THE DISTRIBUTION AND PARTITION OF SOME OF THE TRACE METALS IN SEDIMENTS AND WATERS OF THE COASTAL ENVIRONMENT

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by

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CERTIFICATE

This is to certify that this thesis bound herewith is an authentic record of the research carried out by Smt. V. Rajamani Amma, M.Sc., M. Phil., in the National Institute of Oceanography, Regional Centre, Cochin under my supervision and guidance in partial fulfilment of the requirements for the Ph.D degree of Cochin University of Science and Technology and that no part thereof has been previously formed the basis of the award of any degree, diploma or associateship in any University.

Cochin - 682 018
June, 1994.

Dr. V.N. Sankaranarayanan
(Supervising teacher)

CONTENTS

Page No.

PREFACE

CHAPTER 1. INTRODUCTION 1

CHAPTER 2. MATERIAL AND METHODS

CHAPTER 3. GENERAL HYDROGRAPHY AND MINERALOGY

CHAPTER 4. DISTRIBUTION OF TRACE METALS IN THE WATERS AND SEDIMENTS

PREFACE

The thesis is based on the sampling and analysis of surface and bottom waters, sediments and biomaterials collected from southwest coast of India covering the entire sector of coastal Kerala from Kasaragode to Vizhinjam comprising of eight active coastal zones and from two important highly dynamic estuarine regions namely; Chaliyar and Cochin estuaries. The water samples were analysed for general hydrographic parameters such as salinity, dissolved oxygen, pH as well as dissolved and particulate fractions of trace metals. The sediment texture, organic carbon and various geochemical fractions of metals in the sediment samples were estimated. Trace metals concentrated in various parts of biomaterial were also analysed.

The results of the study are presented in six chapters.

Chapter 1, the introduction reviews the importance of the study and also the geochemical fractionation methods of trace metals in the sediments along with the scope of the present investigation.

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

In Chapter 3, the general hydrographic features of the study area and a brief review of the sedimentological features along with the geological background of the study area are presented and discussed.

Chapter 4 describes the distribution of trace metals in the water and sediments of Kerala coast and the Chaliyar and Cochin estuaries.

In Chapter 5, the results of geochemical partitioning of trace metals, Cu, Zn, Cd, Pb, Fe and Mn are discussed. The various metal fractions studied in different environments are compared. An attempt has also been made to evaluate the significance of geochemical partitioning in the coastal ecosystem. The levels of trace metals observed in the various parts of the body of the biomaterials are also discussed.

Chapter 6 summarises salient features of the investigation.

CHAPTER - 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.

Most of the sediments in coastal zones are enriched with contaminants from municipal, industrial and surface run-off. The chemistry of contaminated sediments is of a complex nature, since the composition of sediment contaminants (such as Cu, Zn, Cd, Pb, Cr, Ni, Co, Fe, Mn, Hg and chlorinated hydrocarbons) varies significantly.

Suspended particulate matter plays a major role in the geochemical cycling of elements. The important role of these particles in regulating the composition of seawater has been recognized (Wangersky, 1986), but the intimate interplay between biological and inorganic processes remains an enigma. It is generally recognized that sediments, both suspended and bottom, constitute a potential source for many dissolved chemical species. Metals in the surface coating of sediments, both in suspension and in bottom deposits, may be brought into solution by changes such as the intrusion of water of significantly different quality (Malo, 1977).

The surplus of metal contaminants introduced into the aquatic system as anthropogenic input usually exist in relatively unstable chemical forms and is not incorporated into crystal lattices of minerals, but tends to accumulate at exchangeable sites of the sediments (Forstner *et al.*, 1982).

According to Forstner and Salomons (1980) principal problems in the environment are: (i) the potential availability of the contaminants in the sediments for aquatic life (bioavailability), (ii) the problem of remobilization, in which form it occurs and under what circumstances.

Use of the total metal concentration as a criterion to assess the potential effects of sediment contamination, implies that all chemical forms of a given metal have equal impacts on the environment, which is highly improbable (Tessier *et al.*, 1979).

Sequential extraction, though more time-consuming and may involve incomplete selectivity of the reagents used, provides much more data on the origin of pollutants, their reaction pathways, biological and physico-chemical availability and possible remobilization, than bulk sample analysis. Another advantage is that the chosen fractions are likely to be affected by various environmental conditions. This means that one can, to a certain extent, simulate natural conditions in the Laboratory (Prohic and Kniewald, 1987).

Analysis of dissolved substances helps to estimate the contamination at the moment of input by a river or a waste disposal, but it can hardly give information about the long term pollution level (Salomons and van Driel, 1980).

Eventhough the content of toxic substances in organisms give direct information as to their impact on biota and the potential risks for human health, it is possible to collect only certain species and make predictions concerning the whole population (Cauwet, 1987).

Analysis of sediments takes a special place in this respect, as sediments can reflect the current quality of an environment and provide a history of the chemical parameters. Study of the sediments collected by coring was proved useful as it provides a historical record of both the natural background and man induced accumulation of metals (Forstner and Schoer, 1984; Thornton and Abrahams, 1984).

Estuaries are precious and productive coastal sites, subject to high demand for a variety of uses. Disposal of sewage and pollutants often results in the degradation of the environmental quality. The scavenging by suspended particles result in large concentrations of pollutants being retained in estuarine sediments (Juracic and Prohic, 1986). Moreover, rivers and other surface waters are by far the most important media for the transport of solids to the sea. Estuaries are, thus an important stage in the global sedimentary cycle (Aston, 1978; Salomons and Forstner 1984). Solids entering the estuary are either products of weathering or are related to human intervention.

The characteristic features of an individual river basin such as its climate, vegetation and morphology, and the mineral composition of its soils and rocks, constitute the background conditions which determine the chemical composition and quantities of material carried by the river and deposited in its estuary. This is probably true for the majority of estuarine systems and is particularly relevant for a polluted area. However, a few attempts have been made to evaluate the partitioning or 'solid speciation' of heavy metals in sediments of the coastal and estuarine systems of Kerala.

1.1 Literature Survey

Most of the studies concerning the behaviour of particulate trace elements in natural systems have been dealt with total elemental concentrations (Landergren 1964)., describing the overall distribution of the chemical elements within it. This means that all forms of a given metal are implicitly considered to have an equal impact on the environment and a similar behaviour in the bio-geochemical cycle. Such a simplification can be accepted over a geologically long time-scale (million years) but is clearly unsuitable for the evaluation of short term processes. Indeed, those elements which are incorporated into crystalline silicates are largely unavailable to either biological or diagenetic processes over a time-scale of a year to a decade (Jenne, 1977).

