higher in Segments III than in Segment I.

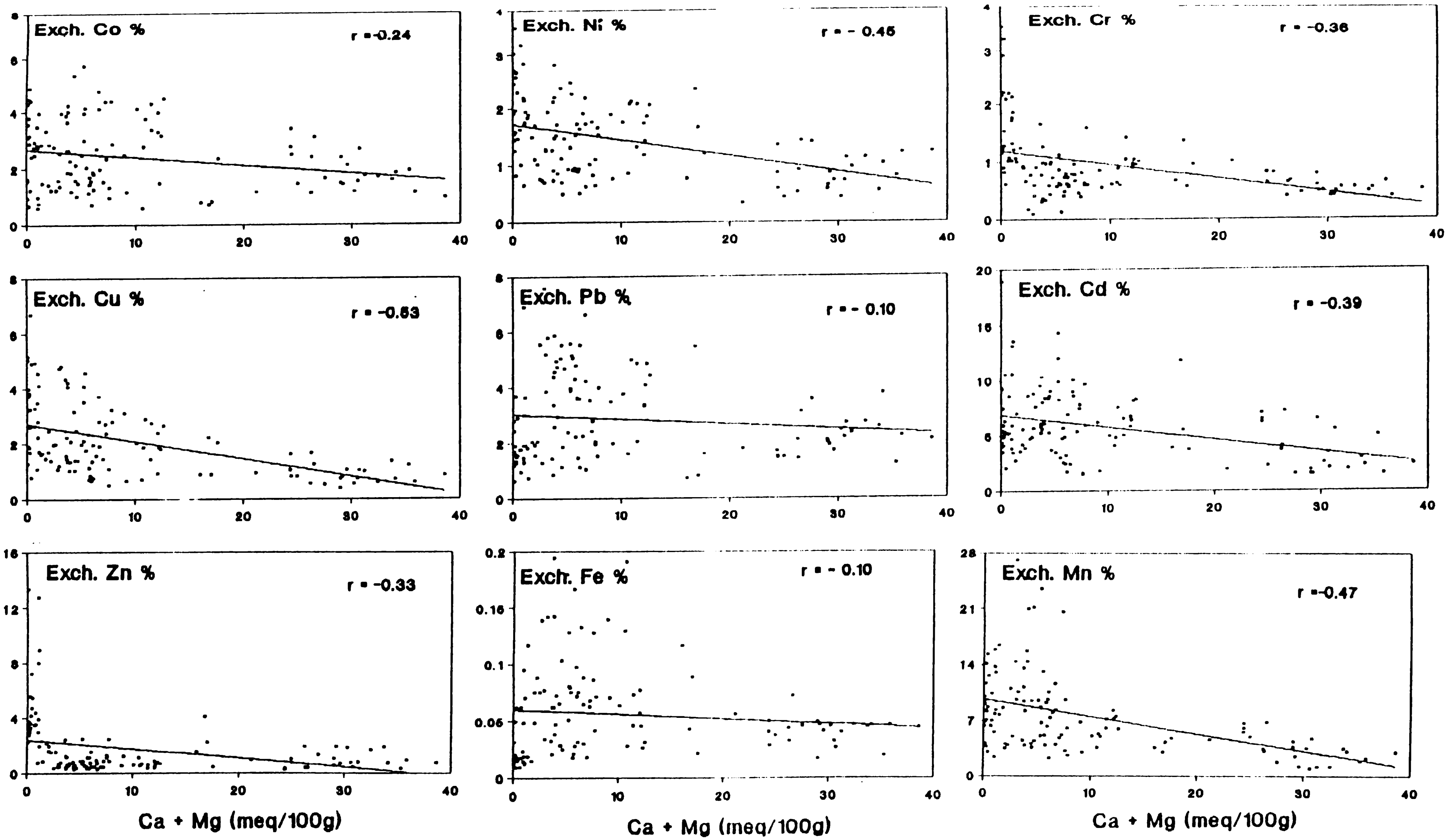


Fig. 5.4 Variations in percentage exchangeable fraction as related to exchangeable Ca + Mg (meq/100g)
(n = 120)

Table 5.3 Annual mean concentration (mg/kg) of the carbonate-bound fraction of trace metals in sediments of the Cochin estuary.

Station		Fe2	Mn2	Zn2	Cu2	Cd2	Pb2	Co2	Ni2	Cr2
1	Mean	1.92	15.38	0.35	0.12	0.03	0.41	0.31	0.28	0.12
	SD	1.43	6.22	0.08	0.03	0.01	0.08	0.09	0.06	0.07
2	Mean	4.36	13.69	0.35	0.13	0.04	0.32	0.20	0.29	0.08
	SD	1.96	4.13	0.07	0.05	0.02	0.14	0.05	0.12	0.03
3	Mean	4.92	5.31	0.50	0.13	0.03	0.56	0.12	0.28	0.13
	SD	4.43	3.22	0.24	0.03	0.01	0.49	0.11	0.09	0.06
4	Mean	5.86	4.67	0.63	0.17	0.07	0.37	0.17	0.26	0.11
	SD	6.19	2.26	0.22	0.08	0.02	0.21	0.10	0.07	0.06
5	Mean	2.13	15.04	2.61	0.27	0.11	1.03	0.22	0.31	0.21
	SD	0.97	5.21	2.51	0.09	0.04	0.52	0.10	0.13	0.05
6	Mean	32.47	22.29	23.52	0.15	0.13	0.80	0.16	0.33	0.11
	SD	14.80	8.00	5.27	0.03	0.08	0.25	0.03	0.16	0.03
7	Mean	9.32	7.03	26.94	0.17	0.12	0.45	0.23	0.15	0.12
	SD	6.10	2.84	5.41	0.07	0.04	0.09	0.12	0.07	0.05
8	Mean	1.93	0.90	4.87	0.22	0.11	0.33	0.09	0.08	0.10
	SD	1.05	0.53	3.49	0.06	0.04	0.23	0.06	0.03	0.03
9	Mean	2.23	0.94	6.36	0.32	0.12	0.92	0.07	0.06	0.11
	SD	0.83	0.88	5.35	0.32	0.08	0.61	0.05	0.05	0.03
10	Mean	0.88	1.84	2.08	0.16	0.04	0.32	0.06	0.13	0.08
	SD	0.40	0.72	0.42	0.04	0.02	0.12	0.03	0.08	0.03
General	Mean	6.60	8.71	6.82	0.18	0.08	0.55	0.16	0.22	0.12
	SD	10.60	8.16	9.97	0.13	0.06	0.42	0.11	0.14	0.06

Table 5.4 Annual mean percentages of the carbonate-bound fraction of trace metals in sediments of the Cochin estuary.

Station		Fe2	Mn2	Zn2	Cu2	Cd2	Pb2	Co2	Ni2	Cr2
1	Mean	0.03	15.18	1.45	2.24	6.29	5.65	4.15	1.77	0.60
	SD	0.02	1.95	0.49	0.64	1.66	1.56	2.03	0.75	0.32
2	Mean	0.05	15.97	1.36	1.86	6.72	3.72	2.12	1.52	0.32
	SD	0.03	2.46	0.29	0.67	2.48	1.16	0.35	0.58	0.13
3	Mean	0.07	11.90	2.11	2.18	5.61	5.29	1.82	1.93	0.58
	SD	0.05	3.19	0.37	0.80	3.34	1.75	0.97	0.70	0.14
4	Mean	0.08	7.96	2.31	2.33	11.01	3.83	3.11	1.79	0.48
	SD	0.08	2.60	0.84	0.90	5.78	1.34	1.61	0.43	0.22
5	Mean	0.01	12.74	2.61	1.58	5.06	4.11	1.38	0.76	0.36
	SD	0.01	3.55	1.98	0.58	2.21	1.00	0.32	0.33	0.15
6	Mean	0.20	16.41	11.81	0.51	2.22	2.23	0.77	0.60	0.16
	SD	0.08	2.63	1.98	0.11	1.00	0.56	0.11	0.22	0.06
7	Mean	0.12	10.04	14.32	0.68	3.76	1.95	1.50	0.60	0.27
	SD	0.07	2.13	2.28	0.30	1.94	0.69	0.73	0.25	0.08
8	Mean	0.04	5.41	9.96	5.53	14.34	3.44	4.08	1.14	0.91
	SD	0.02	1.34	4.99	1.28	3.91	1.63	3.22	0.55	0.30
9	Mean	0.05	5.46	10.83	5.70	12.97	9.48	2.43	1.77	1.41
	SD	0.02	2.55	4.29	1.93	2.96	3.29	1.82	1.50	0.50
10	Mean	0.02	10.50	7.51	4.58	6.80	3.46	2.17	2.14	1.29
	SD	0.01	2.11	2.05	2.63	2.16	0.79	1.05	1.33	0.77
General	Mean	0.07	11.16	6.43	2.72	7.48	4.32	2.35	1.40	0.64
	SD	0.07	4.59	5.35	2.17	4.84	2.57	1.86	0.96	0.53

The precipitation of metal carbonates occurs when the corresponding solubility product is exceeded. The solubility data obtained in pure individual system in distilled water represent only a guide to the conditions existing in natural systems, where the solubility product is influenced by the interplay of a variety of forces. In spite of these limitations, a regression line constructed with the percentage carbonate fraction recorded for the sediments of the Cochin estuary against the negative logarithm of the solubility product of the respective metal carbonates (Fig. 5.5) displayed a significant relationship. The comparatively higher percentages of Zn, Cd, Pb and Cu recorded at the northern riverine Stations could be attributed to the industrial effluents. It was quite probable that phosphate contained in the industrial effluents from the fertilizer factory could contribute to the higher content of this fraction. In order to bring out the influence of phosphates in controlling the metals in the M2 phase, the metal concentration recorded in this phase was compared with the phophorus released from the sediments with the same reagent (sodium acetate, pH=5.0). Significant relationships were recorded for the metals, zinc, nickel, manganese and iron (Fig. 5.6). Church (1986) observed a simultaneous removal of iron and phosphates by flocculation at low salinity regions in Delaware bay. From laboratory simulation studies, Bale and Morris (1981) also demonstrated the affinity of iron for phosphates. Windom et al. (1991) observed that many processes involving flocculation, specific adsorption and precipitation of iron and phosphates were possible and in an estuarine system it was likely that several of these occurred simultaneously. These studies indicated that phosphate could be an important accumulative phase for trace metals in estuarine systems and phosphates as well as carbonates get extracted by sodium acetate. The order of relative abundance of this fraction of metals in the southern parts of the estuary was,