However, such studies do not yield information on the partition of trace elements among the various components of the sediments. Chester and Hughes (1966) have pointed out that unless the various sediment fractions are considered separately, relationships between trace elements and major elements can be marked in sediments.

Early workers who studied the distribution of trace-elements, considered the different sources of elements in the particulate material. They tried to differentiate between broad categories in marine sediments (Goldberg, 1954): the biogeneous portion composed of biological remains; the lithogenous portion of continental origin which does not change during its transfer through the water column; the hydrogeneous portion due to neoformations in the water column; the cosmogenous portion made up of extra terrestrial particles; and the atmogeneous portion produced in the atmosphere.

In order to separate the elements associated with those different phases, selective chemical reactions have been used, especially to isolate lithogenous from the more reactive non-lithogenous forms (Hirst and Nicholls, 1958; Chester, 1965; Arrhenius and Korkish, 1959; Lynn and Bonatti, 1965). Interest in the source, transport, deposition, biological utilization and release of trace metals in the aquatic environment has necessitated the investigation of analytical methods for determining the more readily available forms of metals that are associated with organic and mineral sediments (Malo, 1977). Different reagents have been tried such as weak acids, chelating agents or reducing agents combined with acids (Martin *et al.*,1987, Chester and Hughes, 1967; Gupta and Chen, 1975), for the extraction of non-lithogenous fraction.

Although these one-step extractions present advantages for environmental survey as they are rapid, easy to perform and clearly show contrast between abnormal and normal background levels, certain disadvantages have been encountered (Martin, Nirel and Thomas, 1987)in this method:

(i) The fraction of the total metal extracted by any partial extraction technique will depend upon the type of sample used (Chester and Hughes,1967 Agemian and Chau, 1977).

(ii) Readsorption can occur at neutral pH (Malo, 1977; Rendell *et al.*, 1980)

(iii) The use of a single reagent does not permit the dissolution of all the organic and inorganic labile forms without attacking the detrital ones.

Using EDTA as chelating agent, Golderg and Arrhenius (1958) separated elements of different origin in pelagic clays into an authigenic (biogeneous nad hydrogeneous) and lithogenic fractions. In order to determine the same phase Chester and Hughes (1967) used a reducing agent coupled with a weak acid ($NH_2.OH.HCl$ and CH_3 COOH). The authors noted that opal, montmorillonite and zeolite are not destroyed eventhough these minerals are of hydrogeneous origin. Thus, in sediments where these minerals are present, the method will only discriminate between carbonates (excluding dolomite), Fe and Mn-oxide minerals and adsorbed trace elements.

Agemian and Chau (1977), Loring (1976a) and Malo (1977) used weak and dilute acids (respectively, 0.5N HCl, CH_3 COOH and 0.3M HCl) to determine metals in exchangeable position and those associated with carbonate, easily soluble Fe and Mn oxides and metals weakly attached to organic matter. These metals are considered to be more readily available to mobilization (Malo,1977).

Such procedures that are easy to apply and allow for the contrast between 'abnormal' and 'background' concentrations (Bradshaw *et al.*, 1974) have been considered useful tools to differentiate anthropogenic (Skei and Paus, 1979; Angelidis *et al.*, 1980, 1982) from background levels (Loring 1976b; Piotrowicz *et al.*, 1981). They can also be used as a first stage reconnaissance survey prior to sequential extractions (Chester *et al.*, 1985).

In order to separate more accurately labile (inorganic and organic) from residual phase and to give more insight into particulate speciation, sequential extraction procedures have been developed. These methods are based on a combination of specific extractions often used by soil scientists (Tessier *et al.*, 1979).

Short-term evaluations of trace metals rely upon chemical extractions, the reagent usually being selected according to its ability to allow naturally slower processes, such as cation exchange to occur reasonably rapid although some approaches appear to be totally empirical (Pickering, 1981). One of the major promises of this method was to quantify the 'bioavailability' of different pollutants and trace elements associated with soils and sediments.

Geochemists have also tried to use these methods to estimate either the amount of trace elements involved in authigenesis (removal from the dissolved to the particulate phase)/ remobilization during the early diagenesis/ resuspension of deposited sediments (Martin *et al.*, 1987).

According to the depositional conditions, sediments can be a sink or a source for trace metals in water (James, 1978). Trace metals need not necessarily be definitely fixed in the sediment, and recycling can occur by biological, chemical and physical processes. (Carignan and Nriagu, 1985). According to Jenne's observations (1977), the exchangeable amorphous oxides of Fe, Mn and Al, organic matter, carbonates, phosphates and sulphides can be considered as important sinks for trace elements and/or are susceptable to modification under certain environmental conditions.

Trace metals associated with degradable organics and with the surface coatings of mineral particles are apt to be more available than those incorporated in primary minerals or occluded by secondary mineral structures (Malo, 1977). Strongly acidic or alkaline discharges could dissolve a portion of the surface coatings. Changes in the pH or oxygen regime, also contribute to the solution of metals. In addition, water treatment processes such as chlorination, dialysis, and reverse osmosis may cause solution of surface coatings.

1.2 Sequential Extraction Methods

Most often, extractions consider five or six fractions namely water soluble, exchangeable, carbonate, easily reducible or Fe and Mn hydroxides, organic plus sulphide, and residual. The dissolution of the various fractions is performed in the above sequence which allows the use of progressively stronger reagents whilst minimizing overlaps. (Gibbs, 1973; Gupta and Chen, 1975; Brannon *et al.*, 1976; Tessier *et al.*, 1979 a; Forstner *et al.*, 1981). Martin *et al.*,(1987) has reviewed the different problems involved with several extraction procedures.

1.3 Scope of the present study

Even though a few attempts have been made to evaluate the partitioning of trace metals on the basis of sediment texture (Murthy *et al.*, 1973, 1997 and 1980; Rao *et al.*, 1976 and 1978) no attempt has been made so far on the chemical partitioning of trace metals in the sediments and waters of the coastal ecosystem, comprising of riverine, estuarine and coastal regions of India. A few reports on the partitioning of marine sediments were available . Recently Kunhikrishnan Nair (1992) has reported the various fractions of trace metals in the sediments of the southern and northern arms of Cochin estuary. Shibu *et al.* (1990) carried out an investigation on the speciation of trace metals in the waters of the Periyar and Muvattupuzha rivers and Cochin estuary. The levels of trace metals in the water and particulate matter of Cochin estuary were reported by Nair *et al.* (1990) and in sediments were reported by Nair *et al.* (1991).