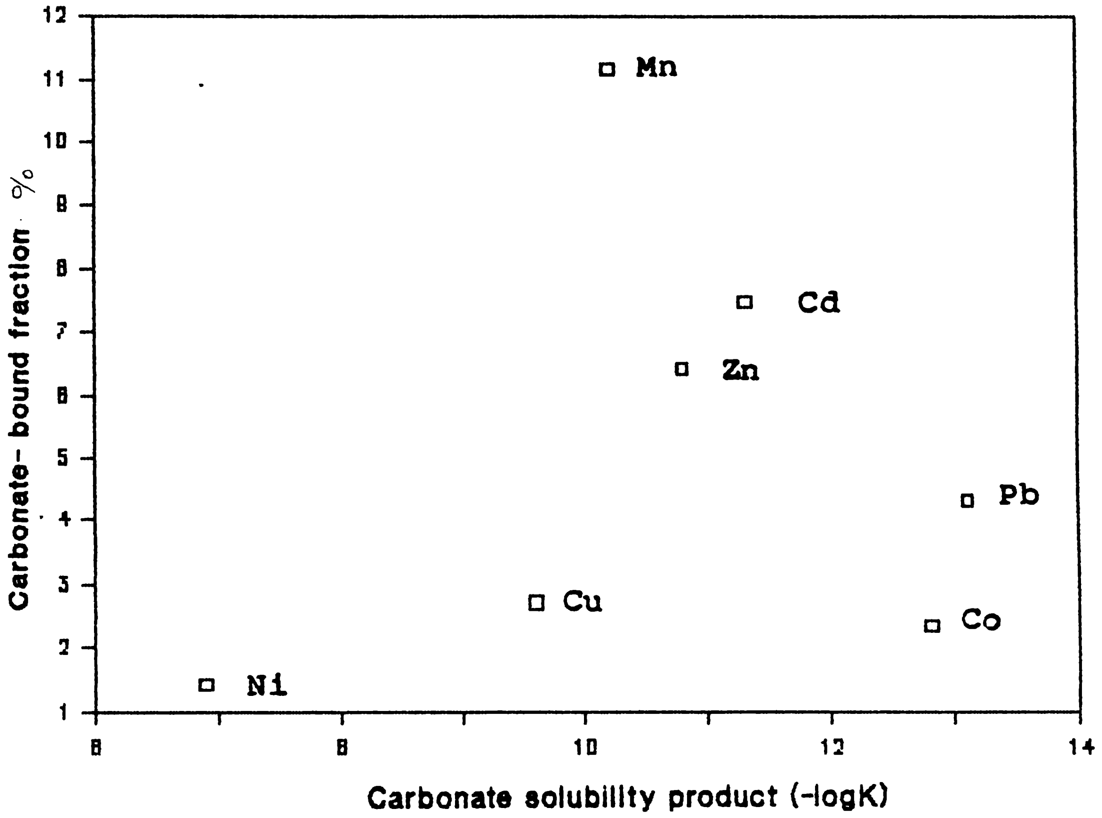


Fig. 5.5 Variations in percentage carbonate- bound fraction as related to the negative logarithm of the solubility product of the corresponding metal carbonates.

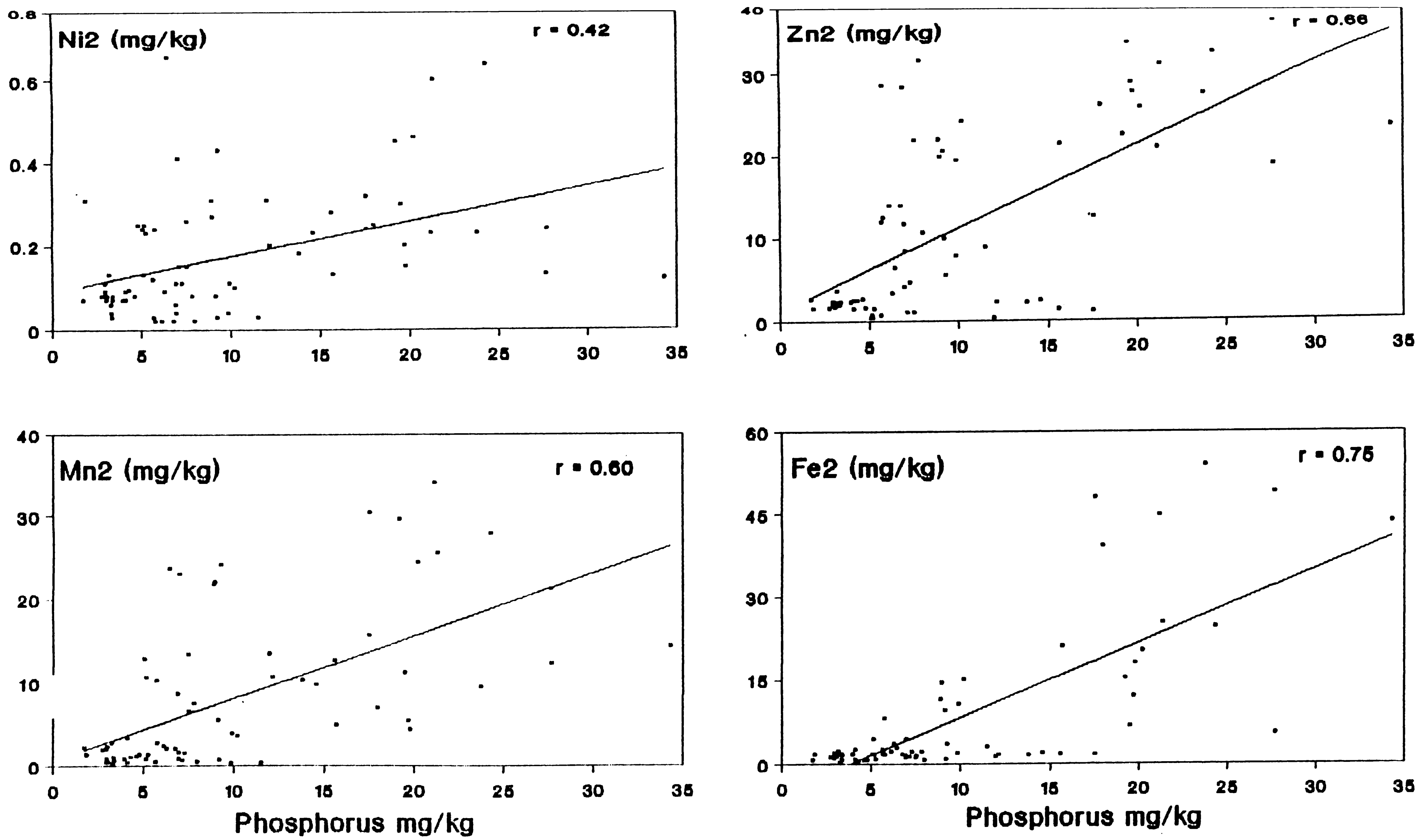


Fig. 5.6 Variations in the concentrations of sodium acetate extractable metals with phosphates extracted by the same reagent. (n = 72)

Mn > Cd > Pb > Co > Cu > Zn > Ni > Cr > Fe

and in the northern part of the estuary was,

Cd > Zn > Mn > Pb > Cu > Co > Ni > Cr > Fe

The shift in the order of abundance signified the anthropogenic input of Cd and Zn to the northern part of the estuary. These results demonstrated that co-precipitation with carbonates would be an important elimination mechanism for metals such as Zn and Cd, particularly when hydrous iron oxides and organic substances were less abundant, especially in slightly higher salinity regions of an estuary. The relatively higher abundance of manganese, zinc and cadmium in this phase was similar to that reported from several other estuaries (Tessier et al. 1980; Prohic and Kniewald, 1987).

5.2.3 EASILY REDUCIBLE PHASE

The hydrous oxides of iron and manganese constitute significant sinks of heavy metals in aquatic systems, particularly under oxidizing conditions. The processes involved are those of adsorption and co-precipitation (Adidiran and Kramer, 1987). Under reducing conditions the sorbed metals are readily mobilized and this phenomenon is the basis of estimation of trace metals in the easily reducible phase. Leaching of sediments with a reducing agent such as hydroxylamine hydrochloride in presence of an acid, which keeps the liberated ions in solution, removes trace metals associated with iron and manganese oxides. Brannon et al. (1977) noted that while the extractant dissolved approximately 85 percent of the manganese oxide, only 5 percent of the iron present was dissolved. Tessier et al. (1979) and Tipping et al. (1985) also observed that manganese oxides were more easily leached than iron oxides. The reagent had minimal effect on sulfides, silicates and organic matter (Tessier et al. 1979).

It has already been pointed out (Chapter 4) that the amount of iron and manganese recovered from this phase was comparatively low in the sediments of the Cochin estuary. While the low levels of manganese in this phase could be attributed to the generally low content of manganese in sediments, the low levels of iron was attributed to the low inputs of soluble iron into the estuary because of the highly oxidizing conditions and turbulence. The low levels of trace metals detected in this phase as compared with values reported from other areas are only a consequence of the characteristic low levels of iron and manganese present in this phase.

The annual mean concentrations as well as percentage contribution of this fraction with respect to total metals, are presented in Tables 5.5 and 5.6 respectively. Significant spatial variations in the percentage distribution of this metal fraction were not detected, except for Cd, Zn, Mn and Pb, which showed significantly higher percentages in the northern part of the estuary. Incidentally, these metals exhibited relatively higher percentages in this phase.

Highly significant correlations were obtained between the pairs Fe3- M3 and Mn3- M3, (M epresents any other metal studied), except for the pairs Fe3- Cu3 and Fe3- Pb3 (Table 5. 11). This behavior was consistent with the assumed composition of the fraction 3 (i.e. Fe- Mn oxide bound) and the known scavenging role of these oxides. In the Cochin estuary, the correlation recorded for the metal pair with Mn was better than that with Fe indicating the higher efficiency of the Mn oxides in scavenging the metals in this estuary. A very high correlation was recorded for the Cd3 - Zn3 pair and thispoints to the similarity in their origin and estuarine behaviour.

The relative abundance of metals determined in this phase was in the order,

Zn > Mn > Cd > Pb > Co > Ni > Fe > Cu > Cr

Table 5.5 Annual mean concentration (mg/kg) of the easily reducible fraction of trace metals in sediments of the Cochin estuary.

Station		Fe3	Mn3	Zn3	Cu3	Cd3	Pb3	Co3	Ni3	Cr3
1	Mean	149.08	7.88	1.25	0.05	0.06	0.38	0.38	0.34	0.03
	SD	26.43	3.71	0.32	0.02	0.03	0.14	0.21	0.08	0.02
2	Mean	149.02	5.13	1.59	0.02	0.07	0.48	0.27	0.29	0.03
	SD	50.08	1.50	0.37	0.01	0.05	0.26	0.07	0.12	0.02
3	Mean	90.33	1.92	1.72	0.12	0.05	0.74	0.25	0.34	0.04
	SD	15.68	0.79	0.64	0.05	0.02	0.44	0.16	0.08	0.02
4	Mean	99.63	3.30	2.10	0.05	0.05	0.44	0.22	0.28	0.04
	SD	31.50	1.79	0.69	0.03	0.02	0.22	0.12	0.08	0.02
5	Mean	78.88	13.35	3.47	0.03	0.18	1.47	0.45	0.82	0.11
	SD	35.81	4.15	1.54	0.01	0.03	0.75	0.12	0.13	0.02
6	Mean	189.75	13.79	25.06	0.03	0.15	1.20	0.41	0.59	0.06
	SD	35.13	4.78	3.66	0.01	0.04	0.42	0.15	0.29	0.02
7	Mean	165.77	8.52	30.93	0.02	0.34	0.72	0.45	0.42	0.06
	SD	43.57	3.60	8.41	0.01	0.24	0.38	0.09	0.11	0.03
8	Mean	44.55	1.02	5.10	0.02	0.06	0.47	0.13	0.11	0.02
	SD	17.03	0.28	2.57	0.02	0.02	0.36	0.05	0.09	0.01
9	Mean	30.05	1.71	5.71	0.06	0.08	1.21	0.17	0.15	0.02
	SD	9.59	1.70	5.16	0.02	0.05	1.53	0.07	0.11	0.01
10	Mean	35.19	1.95	4.29	0.02	0.06	0.37	0.13	0.16	0.01
	SD	8.42	0.36	1.18	0.01	0.02	0.20	0.02	0.06	0.00
General	Mean	103.23	5.86	8.12	0.04	0.11	0.75	0.29	0.35	0.04
	SD	62.54	5.33	10.71	0.04	0.12	0.72	0.17	0.24	0.03

Table 5.6 Annual mean percentages of the easily reducible fraction of trace metals in sediments of the Cochin estuary.