The aim of the present study is to trace out the pathway and the fate of some of the heavy metals in the various aquatic environments viz. riverine, estuarine and coastal regions of Kerala by subjecting the sediment samples to partition studies.

CHAPTER - 2

Material and Methods

2.1 Description of the study area:

The area of the study, the Kerala coast, the Cochin and Chaliyar estuaries and the stations sampled are shown in figs.2.1, 2.2 and 2.3. The stations were fixed on the basis of specific geographical features, water flow regimes and anthropogenic activities. Water and sediment samples were collected from eight coastal sections along the Kerala coast as shown in Fig.2.1.

The Cochin estuary is the largest of the estuaries along the Kerala Coast. Two major rivers Periyar and Muvattupuzha drain into the northern and southern parts of the estuary respectively. The southern part also receives discharges from four other rivers namely Manimala, Pampa, Achancoil and Meenachil.

The industrial belt of the Greater Cochin is situated on either banks of Periyar river. Large quantities of industrial effluents from these factories along with the effluents from the sewage treatment plant of Cochin city make the northern part of the estuary heavily polluted, while in the southern part the point sources of pollution can hardly be detected, since this part receives water that drains through vast areas of agricultural land.

As the northern part is highly under the influence of the industrial discharges the southern part which is relatively free of industrial pollution is selected for the present investigations. Samples were collected from seven stations as shown in Fig.2.2.

Chaliyar estuary situated in Calicut at the northern part of Kerala is formed by two rivers, the Chaliyar and Cherupuzha, a tributory of river Chaliyar. The Chaliyar is the third largest river of Kerala state. It originates from the Ilambaliri hills in Gudalur Taluk of Nilagiri district in Tamil Nadu at an elevation of 2066 m above mean sea level. Chaliyar flows towards the west from the Western Ghats and joins the Arabian Sea at Beypore near Calicut. The chaliyar river estuary enters the sea in a south westerly direction and this inlet is situated in a stable region. The Chaliyar river estuary has a port handling cargo and fishery harbour at Beypore situated at 11°08'N lattitude and 75°51'E longitude.

Bottom sediments in the estuary is composed of silty sands in shalow areas and clayey silts in deeper areas. Towards upstream of the river, the bottom is mainly sandy with a small percentage of silt. Four stations as shown in Fig.2.3 were selected for sample collections. This is about 10 Km from the river mouth and beyond this point the river bed sediment consists of fine to coarse sand with pebbles.

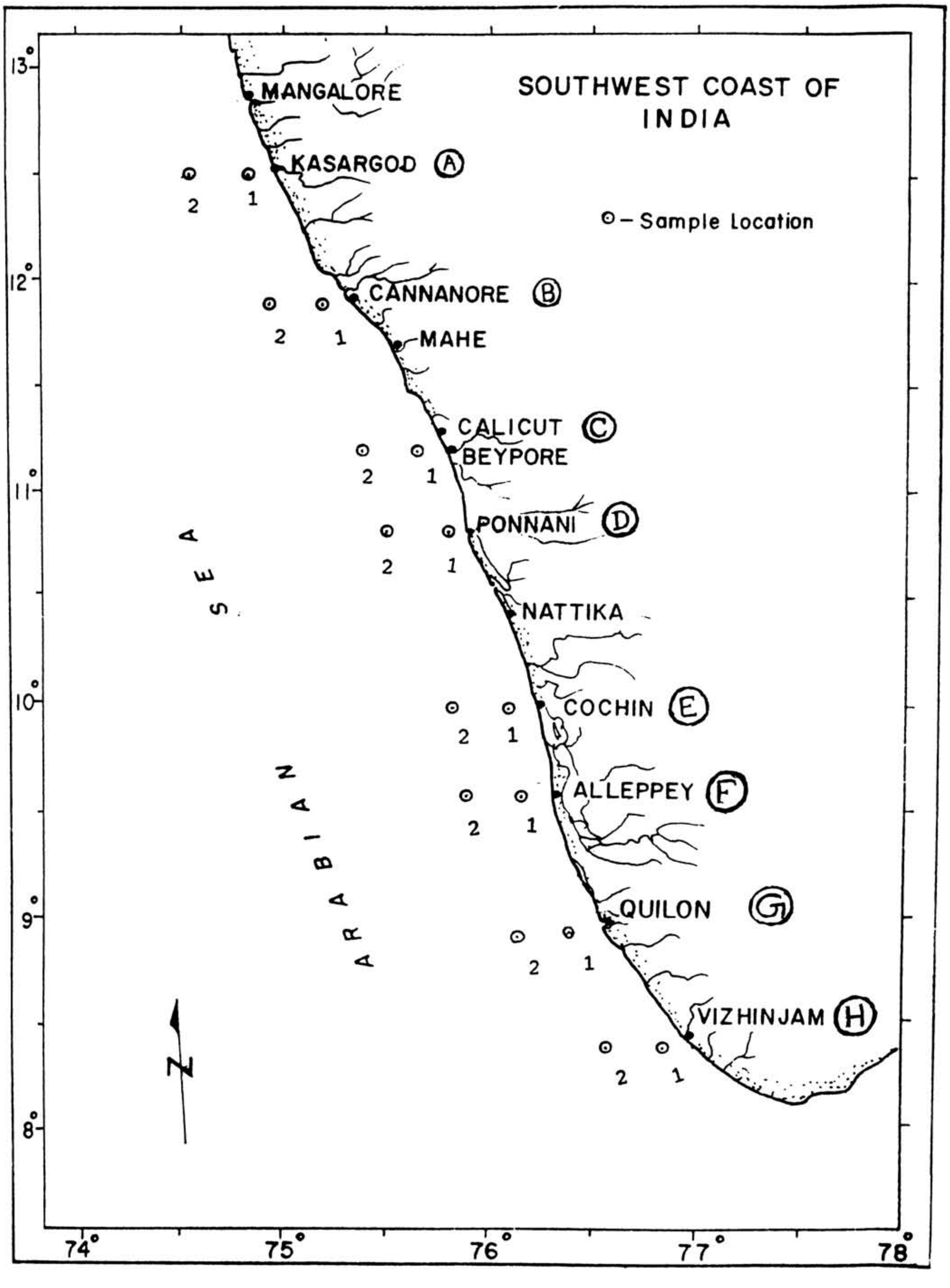

FIG. 2.1 MAP SHOWING SAMPLE LOCATIONS

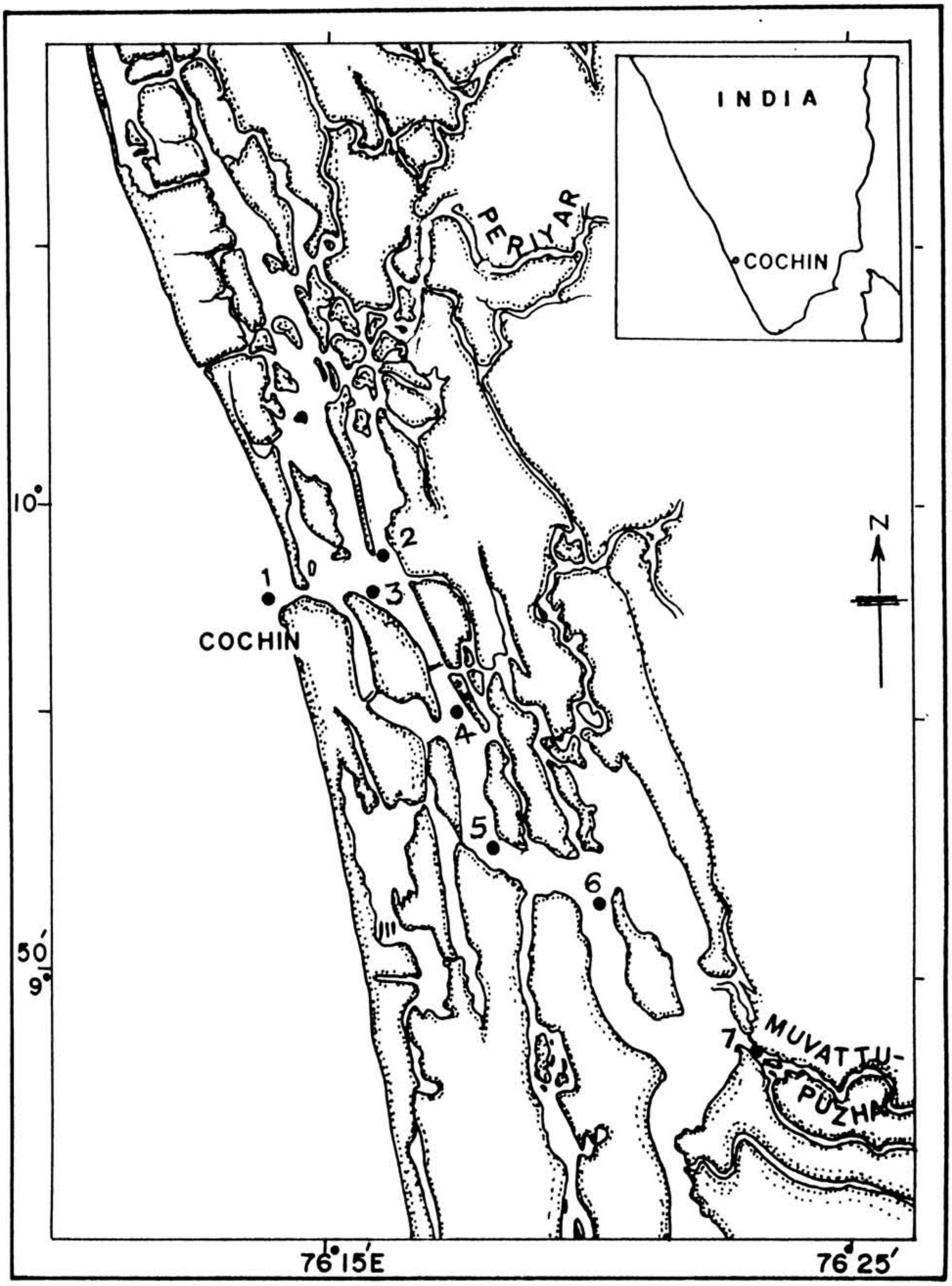
INDIA
COCHIN
PERIYAR
10°
1
2
3
COCHIN
4
5
6
7
MUVATTU-
PUZHA
N
50′
9°
76°15′E
76°25′