Station		Fe3	Mn3	Zn3	Cu3	Cd3	Pb3	Co3	Ni3	Cr3
1	Mean	1.96	7.61	5.14	0.89	11.09	5.15	4.56	2.00	0.13
	SD	0.52	1.58	1.97	0.32	6.95	1.87	2.06	0.54	0.08
2	Mean	1.77	6.13	6.08	0.29	9.79	5.67	2.82	1.53	0.12
	SD	0.44	1.36	1.14	0.13	5.70	2.83	0.62	0.57	0.07
3	Mean	1.40	4.85	7.60	2.13	6.41	7.27	4.21	2.47	0.17
	SD	0.30	1.33	1.34	1.21	2.37	2.40	2.00	0.94	0.09
4	Mean	1.45	6.14	7.59	0.73	6.42	4.82	3.96	1.90	0.18
	SD	0.44	2.99	1.63	0.54	2.46	1.95	2.60	0.47	0.11
5	Mean	0.53	11.24	3.86	0.17	9.33	6.16	3.48	2.18	0.21
	SD	0.20	2.90	0.73	0.13	4.64	2.17	2.12	1.14	0.13
6	Mean	1.21	10.46	12.64	0.11	2.95	3.36	2.14	1.10	0.09
	SD	0.26	2.25	1.16	0.06	0.74	1.02	1.10	0.48	0.04
7	Mean	2.19	12.99	16.14	0.11	8.64	2.68	3.02	1.72	0.13
	SD	0.61	5.44	2.30	0.07	4.44	0.61	0.94	0.56	0.06
8	Mean	0.89	7.33	10.36	0.42	8.23	7.12	5.03	1.43	0.14
	SD	0.33	2.84	2.28	0.46	2.68	6.96	2.04	0.92	0.08
9	Mean	0.66	10.36	9.68	1.81	8.62	9.36	6.43	2.63	0.21
	SD	0.17	8.10	3.49	1.22	1.80	5.75	3.72	1.00	0.08
10	Mean	0.65	11.96	14.64	0.71	9.87	5.22	5.25	2.83	0.18
	SD	0.21	3.81	2.15	0.49	2.01	4.86	1.43	1.11	0.07
General	Mean	1.27	8.91	9.37	0.74	8.13	5.68	4.09	1.98	0.16
	SD	0.67	4.67	4.35	0.91	4.45	4.08	2.39	0.97	0.09

and this order agreed quite well with that reported by Tessier et al. (1980) from Yamaska and St. Francois river sediments, except for Cd and Cu. For amorphous oxides of iron in soils, the affinity series established (Elliot et al. 1986) was

Pb > Cu > Zn > Cd.

The low affinity of Cu, Co, Pb, Ni and Zn for this phase has been indicated for river sediments (Tessier et al. 1980). The higher levels of Zn and Cd observed in this phase in sediments of the Cochin estuary, could only be a reflection of the anthropogenic inputs. Fig. 5.7 depicts the relation between the negative logarithm of the solubility product of the respective metal hydroxide and the percentage abundance of the metals in the M3 phase. The relationship indicated was remarkably significant, suggesting that the metal fractions determined truly represented the hydroxide precipitation behaviour in this tropical estuary.

5.2.4. ORGANIC/SULFIDE PHASE

The trace metals solubilised after the destruction of organic matter constituted the organic phase. The reagent used was hot acidified hydrogen peroxide, originally suggested by Gupta and Chen (1975).Sulfide minerals also could be extracted with this reagent. In the Cochin estuary, during the survey the bottom water was never been found to be depleted of dissolved oxygen, so as to cause sulfide precipitation, and hence, the metals extracted at this stage could be regarded as a good estimate of the metals bound to the organic fractions of the sediments. In sediments, the metals may be bound to various forms of organic matter, such as living organisms, detritus, organic coating on mineral particles, etc.

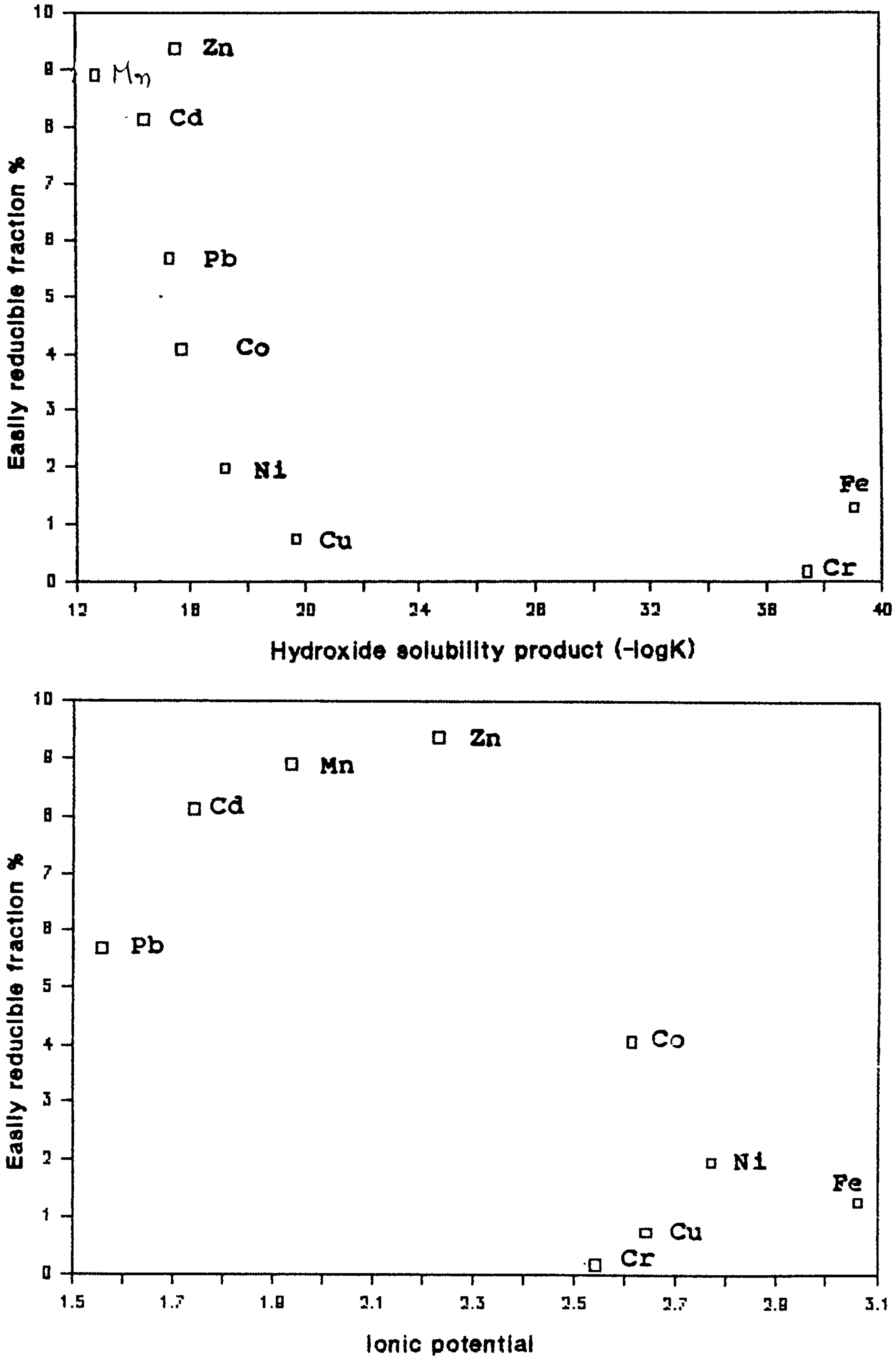


Fig. 5.7 Variations in the percentage of easily reducible fractions with (a) negative logarithm of the solubility product of corresponding metal hydroxide and (b) ionic potential

Data on the spatial distribution of organically bound trace metals in the sediments of Cochin estuary are presented in Tables 5.7 (absolute values) and 5.8 (percentage values). For all the metals, the highest concentration in this fraction was detected in Segment II signifying the influence of estuarine processes in controlling the spatial distribution of organically bound metals. As the river water carrying clays and organic matter entered the brackish water region in the estuary, the changed chemical environment caused coagulation and flocculation of these colloidal particles. However, a significant spatial variation in percentage-wise distribution was noted only in the case of Zn and Cr, both having higher percentages in Segment II. The observed minimum spatial variation in percentage values indicated that the variations in the total content of metals were always associated with a variation in the organic phase of the metal and that both were related to the estuarine processes.

The order of relative abundance of trace metals in this fraction, in the sediments of the Cochin estuary was,

Cd > Mn > Zn > Co > Cu > Pb > Ni > Cr > Fe.

The relative concentration of each metal in this fraction depended upon the free metal ion and the equilibrium constant for metal organic complexes, the ligand concentration being the same for all metals. Based on the model suggested by Tessier et al. (1980), the comparative stability constants of the metal organic complexes (with respect to manganese complexes),in estuarine sediments were calculated and the same is presented below.

	Fe	Zn	Cu	Cd	Pb	Co	Ni	Cr
Segment I	-0.23	0.31	0.70	0.36	0.12	0.46	0.42	0.92
Segment II	0.14	0.11	1.06	0.58	-0.32	0.55	0.65	1.28
Segment III	0.05	0.08	0.56	0.13	-0.17	0.37	0.25	0.48

Table 5.7 Annual mean concentration (mg/kg) of the organic/sulfide bound fraction of trace metals in sediments of the Cochin estuary.