Fig. 2.2

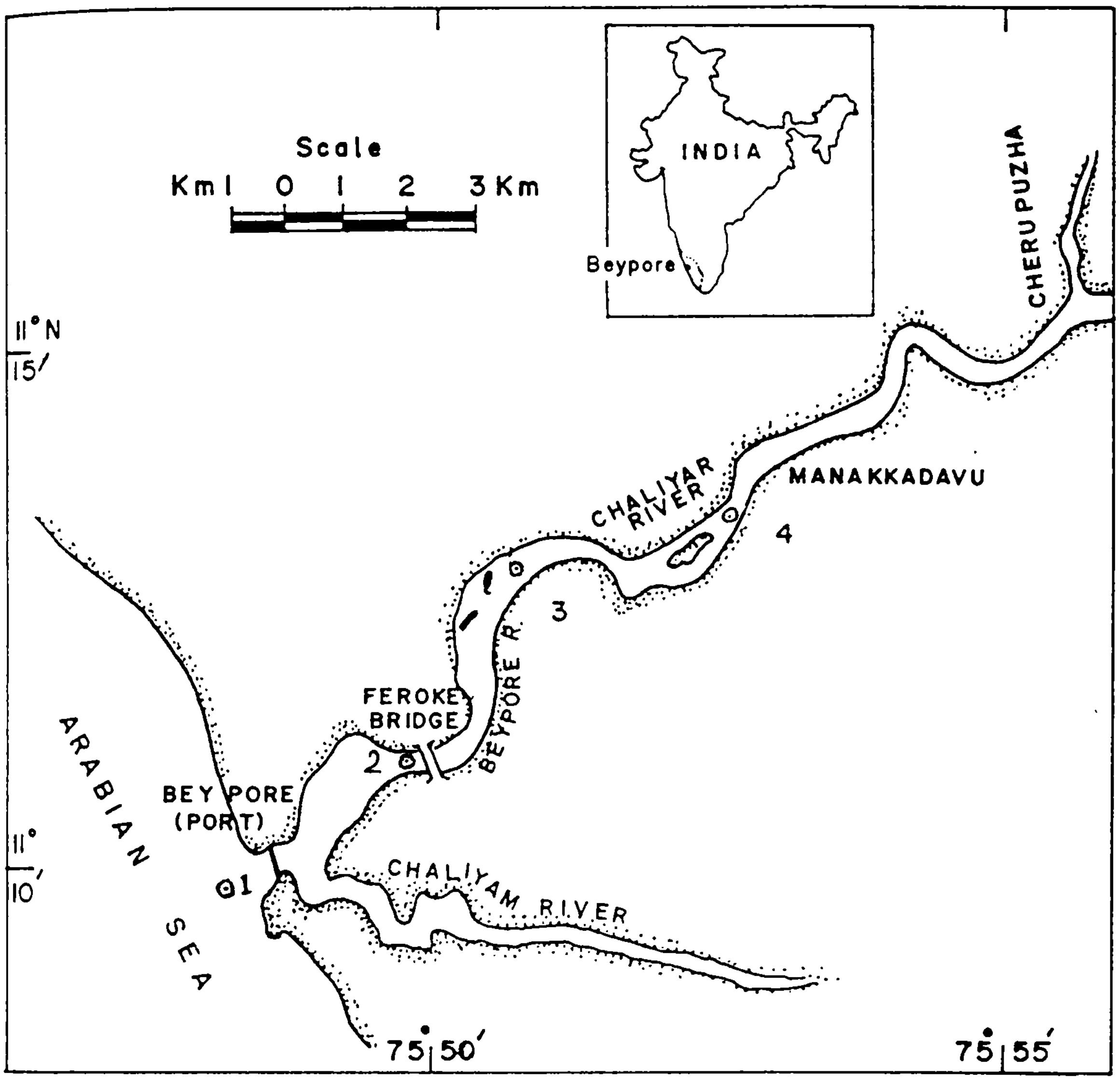

Fig. 2.3. Observation stations in Chaliyar river estuary.

2.2 Sampling procedure

Extreme care was taken in sampling and subsampling being the first crucial point influencing the results.

Water samples were collected in 5 litre polythene jerry cans. The sample containers were soacked in 6N HNO_3 overnight and rinsed with the sample prior to collection. After filling, the bottles were wrapped in polythene covers and kept frozen until the analysis.

Sediment samples were collected using a van-veen grab. Undistrubed subsamples were taken immediately from the centre with a polythene scoop. The sediment was placed in pre-rinsed, 1 litre wide mouth polythene bottles and the bottles filled without trapping any air bubbles. The samples were kept frozen below - 5 degree Centigrade till the analysis.

Common species of fish samples in the estuarine and marine regions were caught using nylon nets from the study area of Cochin. Subsamples of flesh and alimentary canal with liver were kept for oven drying as soon as the samples reached the laboratory.

2.3 Methods of Analysis

All glasswares and polythenewares used in the experiments were previously washed, soaked in 6N nitric acid and then rinsed with denionized water. All the reagents used were of analytical grade and the reagents and standards were prepared with deionized water. Laboratory grade MIBK was double distilled and the APDC solution used was extracted with redistilled MIBK to get rid off any metal contaminants present.

Dissolved and particulate metals.

Three aliquots of each water sample were filtered through 0.45 micron millipore filter paper. The suspended particulate matter retained on the filter was dried at 40-50 degree centigrade, weighed and digested with HF-aquaregia mixture in a teflon bomb and the digested solution made upto 25 ml in boric acid matrix (Loring and Rantala, 1977). The dissolved fraction of metals were determined by re-extraction with 1% (v/v) nitric acid of the preconcentrated filtered water samples by APDC-MIBK extraction (Smith and Windom, 1972, Brook *et al.* 1967).

In addition to the geo-chemical partitioning the sedimment samples were also analysed for gross heavy metal concentration, total organic carbon and grain size distribution. The total metal analysis was carried out by the digestion of the sample with a mixture of acids in a teflon bomb (Loring and Rantala, 1977). The organic carbon analysis was by wet oxidation method with chromic acid (Elwakeel and Riley, 1957) and the texture analysis of sediment samples was conducted by wet sieving and by pipette method (Krumbein and Petti John, 1938).

2.3.1. Procedures

2.3.1.1 Geo-chemical partitioning.

The partitioning of the tracemetals among the various geochemical phases of the sediment sample is achieved by subjecting a known quantity of the wet sediment sample to a series of chemical reactions. These components include:-

(i) Ions on exchangeable sites (Exchangeable phase)
(ii) metal carbonates
(iii) easily reducible fraction
(iv) moderately reducible phase
(v) Organic and sulphides
(vi) lithogenous (mineral residual) fractions.

Sequential Extraction Procedure.

Subsamples of the sediments were taken from the centre of the bottles, where they are protected against oxygen contact during sampling and transport. Manipulations during extraction of the subsamples were continued up to the 4th fraction in a glove box, providing an inert atmosphere of nitrogen gas. The extractions were done in 125 ml polypropylene tubes closed with air tight screw caps to ensure integrity of the sample solution during the mechanical shaking and centrifuging procedure. The phases were separated by centrifugation at 6000 rpm for 20 minutes. The samples were analysed in triplicate and the analysis was repeated when the values differed by over 15 percent. The mean of the three determinations has been reported. The various steps involved in the fractionation are as shown below:-

(i) Exchangeable phase: About 10 g of wet sediment samples was placed in the pre-weighed and pre-rinsed polypropylene tube and shaken with 50 ml of deaerated 1M. ammonium acetate solution for two hours in a mechanical shaker. The phases were seperated by centrifugation and the extract collected in a 100 ml standard flask. Once again the extraction was repeated with 50 ml of the ammonium acetate, shaking for one hour. The combined extracts collected in the standard flask was made up to the mark and kept in the refrigerator in polythene bottles till analysis.

The moisture content of the sample is also determined using another subsample.

(ii) Carbonate Phase: The above residue was washed with nitrogen sparged glass distilled water and centrifuged. The supernatant was discarded and the residue was extracted twice with 50 ml lots of deaerated IM sodium acetate solution (pH adjusted to 5 with acetic acid), shaking for 5 hours.

A chelator (10 mg EDTA) was added to the ammonium and sodium acetate extracts to prevent precipitation of metals during storage in the refrigerator. Acidification of these solutions was found to be inadequate due to precipitation of humid acids, leached by the first two steps (Kersten and Forstner, 1987)

(iii) Easily reducible fraction: The residue from the previous step, washed with deaerated glass distilled water was shaken for 12 hours with 50 ml aliquot of deaerated 0.1M hydroxylamine hydrochloride in 0.01M nitric acid, twice.

(iv) Moderately reducible fraction : A 2g subsample of the previous residue was extracted twice by shaking with 50 ml lots of nitrogen sparged 0.2M ammonium oxalate in 0.2M oxalic aicd, for 12 hours. Another subsample of the residue of the (iii)rd step was kept for moisture content determination.

(v) Organics and sulphides: To the above residue added 6 ml of 0.02M nitric acid and 10 ml of acidified (pH2, HNO_3) 30% of hydrogen peroxide. The mixture was heated to 85 degree centigrade. After two hours of heating 5 ml of 30% H_2O_2 (PH-2) was added. The mixture was allowed to cool and extracted with 100 ml of IM ammonium acetate in 6% nitric acid.

(vi) Residual fraction: The residue was washed with glass distilled water, dried and digested with a mixture of 1 ml aquaregia and 6 ml HF in a teflon digestion bomb, at 90 degree centrigrade. After digestion, the contents of the teflon bomb were transferred into a 100 ml standard flask containing 5.6 g boric acid and 10 ml glass distilled water, and the solution made up to 100 ml.

Fig.2.4 represents a schematic diagram of the overall sequential extraction procedure adopted for the present investigation.

2.3.1.2 Digestion procedure for total metals in sediments, suspended particulate matter and in biomaterials.

A finely ground, dried sediment sample of 1g was weighed accurately in a teflon bomb and wetted with 1 ml of aquaregia, 6 ml of con.HF were added slowly and the bomb was heated in an air oven (90-100°C) for one hour. After cooling the contents were washed into a 100 ml volumetric flask containing 5.6g of boric acid that has been shaken with 20 ml of glass distilled water. The flask was shaken to complete the dissolution and made up to volume (Loring and Rantaia, 1977). The filter was transferred into the teflon vessel with plastic tweezers and squashed it at the bottom of the vessel, wetted with 1 ml of aquaregia and 2 ml of HF was added, heated the bomb in an air oven (90-100°C) for one hour. After cooling the contents were decanted through a funnel into a 25 ml volumetric flask containing 0.93 g boric acid and 5 ml glass distilled water. The filter paper remaining in the teflon vessel was washed several times with small volumes of water. Finally the flask was shaken to complete the dissolution and made up to volume. The blank solution was preapred in the same manner but omitting the sample. About 0.3g of dried biomaterial sample was digested

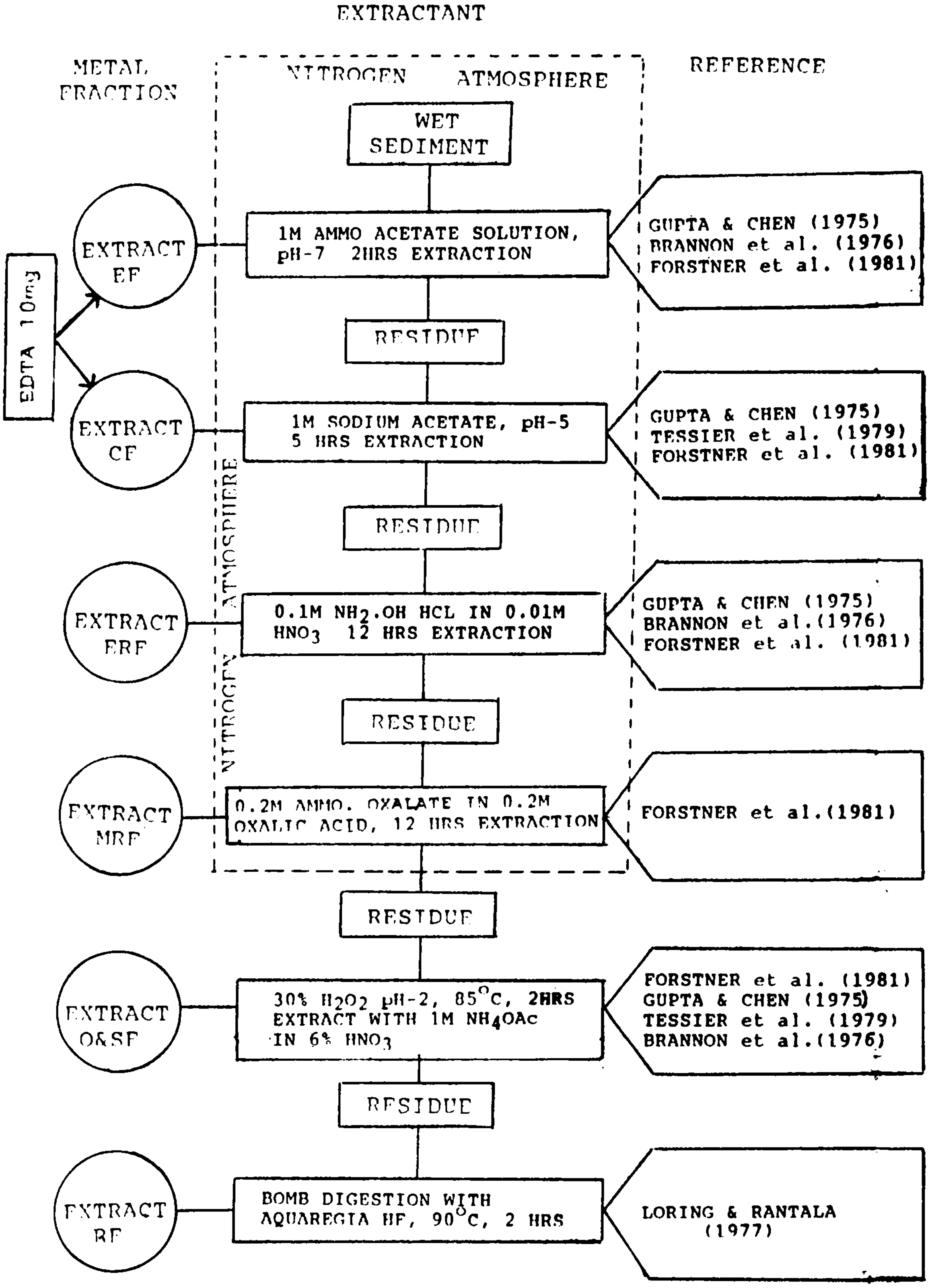

Fig.2.4 Schematic diagram - Sequential extraction proceedure

EF - EXCHANGEABLE FRACTION

CF - CARBONATE FRACTION

ERF - EASILY REDUCIBLE FRACTION

MRF - MODERATELY REDUCIBLE FRACTION

O & SF - ORGANICS & SULPHIDES FRACTION

RF - RESIDUAL FRACTION

with 3ml of conc. nitric acid in a teflon bomb at 120°C for 2 hours. After cooling the digestive was quantitatively made up to 25ml with glass distilled water, in a standard flask. Blank was also prepared in the same manner but omitting the sample (Paus, 1972).

Trace metal analysis: The analysis of trace metals in all the extracts were performed in an atomic absorption spectrophotometer (Perkin Elmer Model 2380) involving direct aspiration of the solution into an air-acetylene flame. A standard spiking method was used for the determination of cadmium and lead in all the fractions and for copper and zinc in the first three fractions. The extracts were suitably diluted with glass distilled water for the determination of iron and manganese. Reagent blanks were aspirated for all the solutions.