Station		Fe4	Mn4	Zn4	Cu4	Cd4	Pb4	Co4	Ni4	Cr4
1	Mean	55.08	23.52	2.54	1.76	0.17	1.35	1.80	1.58	2.20
	SD	23.60	5.30	0.78	0.53	0.04	0.54	0.52	0.36	0.41
2	Mean	66.35	22.68	2.97	1.35	0.18	1.33	1.88	1.53	1.80
	SD	30.05	4.78	0.67	0.51	0.05	0.72	0.34	0.32	0.38
3	Mean	68.27	12.79	4.89	1.23	0.25	1.41	1.57	2.21	2.19
	SD	40.11	10.04	2.25	0.72	0.10	0.79	1.27	1.12	1.33
4	Mean	67.13	15.56	4.89	1.35	0.23	1.56	1.24	1.86	1.75
	SD	36.94	7.10	2.03	0.47	0.09	0.80	0.30	0.53	0.55
5	Mean	202.38	36.03	28.53	2.14	1.21	1.04	2.73	6.52	6.21
	SD	88.12	13.21	8.25	1.01	1.18	0.52	1.21	3.11	3.51
6	Mean	318.43	38.70	67.21	4.61	2.47	1.26	3.88	8.21	16.34
	SD	38.08	12.19	6.29	0.59	1.09	0.45	1.02	1.73	4.13
7	Mean	185.82	19.27	61.15	8.77	1.59	1.33	3.25	2.32	10.62
	SD	34.03	6.32	12.65	4.92	0.89	0.32	1.49	0.81	4.18
8	Mean	56.28	4.53	13.97	0.76	0.25	0.84	0.46	0.53	0.69
	SD	17.06	1.19	5.60	0.53	0.10	0.46	0.14	0.14	0.39
9	Mean	32.18	2.73	14.90	2.26	0.28	1.06	0.82	0.38	0.56
	SD	23.87	1.10	9.20	2.77	0.17	0.67	0.50	0.27	0.38
10	Mean	23.20	3.26	6.02	0.81	0.19	0.46	0.44	0.62	0.65
	SD	10.62	0.67	2.13	0.35	0.06	0.17	0.09	0.17	0.43
General	Mean	107.51	17.91	20.71	2.50	0.68	1.16	1.81	2.58	4.30
	SD	99.21	14.29	23.87	2.99	0.96	0.65	1.39	2.79	5.48

Table 5.8 Annual mean percentages of the organic/sulfide bound fraction of trace metals in sediments of the Cochin estuary.

Station		Fe4	Mn4	Zn4	Cu4	Cd4	Pb4	Co4	Ni4	Cr4
1	Mean	0.69	25.09	9.83	32.07	33.45	18.02	22.01	9.19	10.87
	SD	0.24	5.59	2.14	10.65	6.28	7.27	4.40	1.66	1.02
2	Mean	0.81	27.03	11.46	19.62	28.87	15.44	20.11	8.26	7.35
	SD	0.37	3.48	2.69	6.35	7.32	5.77	2.48	1.58	1.76
3	Mean	1.01	26.54	20.65	17.29	35.88	14.07	21.89	14.11	9.87
	SD	0.53	4.20	3.12	7.32	6.95	2.76	4.55	2.98	2.64
4	Mean	0.96	27.03	16.81	17.75	33.00	16.14	21.57	12.73	8.03
	SD	0.48	6.06	3.18	3.97	4.65	5.34	4.31	2.45	1.87
5	Mean	1.37	28.55	32.65	11.28	35.93	4.58	16.44	13.56	8.57
	SD	0.44	4.51	1.65	2.84	10.32	2.23	2.44	1.93	2.84
6	Mean	2.04	28.94	34.05	15.34	44.88	3.60	18.98	15.77	21.99
	SD	0.40	3.68	2.35	1.97	12.65	1.39	3.27	2.75	2.87
7	Mean	2.48	28.07	32.17	30.55	40.92	5.62	19.67	8.86	23.52
	SD	0.60	4.50	3.26	4.56	8.74	1.66	3.30	1.65	3.25
8	Mean	1.15	29.98	30.44	16.64	33.40	9.79	17.18	7.20	5.31
	SD	0.38	3.20	6.86	5.43	5.85	2.42	3.99	1.21	1.86
9	Mean	0.72	20.07	33.37	25.03	30.69	11.10	23.45	8.85	6.46
	SD	0.53	7.36	6.29	10.37	5.39	5.64	4.76	4.12	3.61
10	Mean	0.41	19.81	21.39	17.83	31.97	5.32	16.83	10.85	8.15
	SD	0.16	5.40	8.16	3.81	4.71	1.91	3.38	3.81	3.89
General	Mean	1.16	26.11	24.28	20.34	34.90	10.37	19.81	10.94	11.01
	SD	0.75	5.98	10.01	9.03	8.94	6.58	4.42	3.79	6.64

The stability ratios so worked out followed the lrwing William order for the complexation of divalent metals (Irving and Williams, 1948), namely,

Cu> Ni> Zn> Cd> Fe >Mn.

5.2.5 RESIDUAL PHASE

This phase contains primary as well as secondary weathered minerals which are for most part a very stable portion of the elemental constituents (Brannon et al. 1977). Since metals found in this phase were expected to be chemically stable and biologically inactive, strong acid digestion was required to dissolve the metals out of this phase.Hot nitric acid utilized in the scheme was expected to bring about a near total digestion, with the reaction being vigorous enough to dissolve all the heavy metals except that bound to silicate phases (Ure, 1990). The heavy metals considered in the present study were not likely to be associated to any appreciable degree with silicate minerals.

Fraction 5 represented an essentially non-labile component, and the results confirmed that this form, which was usually designated as residual was an important sink for trace metals in sediments. Without exception, trace metal concentrations found in this fraction (Table 5.9 and 5.10) were higher than those observed in any of the other fractions. For iron, more than 95% was detected in this phase; chromium and nickel also followed the same trend, with the percentages recorded above 75 at all Stations. The residual component in the distribution of cobalt, lead and copper in sediments of the Cochin estuary was between 60 and 90 percent, the percentage values being comparatively lower in the industrial and sewage effluent receiving Stations in the northern parts of the estuary. Of the remaining metals, zinc exhibited significant spatial variations, showing higher percentage contribution (above 70 percent) in the southern parts and lower percentage contribution (less than 50 percent) in the northern parts, and

Table 5.9 Annual mean concentration (mg/Kg) of the residual fraction of trace metals in sediments of the Cochin estuary.

Station		Fe5	Mn5	Zn5	Cu5	Cd5	Pb5	Co5	Ni5	Cr5
1	Mean	7686	35.57	21.63	3.57	0.22	5.15	5.77	15.51	17.65
	SD	1640	10.94	5.38	1.15	0.06	1.30	2.09	5.65	2.47
2	Mean	8078	34.80	21.03	5.24	0.30	5.77	6.84	16.30	22.67
	SD	816	5.81	2.20	0.75	0.06	0.82	0.93	1.59	2.26
3	Mean	6416	21.27	16.16	6.86	0.35	6.99	5.31	13.34	18.95
	SD	907	12.29	5.82	6.87	0.22	4.09	4.40	7.63	6.69
4	Mean	6750	30.75	20.86	5.95	0.30	6.47	3.94	11.85	19.87
	SD	929	14.32	7.50	2.00	0.10	1.95	0.90	1.45	4.78
5	Mean	14254	54.82	51.46	16.69	1.34	20.31	12.50	38.39	58.84
	SD	2095	18.67	10.38	6.57	1.19	6.94	4.78	15.23	19.86
6	Mean	15435	54.91	80.00	25.33	2.38	31.68	15.47	43.48	57.29
	SD	2416	18.25	6.94	3.83	0.51	4.32	2.22	10.19	13.88
7	Mean	7332	30.22	68.22	19.20	1.56	22.85	12.02	23.15	33.12
	SD	1090	9.41	13.41	9.85	0.46	9.81	4.02	8.35	8.75
8	Mean	4902	7.64	22.18	3.03	0.28	6.75	1.97	6.48	11.30
	SD	812	2.62	9.37	0.94	0.05	3.67	0.65	1.29	4.35
9	Mean	4590	9.37	18.46	3.74	0.29	6.58	2.16	4.39	7.29
	SD	1452	5.69	11.70	3.24	0.12	3.82	0.95	2.78	3.04
10	Mean	5582	8.37	15.75	3.45	0.28	7.71	2.03	4.82	6.39
	SD	1159	3.24	5.01	1.60	0.06	2.11	0.71	0.68	1.88
General	Mean	8103	28.77	33.57	9.31	0.73	12.03	6.80	17.77	25.34
	SD	3828	20.19	24.14	8.96	0.85	10.05	5.34	14.70	19.99

Table 5.10 Annual mean percentages of the residual fraction of trace metals in sediments of the Cochin estuary.

Station		Fe5	Mn5	Zn5	Cu5	Cd5	Pb5	Co5	Ni5	Cr5
1	Mean	97.25	36.16	82.98	62.48	42.06	67.27	67.43	85.80	87.75
	SD	0.48	5.87	3.14	10.01	8.17	9.00	6.94	2.87	1.28
2	Mean	97.32	41.91	80.72	76.75	48.71	70.93	72.92	87.66	91.72
	SD	0.40	6.14	2.17	6.56	5.59	7.63	2.42	1.33	2.01
3	Mean	97.44	48.69	69.64	76.41	44.80	69.02	68.40	79.66	88.43
	SD	0.61	3.60	4.29	8.65	9.37	3.03	5.57	4.29	2.65
4	Mean	97.43	53.17	72.64	76.87	43.17	71.15	67.68	81.75	90.66
	SD	0.93	6.22	2.68	4.67	6.74	7.47	5.26	2.67	2.05
5	Mean	98.05	44.02	60.07	85.86	44.94	83.29	76.66	82.70	90.27
	SD	0.61	4.20	3.50	3.22	4.79	2.00	3.48	1.62	2.51
6	Mean	96.51	41.00	40.53	83.32	48.10	88.46	76.54	81.62	77.18
	SD	0.59	4.35	2.41	2.06	13.30	1.94	2.83	2.41	2.83
7	Mean	95.11	43.89	35.98	67.69	43.58	88.17	74.74	87.91	75.46
	SD	1.14	5.13	3.04	4.79	7.95	1.95	3.36	1.76	3.32
8	Mean	97.87	49.73	46.29	74.75	38.02	77.63	70.13	88.36	92.49
	SD	0.67	4.80	3.36	4.69	5.82	6.20	7.29	1.88	1.97
9	Mean	98.54	57.21	39.96	63.65	37.19	67.15	66.24	84.39	89.60
	SD	0.44	14.08	5.99	8.51	11.91	8.77	4.73	5.50	3.54
10	Mean	98.90	47.27	53.43	74.34	46.75	84.73	72.73	82.48	88.89
	SD	0.29	8.64	8.55	5.61	5.38	5.93	4.98	3.96	3.04
General	Mean	97.44	46.30	58.22	74.21	43.73	76.78	71.35	84.23	87.25
	SD	1.21	9.10	17.19	9.66	9.13	10.24	6.17	4.25	6.22

this signified the anthropogenic input of zinc to the northern parts of the estuary. Cadmium and manganese seemed to be the most loosely bound metals of the environment, since the percentages of residual fraction of these metals detected was the lowest in all the Station in the south (S1 to S4) and was comparable with that of zinc in the northern parts.