2.4 Precision:

The precision of the analytical techniques and the reproducibility of data were checked by comparing the values of each fraction for the triplicate analysis of every sample. It was found that the percentage variations recorded for most of the samples for the metals Cu, Zn, Fe and Mn was less than 10% while Cd and Pb showed variation up to 20% for a number of samples. This indicates low precision coupled with very low concentrations of the analytics. The reproducibility of the data was quite good and comparable with values reported in literature for similar studies (Gupta and Chen, 1975:

		E.F. /ug/g	C.F. /ug/g	E.R.F. /ug/g	M.R.F. /ug/g	C & S.F. /ug/g	R.F. /ug/g	Sum /ug/g	Total metal /ug/g
Iron									
Chaliyar estuary									
	1	0.8933	3617.97	714.66	35010.32	8562.31	11796.96	59703.11	57781.10
	2	0.4286	2357.14	878.57	26763.60	4439.46	18645.73	53084.92	49978.4
Cochin estuary									
"	1	1.4066	1406.5	668.1	18108.2	7006.03	7437.3	34627.8	32947.5
"	3	1.9896	1840.3	746.2	22717.0	13067.1	7840.2	46212.7	43116.278
"	4	0.6014	751.7	721.42	22452.0	18924.7	12733 .2	55583.62	54651.16
Manganese									
Off Alleppey	1	0.7735	5.4146	4.3832	11.3449	73.7417	92.0885	187.7479	193.0423
Off Cochin	1	11.2345	27.489	15.5371	12.1907	90.3544	54.7190	211.5257	201.9119
Off Ponnani	1	1.0956	16.709	10.9567	20.5438	54.7836	76.0037	180.0924	176.0859
Off Calicut	1	2.2540	51.6895	3.005	14.2750	61.3148	186.0111	318.5494	309.53
Copper									
Off Kasargode	1	------	0.5070	0.0172	4.9791	6.0284	7.8369	19.3686	23.9129
"	2	------	0.3979	0.0199	2.5862	25.2464	19.8365	48.0869	45.6519
Off Canannore	1	------	------	------	9.8911	12.6610	19.7252	42.2773	41.526
Off Calicut	1	------	0.6860	0.0232	5.5787	10.0641	4.4030	20.752	21.7390

? Reporting [illegible] up to [illegible]

Contd......2

		E.F. µg/g	C.F. µg/g	E.R.F. µg/g	M.R.F. µg/g	C & S.F. µg/g	R.F. µg/g	Sum µg/g	Total metal µg/g
Zinc									
Off Quilon	2	-----	-----	0.46	8.94	19.25	30.61	59.26	56.85
Off Alleppey	1	0.041	0.2247	----	6.0980	38.876	24.471	69.7107	76.760
Off Cochin	1	0.2083	2.6041	6.250	5.8331	89.580	44.284	148.7595	140.4208
Off Ponnani	1	------	0.3581	0.8356	3.5810	26.738	27.3018	58.8145	62.8628
Lead									
Off Quilon	1	------	1.705	-----	0.8527	20.4658	14.9067	37.9307	43.4782
Off Alleppey	1	-------	4.6769	2.3385	9.3538	23.3846	28.1527	67.9065	65.2174
Off Cochin	1	-------	2.1679	2.1679	8.6716	17.3433	50.640	80.9997	76.0870
"	2	-------	------	------	------	7.975	15.950	23.925	26.04
Cadmium									
Off Quilon	1	0.6142	------	------	0.57	1.2866	------	2.4708	2.128
Off Alleppey	1	1.1249	0.4184	------	---	1.4704	1.5281	4.5418	4.256
Off Cochin	1	0.7496	0.6542		0.2776	1.6542	------	3.3356	3.192
"	2	0.6034	0.5593	-------	0.2797	1.16	------	2.6024	2.7134

Table 2.1

(-----) below detectable limit

Chester *et al.*, 1988).

The sum of the values of all the fractions and the total metal concentrations when compared as presented in Table 2.1 were found to be in good agreement and the variation was below 10% for 95% of samples, which also appraises the precision of the analytical techniques.

2.5 General Hydrographic and other parameters:

Concurrent to trace metal analysis, water quality parameters such as salinity, pH, dissolved oxygen, suspended solids, Eh of the sediments etc, were estimated by standard procedures as detailed below:-

Eh and PH - Philips pH meter
Salinity - Autosal
Dissolved oxygen - Iodometry (strickland & Parasons,1977)
Suspended solids - Gravimetry (Butler and Mc Manus, 1979)

The moisture content of the sediments were determined gravimetrically by oven drying of the accurately weighed wet samples to constant weight at 105^{o}C (Hakanson and Janssson, 1983). The moisture content was expressed as the percentage weight of water in the wet sediment and from this the sediment metal values were computed and expressed on dry weight basis. Total sulphide in sediments were determined gravimetrically after oxidation and extraction with acidified hydrogen peroxide (Vogel, 1967). Total-P was determined by phosphomolybdic method. (Strickland and Parsons, 1977).

CHAPTER - 3

General Hydrography and Mineralogical aspects of sediments

The hydrographical features along with mineralogical characteristics of sediments constitute an essential and useful basis for the partitioning of trace metals among various geochemical fractions being influenced by the parameters like. pH , Eh, salinity, dissolved oxygen, organic matter content grain size etc. and anthropogenic input. Therefore a prior knowledge of environmental characteristics and the mineralogy of sediments is essential for the interpretation of trace metal concentrations in various geochemical fractions of the sediments. In this chapter the data on some important hydrographic parameters like salinity, dissolved oxygen, pH and a brief review on the sedimentological features along with the geological background of the study area are presented and discussed.

3.1 Hydrographical features of Kerala Coast.

Kerala has a number of river openings along its coast line. Some of these drain into the backwaters or lakes prior to emptying into the Arabian Sea (fig.1). Certain features that most of these rivers share are short length, leanflow during non-monsoon months, connection with back-waters and the tidal nature of mouths (Sarala Devi, *et al.*, 1983). The