The overwhelming importance of residual metals was pointed out in studies on other estuarine sediments too (Brannon et al. 1976; Gibbs, 1977; Tessier et al. 1980; Yetang and Forstner, 1984; Lee, 1985; Martin et al. 1987). The results, thus, clearly illustrated the difficulty of distinguishing between background and anomalous levels of trace metal contamination when only total metal analyses were performed. The order of abundance of metals in the residual phase of the sediments of the Cochin estuary was,

Fe> Zn> Mn > Cr> Ni> Pb> Cu> Co> Cd,

and with the exception of zinc, this represented the order of crustal abundance of these metals. Similar observations, where zinc exceeded manganese in abundance, were reported from the Sepitiba bay (Lacerda et al. 1987), a polluted estuary on the Brazilian coast. However, when the percentage values were considered the order of abundance was,

Fe> Cr> Ni> Pb> Cu> Co> Zn> Mn> Cd

and this signified the high environmental mobility of zinc, manganese and cadmium. Low percentages of zinc, cadmium and manganese in the residual fraction were reported for several other estuaries (Grieve and Fletcher, 1976; Forstner, 1982; Calmano and Forstner, 1983; Lee, 1985; Rosental et al. 1986; Samanidou and Fytianos, 1987; Prohic and Kniewald, 1987; Pardo et al. 1990; Elsokkary and Muller, 1990; Bradley and Cox, 1990). The selective extraction thus showed the existence of a category of transition metals which were relatively depleted in the residual fractions.

Table 5.11 Correlation matrices of metal pairs extracted by different extractants (n = 120; all values +ve)

	Cu1	Cd1	Co1	Pb1	Zn1	Ni1	Mn1	Cr1
Fe1	0.13	0.19	0.43	0.36	0.07	0.37	0.57	0.34
Cr1	0.28	0.58	0.57	0.65	0.20	0.67	0.05	
Mn1	0.01	0.10	0.23	0.06	0.17	0.06		
Ni1	0.21	0.38	0.69	0.76	0.05			
Zn1	0.78	0.57	0.17	0.30				
Pb1	0.39	0.57	0.66					
Co1	0.16	0.28						
Cd1	0.55							

	Cu2	Cd2	Co2	Pb2	Zn2	Ni2	Mn2	Cr2
Fe2	0.15	0.10	0.03	0.16	0.54	0.17	0.44	0.05
Cr2	0.23	0.23	0.44	0.49	0.05	0.35	0.18	
Mn2	0.09	0.11	0.44	0.26	0.25	0.61		
Ni2	0.13	0.06	0.53	0.22	0.01			
Zn2	0.14	0.56	0.07	0.23				
Pb2	0.58	0.46	0.19					
Co2	0.09	0.04						
Cd2	0.45							

	Cu3	Cd3	Co3	Pb3	Zn3	Ni3	Mn3	Cr3
Fe3	0.10	0.23	0.50	0.06	0.51	0.38	0.43	0.27
Cr3	0.05	0.41	0.54	0.30	0.25	0.70	0.52	
Mn3	0.21	0.38	0.56	0.33	0.42	0.77		
Ni3	0.03	0.44	0.50	0.37	0.30			
Zn3	0.23	0.74	0.36	0.28				
Pb3	0.04	0.26	0.22					
Co3	0.05	0.38						
Cd3	0.21							

Contd....

Table 5.11 contd.....

	Cu4	Cd4	Co4	Pb4	Zn4	Ni4	Mn4	Cr4
Fe4	0.50	0.79	0.74	0.11	0.82	0.82	0.69	0.84
Cr4	0.68	0.91	0.86	0.16	0.89	0.80	0.68	
Mn4	0.32	0.64	0.79	0.31	0.49	0.82		
Ni4	0.32	0.75	0.77	0.14	0.63			
Zn4	0.75	0.85	0.72	0.11				
Pb4	0.29	0.07	0.33					
Co4	0.68	0.81						
Cd4	0.60							

	Cu5	Cd5	Co5	Pb5	Zn5	Ni5	Mn5	Cr5
Fe5	0.69	0.69	0.75	0.71	0.70	0.82	0.75	0.83
Cr5	0.84	0.80	0.89	0.82	0.78	0.95	0.84	
Mn5	0.68	0.62	0.80	0.60	0.60	0.86		
Ni5	0.86	0.80	0.93	0.82	0.77			
Zn5	0.89	0.86	0.83	0.92				
Pb5	0.95	0.88	0.86					
Co5	0.92	0.82						
Cd5	0.85							

Martin et al. (1987) opined that characterization of the `residual' background on relative basis might be misleading so far as a decrease in residual fraction could only result in the instance of an additional input of an anthropogenic labile material. An operationally defined background level, can however be, presented, on concentration basis, integrating various lithologic and climatic variations. The mean data on residual trace metal concentration recorded at the three segments of the Cochin estuary are presented in Table 5.12. For comparison, the average values for Indian river sediments (Subramanian et al. 1985), world surface soils and earth's crust (Martin and Whitfield 1983) are also presented. Except for manganese and cadmium, the values recorded in Segment II were comparable to that of crustal abundance indicating that the major source of the trace metals studied was weathered products of earth's crust. In comparison to the average values for Indian sediments, the sediments in Segment II of the Cochin estuary were enriched in zinc and cadmium. In the other two segments the values were comparatively low because of the coarse texture of the sediments, but the order of abundance was the same as recorded in earth's crust. Further, the significant positive correlation (Table 5.11) recorded between different metal pairs determined in this fraction testified that the metals studied had a common source, and this metal phase underwent little chemical transformation within the estuarine environment.

5.3 PHASE CONCENTRATION FACTOR

Forstner (1979c) introduced the concept of phase concentration factor (PCF) to compare the metal enrichment in samples with large differences in metal concentrations. PCF is a relative value, and is not influenced by the total metal content. The PCF is the ratio between the percentage of a certain metal association to the percent content of the respective carrier material. If the computed value is above 1,

Table 5.12 Mean residual metal content in sediments of the Cochin estuary (segment-wise) [mg/kg]

Metal	Seg I	Seg II	Seg III	Indian Sediments*	World Soils **	Earth Crust **
Fe	7429	12742	5102	29000	40000	35900
Mn	72	108	16	605	1000	720
Zn	26	158	42	16	90	127
Cu	7	26	5	28	30	32
Cd	0.64	3.96	0.74	NA	0.35	0.20
Pb	9	29	9	NA	35	16
Co	8	18	3	31	8	13
Ni	17	42	6	37	50	49
Cr	22	61	9	87	70	71

NA = Data not available

* = Subramaniam, et al. 1985, ** = Martin and Whitfield, 1983

an enrichment in the studied phase is inferred; if the value is less than 1, then , it is indicative of dilution of metal concentration in the sample due to the presence of that phase.

Enrichment of all the metals in the organic phases have been worked out, on the basis of above principles. The organic carbon values were used to quantify the organic phase. The PCF of all the samples studied were worked out, and the averaged, season-wise and segment-wise, values are plotted in Fig. 5.8 All the metals, except iron, showed a factor above 1 indicating that the metal values were enriched by the presence of organically bound metals. This enrichment was a maximum for the sediments of Segment III and a minimum for Segment II. Seasonally, it was during the monsoons, when estuarine environment was dominated by the riverine inputs from terrestrial sources that the influence of organic bound metals on the total pool was a maximum.

5.4 ESTUARINE ENRICHMENT

For studying the estuarine behaviour of the various metal phases determined, the metal values recorded at the middle estuary (ME) were compared to that of upper estuary (UE) and lower estuary (LE). Values from Station 1 in the southern end and Station 10 in the northern end were taken as representative of the upper estuarine regions. Station 3 values in the southern arm and Station 7 values in the northern arm represented the middle estuarine region. Metal content at Station 5 (barmouth) was the common factor representing lower estuarine region of both arms of the estuary. To nullify the effects of other sedimentological parameters on chemical partitioning, the ratios of the metal fractions between the two sites were compared to the ratio of total metal between the respective sites and the relationship so obtained is plotted in Fig.5.9 to 5.13.

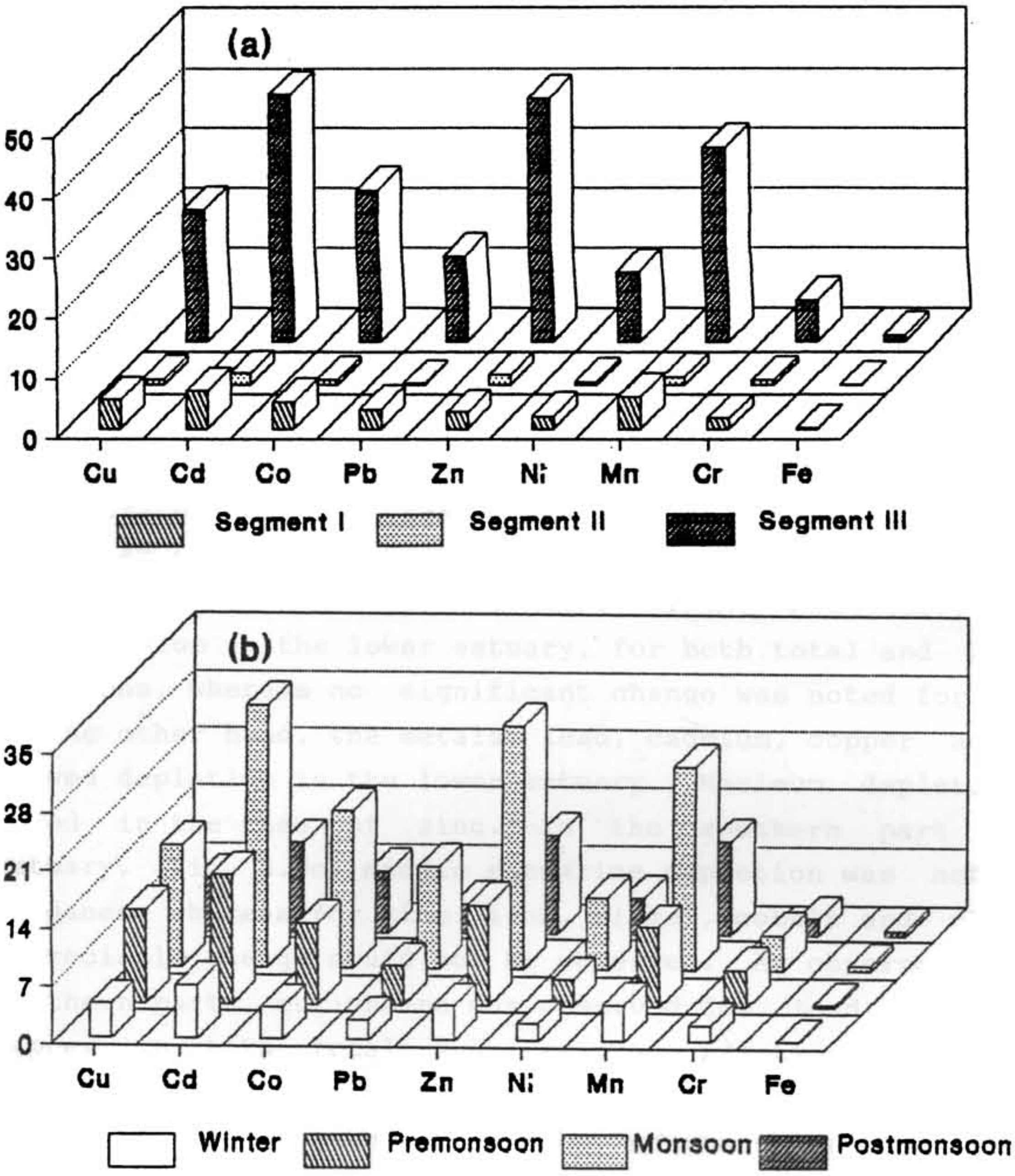


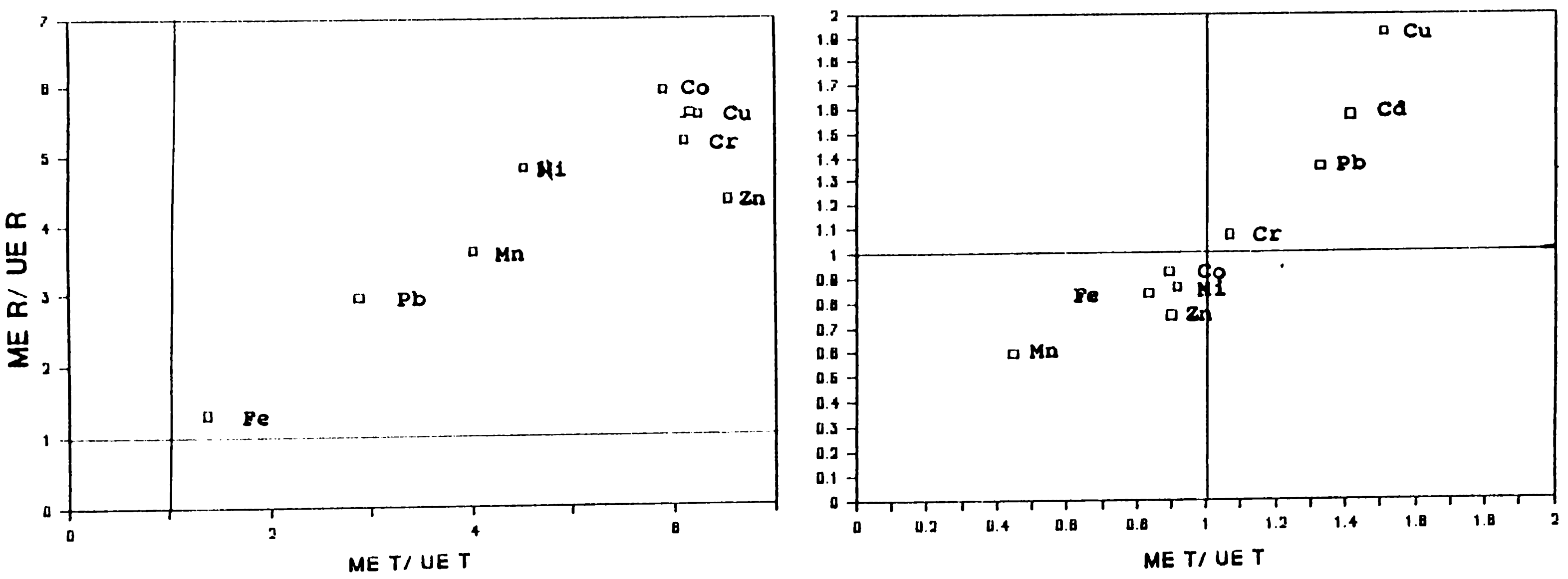
Fig. 5.8 Phase concentration factor, (a) spatial variation and (b) seasonal variation

Figure 5.9a on residual metals indicated that, between the upper estuary and middle estuary, in the northern part, the total concentration of all the metals showed enrichment in sediments in the middle estuary. The enrichment was minimum for iron, but was 6 to 7 times for the metals, zinc, chromium, cobalt and copper. Lead, manganese and nickel showed 3 to 5 times enrichment. The residual fractions also exhibited, a similar enrichment and suggested that this fraction had not undergone any appreciable change in this part of the estuary. The enrichment in total metal concentration could be attributed to the difference in particle size distributions whereas the variations in the magnitude of enrichment for various metals could be traced to the segregation of metals by coagulation, as demonstrated by Gibbs (1986). Between the middle estuary and the lower estuary on the northern part (Fig. 5.9b) appreciable enhancement was noted for the metals, iron, manganese, nickel and chromium in the lower estuary, for both total and residual fractions, whereas no significant change was noted for cobalt. On the other hand, the metals, lead, cadmium, copper and zinc showed depletion in the lower estuary. Maximum depletion was noted in the case of zinc. In the southern part of the estuary, (Fig. 5.9c) middle estuarine depletion was noted for manganese whereas for zinc, iron, nickel, cobalt and chromium, appreciable change could not be observed. As observed in the northern parts, enrichment was observed for, lead, cadmium and copper in both total and residual fraction although the enrichment was only 1.5 to 2.0 times. Between the middle estuary and lower estuary in the southern part(Fig. 5.9d), enrichment was noted in the lower estuary, for the total trace metals and the residuals co-varied with totals, signifying the minimal reactivity of residual phase under estuarine conditions.

The estuarine reactivity of organically bound metals is depicted in Fig. 5.10 (a - d). The enrichment of lead, nickel, and cobalt in this phase paralleled that of total metals in the middle estuary (Fig. 5.10a) of the northern arm, indicating

(a) ME/UE - North

(c) ME/UE -South



(b) LE/ME -North

(d) LE/ME - South.

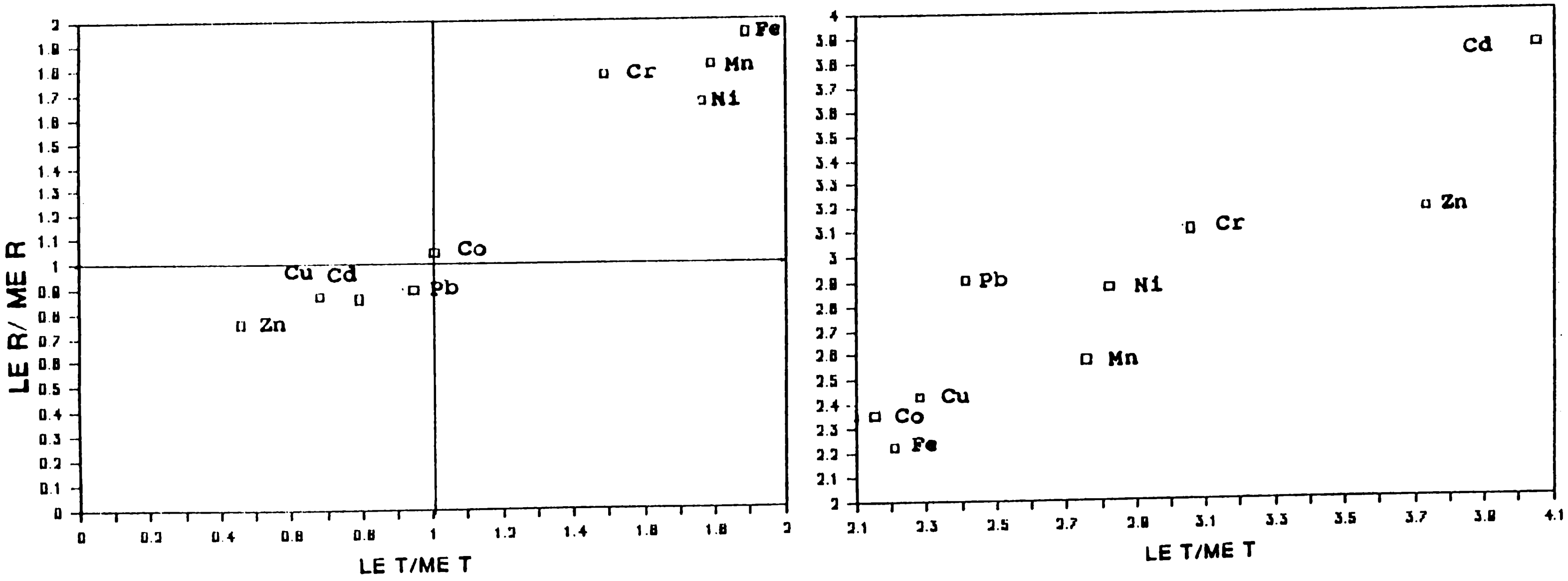


Fig. 5.9 Estuarine enrichment of residual fractions
(UE = Upper estuary; ME = Middle estuary; LE = Lower estuary
T = Total metal; R = Residual metal)

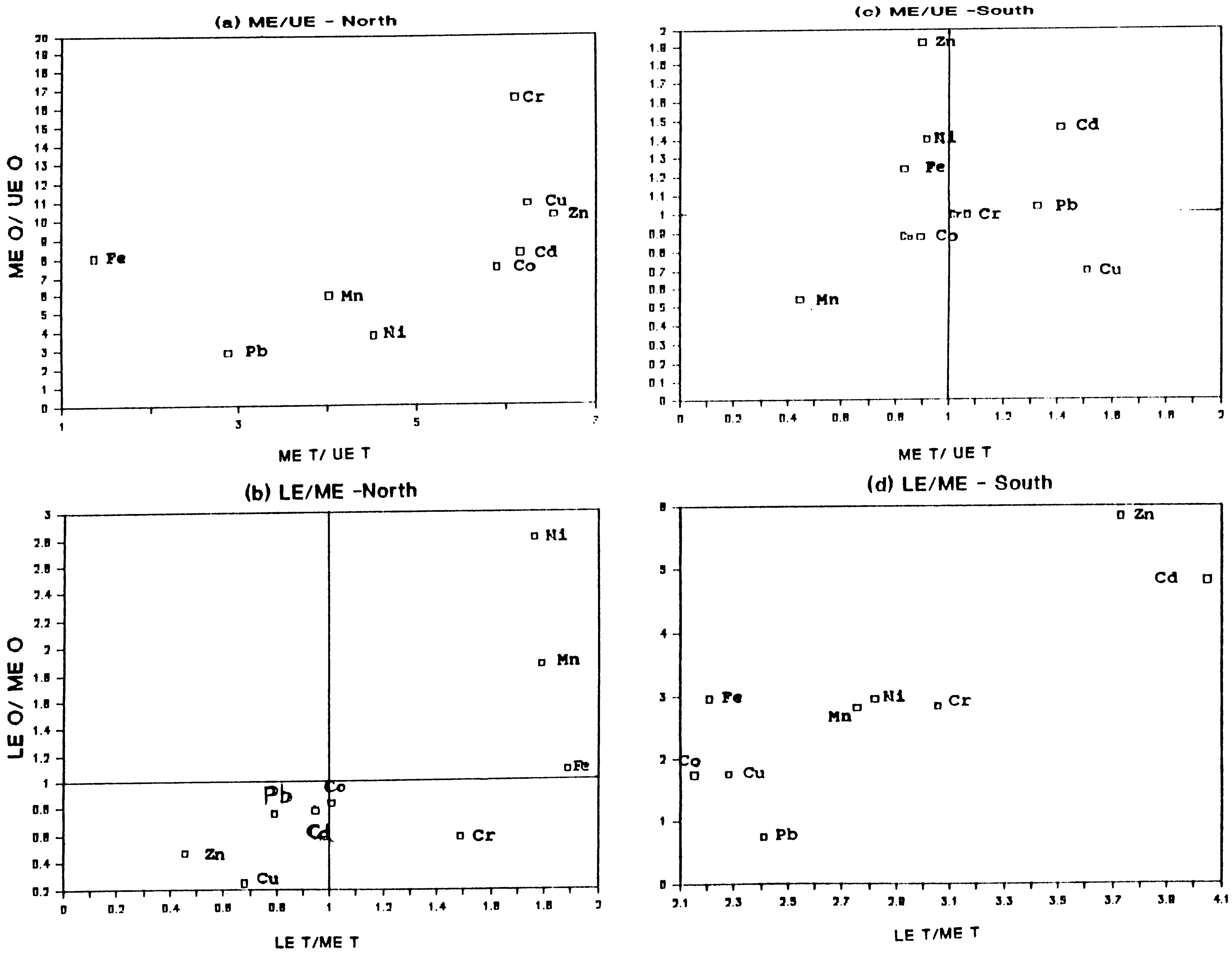


Fig. 5.10 Estuarine enrichment of organic-bound metals
(UE = Upper estuary; ME = Middle estuary; LE = Lower estuary
T = Total metal; O = Organic-bound metal)

that these metal had undergone little change through organic recycling. For iron and manganese, the enhancement in organic phase was slightly higher (8 and 6 times, respectively) when compared with enrichment (1.5 and 4 times) in the total amounts. Maximum enrichment was recorded for chromium (17 times). Cadmium, zinc and copper were more enriched in the organic phase than the enrichment recorded in total metals. Between the middle estuary and lower estuary in the northern part (Fig. 5.10b), organic phase of copper and chromium showed depletion in the lower estuary, and the depletion was 3 and 2 times higher, respectively, than that recorded for total metals. Organically bound iron also exhibited slight depletion in the lower estuary. For the other metals depletion/ enrichment recorded was parallel to that of total trace metals. As observed for residual manganese, organic bound manganese also was depleted in the middle estuary in the southern arm (Fig 5.10 c). Although total copper was enriched in the middle estuary, corresponding increase in the organic phase was not noted, signifying phase transfer during estuarine processes. For iron, nickel and zinc, the enrichment in organic phase was slightly higher than the corresponding increase in total trace metal levels, but for cobalt, chromium, lead and cadmium, increase in organic phase paralleled that of increase in total metal. Between the lower and middle estuary in the southern part (Fig. 5.10d) enrichment was noted for all the metals (except lead) in the organic phase, as also noted for total metal concentration indicating that dynamic equilibrium was attained in phase transformation through organic cycling.

The behaviour of easily reducible forms of trace metals is depicted in Fig. 5.11 (a- d). The inadequacy of data on copper in this phase has already been pointed out (Chapter 4). For iron, 5 times enrichment was recorded in this phase in the middle estuary (Fig. 5.11a) which was 4 times higher than the enrichment in totals. For zinc and cadmium also slightly high enrichment in this fraction was noted than the increase in totals. For the remaining metals, the enrichment in this phase

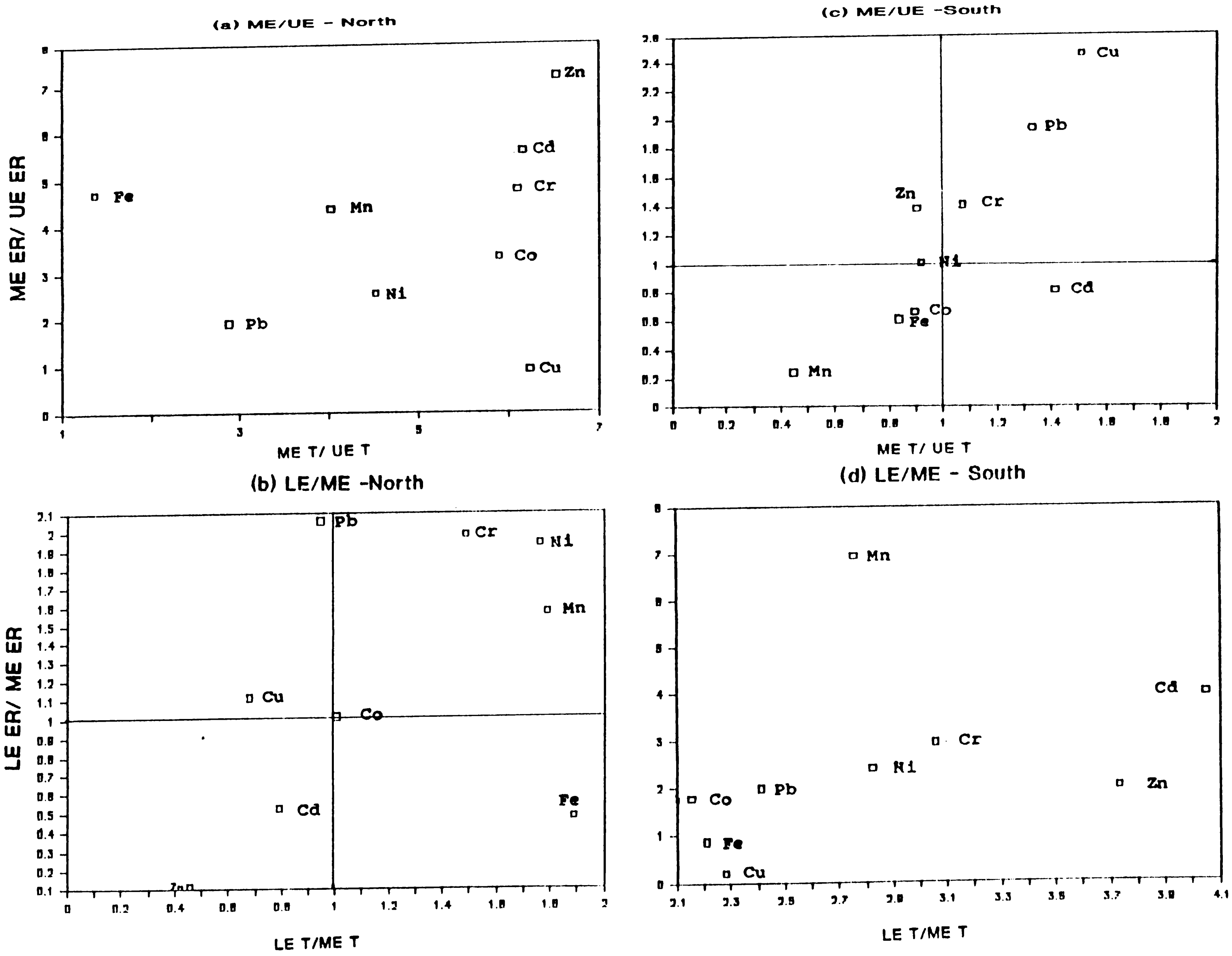


Fig. 5.11 Estuarine enrichment of easily reducible metals
(UE - Upper estuary; ME - Middle estuary; LE - Lower estuary
T - Total metal; ER - Easily reducible metal)

was paralleled by an enrichment in totals also, in the northern part of the estuary. However, between middle estuary and lower estuary, in the north, appreciable depletion was noted in the lower estuary for iron, zinc and cadmium in this phase (Fig. 5.11b), whereas, lead recorded enrichment. Chromium, nickel and manganese covaried with totals and cobalt concentrations were unchanged. Between upper and middle estuary in the south (Fig. 5.11c), the depletion/ enrichment in this phase followed the same trend, as was recorded for totals. Between middle and lower parts of the southern estuary (Fig. 5.11d), manganese showed enrichment in this phase; iron and copper exhibited depletion. Other metals did not exhibit any changes between the sites compared.

Except for iron, manganese and zinc, the trace metals in the carbonate bound phase exhibited depletion in the middle estuary, when compared with the status of total trace metals, in the northern arm of the estuary (Fig. 5.12a). While, manganese showed little change, iron fraction showed maximum enrichment (10 times) in the middle estuary, followed by zinc (2 times). Maximum depletion was noted for the carbonate bound iron, and zinc in the lower estuary (Fig. 5.12b) whereas copper and lead in this phase was found to increase. In the southern parts, iron and zinc in this phase (Fig. 5.12c) showed enrichment in the middle estuary when compared to the upper estuary and manganese and cobalt exhibited depletion. No significant changes could be detected for other metals in this phase. Between middle and lower estuary in the south, iron, nickel and chromium showed depletion, while zinc in this phase showed an enhancement in the lower estuary. The carbonate phase of all other metals paralleled the distribution of the total content.

Significant estuarine reactivity was recorded for the metals in the exchangeable phase (Fig. 5.13 a-d). Between middle and upper estuary in the north, the enhancement in the total metals was not followed by a similar enhancement in exchangeable

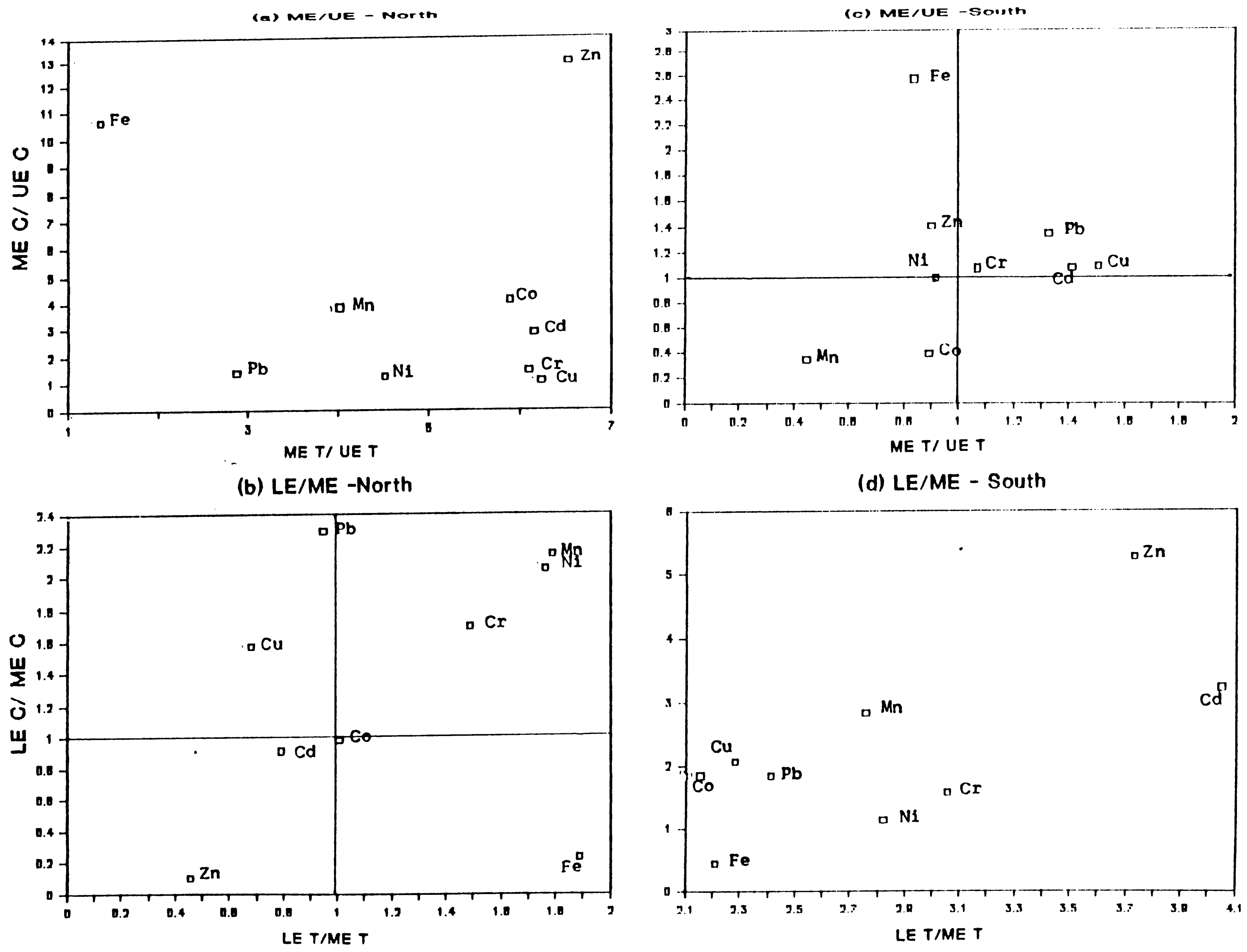
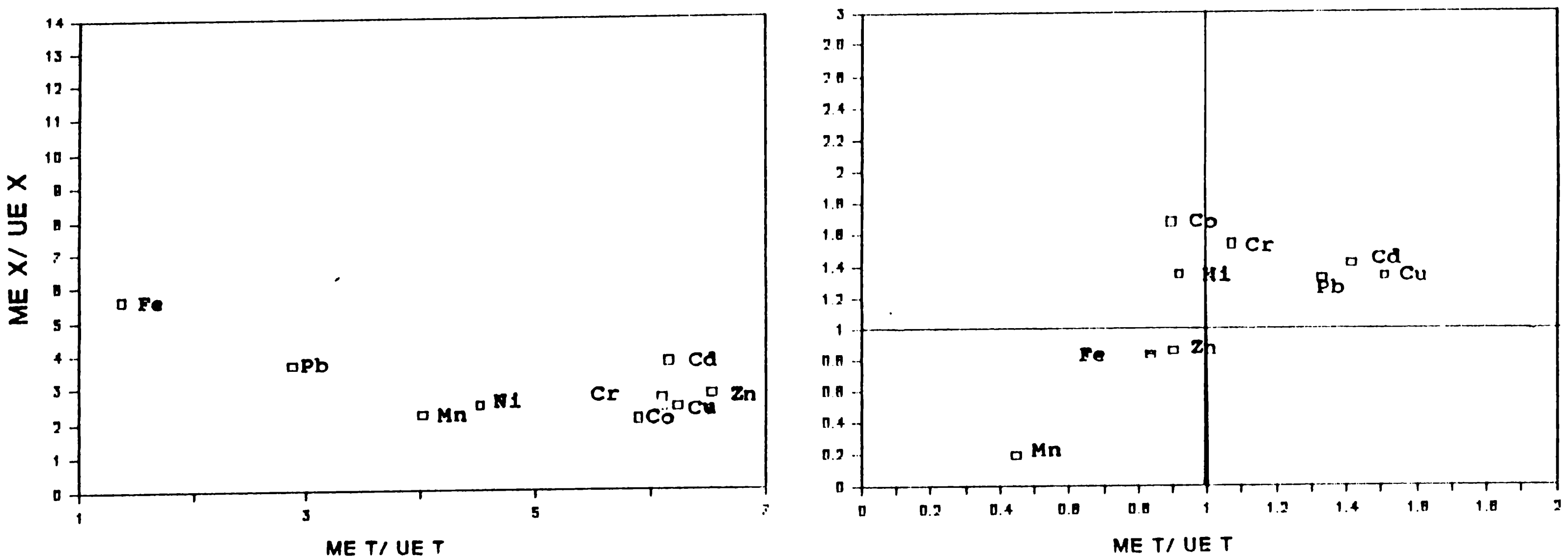


Fig. 5.12 Estuarine enrichment of carbonate-bound metals
(UE - Upper estuary; ME - Middle estuary; LE - Lower estuary
T - Total metal;C - Carbonate-bound metal)

(a) ME/UE - North (c) ME/UE -South



(b) LE/ME -North (d) LE/ME - South

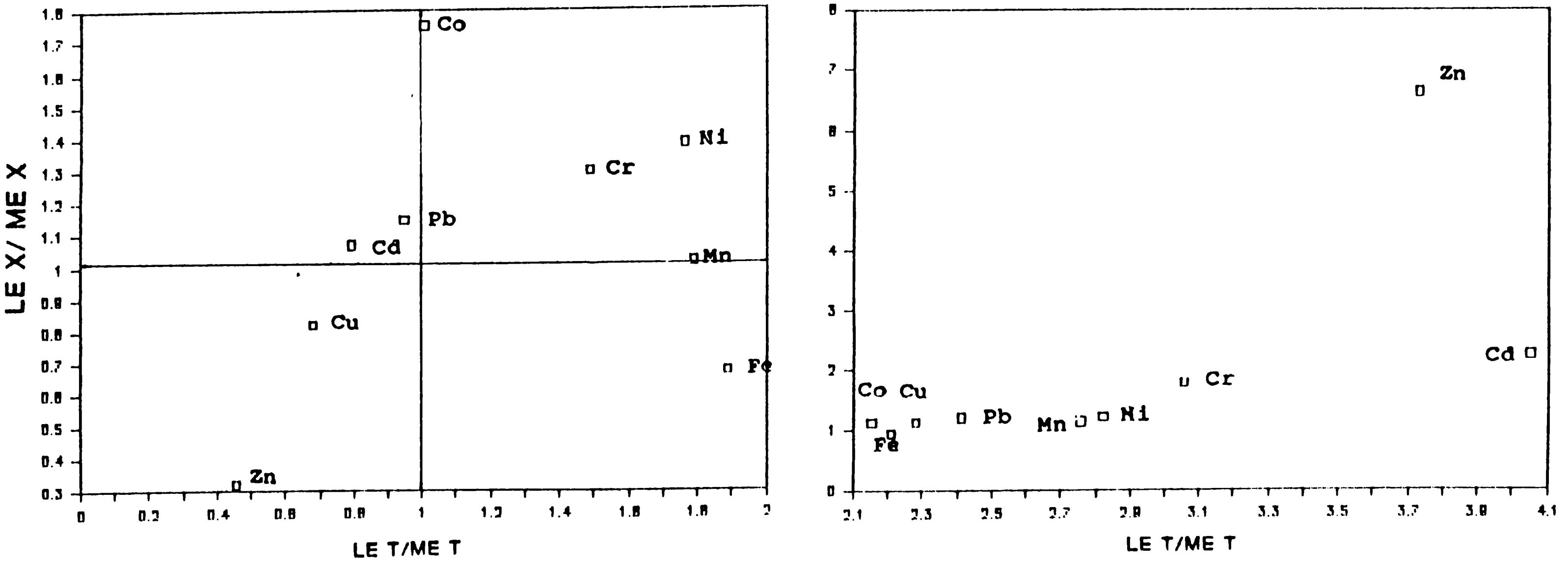


Fig. 5.13 Estuarine enrichment of exchangeable metals
(UE = Upper estuary; ME = Middle estuary; LE = Lower estuary
T = Total metal; X = Exchangeable metal)

phases, indicating that this phase had undergone rapid transformation between these two segments in the estuary. Iron in this phase was found to get enriched (Fig. 5. 13a) in the middle estuary ; lead also recorded slight enrichment, but, depletion was noted for all other metals. On the other hand, the `totals' of all the metals had recorded enrichment in the middle estuary, and the depletion in the concentration of exchangeable fraction was a convincing evidence for the desorption of trace metals from sediments in lower saline regions of this tropical estuary. This depletion was further aggravated in the lower estuary for all the metals, and the depletion was maximum for zinc (Fig. 5.13b). In the southern parts, however, the exchangeable fraction was found to co-vary with totals between the upper and middle estuary (Fig 5.13c), except for manganese , which exhibited depletion and cobalt, chromium and nickel, which showed enrichment. Between middle and lower estuary in the south, all the metals ,excepting zinc, exhibited depletion in this phase. Similar observations were recorded by Fletcher et al. (1983) at the Fraser estuary. The reduction in exchangeable trace metals under the influence of salinity was attributed to desorption. However, an alternative explanation for these observations could include the landward transport of compositionally distinct marine particles in the saltwater intrusion as suggested by Forstner et al. (1990) for the Elbe estuary, or compositional variation reflecting changes in the size distribution of sediments, as pointed out by Nolting et al. (1990) for the Rhine and Meuse estuaries. Textural analysis had shown that the sediments at Station 5 (lower estuarine station) contained relatively higher proportion of coarser particles than that at Station 6, except during the monsoon season (Fig. 3.2). Consequently the relatively low extractable metals observed in this region of salt intrusion might simply reflect the increased proportion of coarse particles. However, a comparison of the reduction in total metals with that of metals in the exchangeable phase showed that desorption was a major process deciding the fate of trace metals in this tropical estuary.

The sequential analysis, thus clearly brings out the estuarine reactivity of trace metals. While the residual fractions had undergone little chemical change, within this estuary, all the other fractions exhibited notable changes. But the direction and magnitude of the change varied widely between the metals studied and also between the two arms of the Cochin estuary.

5.5 THE OUTLOOK

Sequential chemical extraction schemes have opened up new vistas for closer examination of the fate of trace metals in the environment. The techniques have become invaluable in studying the terrestrial transport and ultimate removal/ transformation of trace metals. Chemodynamics of trace metals in the continuously changing environment of a tropical estuary, now stand highlighted.

Environmental behaviour of trace metals is receiving increased attention with added emphasis on sources, sinks, contamination levels and bioavailability. This necessitates rapid advancements in developing simpler, reliable and affordable methodologies. Although, the sequential extraction techniques, employed herein, can be advantageously used in delineating the boundaries and also in predicting the transfer processes between various media in the environment, refinement of techniques, both in analytical terms and conceptual lines, need to be made. Techniques for physical fractionation, sub-phase fractionation, and mathematical systems modeling are potential areas for further exploration. There is also a need to coordinate and integrate the various approaches in chemical fractionation so as to define the bio-geo-physico-chemical factors that influence and regulate the environmental impact of trace metals.

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