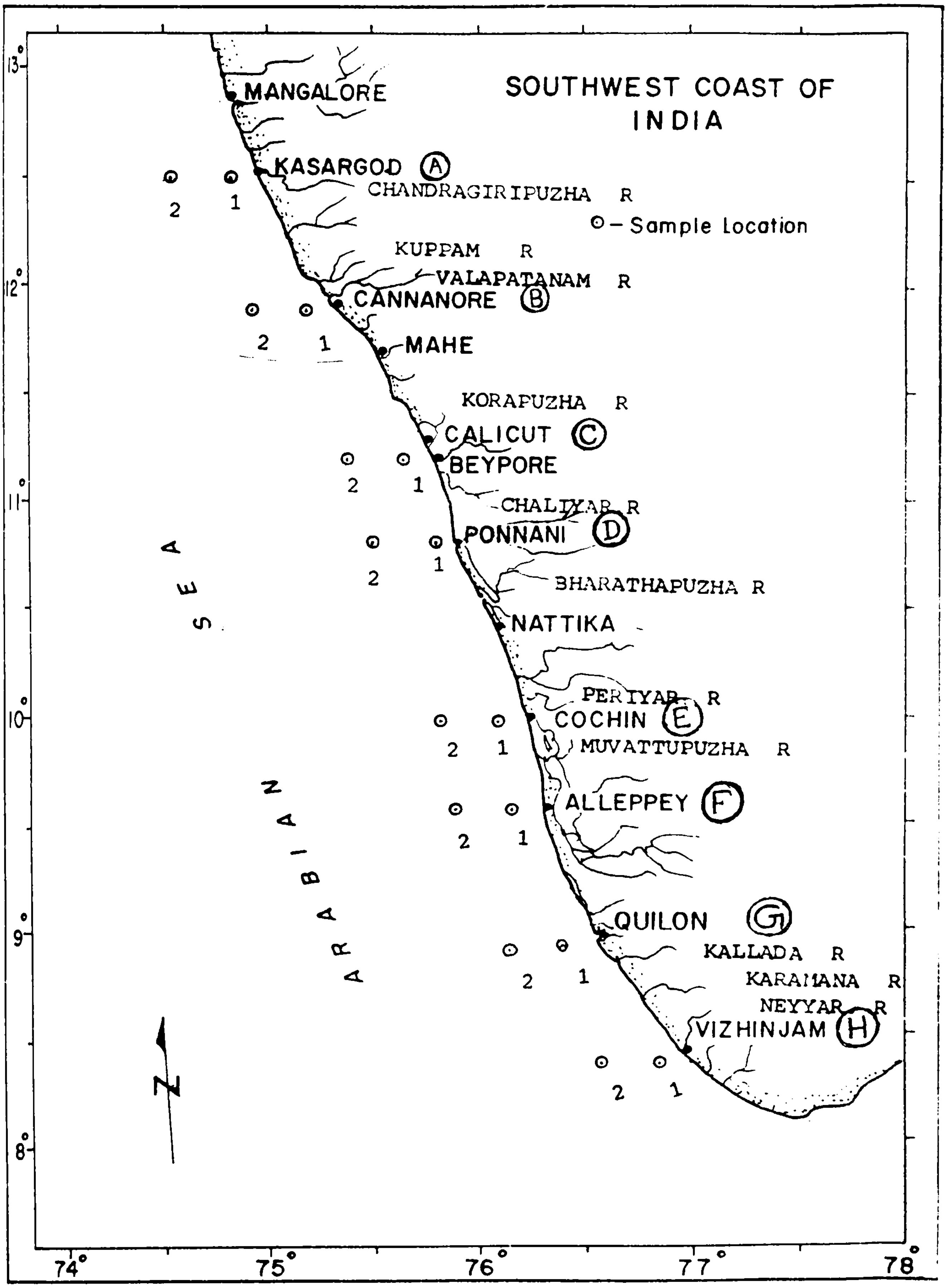

FIG.1. Draining sites of some important rivers of Kerala.

distribution pattern of salinity, dissolved oxygen and pH of the coastal waters are shown in Figs. 3.1.1, 3.1.2 and 3.1.3.

3.1.1 Salinity.

During the monsoon season the surface salinity is low (<32%) at all stations due to the influence of river run off and precipitation, as compared to other seasons. The salinity distribution in the area of study is uniform during the pre-monsoon and post-monsoon seasons. The minimum surface salinity was recorded off Calicut at station 1 and (33.03x10-3) a maximum of 35.75 at Vizhinjam Station No.2 during the pre-monsoon season and a minimum of $28.36\text{x}10^{-3}$ at Kasargode station No.1 and maximum of 34.4 at Station No.2 off Kannur during the post-monsoon season. The present data shows a well defined horizontal stratification for all the coastal stations during the monsoon and non-monsoon seasons. The spatial variation was found to be more in the post-monsoon than in the pre-monsoon season and it is attributed to the influence of the influx of fresh water. The values are comparable with those recorded by previous investigators for the study area (Sen Gupta *et al.*, 1979)

3.1.2. Dissolved Oxygen

Dissolved oxygen plays a vital role in the marine environment. Oxygen is dissolved directly from the atmosphere at the air-sea interface or is made available chemically by photosynthetic activity of marine plants. The amount of oxygen present in solution is governed by a number of factors such as temperature, partial pressure of the gas in the atmosphere, bio-chemical degradation of organic matter, respiration, photosynthesis etc. High photosynthetic activity due to the abundant phytoplankton production enhances the oxygen content of water, especially the surface layers wherein photosynthetic activity is maximum (Tait, 1968).

Dissolved oxygen values of both surface and bottom exhibited significant spatial and seasonal variations. The variation between the surface and bottom values are insignificant during the pre-monsoon season while marked difference was observed during the post monsoon season. The dissolved oxygen values varied from 5.08 ml/l to 2.9 ml/l and from 4.45 ml/l to 1.35 ml/l respectively for surface and bottom waters during post-monsoon period. The low temperature of surface water during the post-monsoon season enhances the solubility of atmospheric oxygen in the surface waters (Riley and Chester; 1971), and the settling of the organic matter rich particulates brought to the coastal region by monsoon flushing causes depletion in dissolved oxygen content of the bottom along with the upwelled water which has low water temperature and dissolved oxygen during the post-monsoon season.

During pre-monsoon season the high surface water temperature reduces the solubility of the oxygen in surface waters thereby causing a decrease in dissolved oxygen content of the surface waters. The observed data showed that only at four sections along the coast viz. off Kasargode, Ponnani, Cochin and Vizhinjam exhibited the general trend of dissolved oxygen content of the surface waters being more than that at the bottom.

During the pre-monsoon season the dissolved oxygen values for surface and bottom waters ranged from 4.69 ml/l to 3.92 ml/l and 4.69 to 3.51 ml/l respectively, with most of the values falling between 4.69 and 4.25 ml/l. The dissolved oxygen content of the coastal waters were comparatively higher during the pre-monsoon season especially for bottom waters.

During the monsoon season the influence of upwelled water was seen in the dissolved oxygen values of the entire area of study (Bhargava *et al.*, 1973; Rao *et al.*, 1972; Jayaraman and Gogate, 1957; and Banse, 1959).

3.1.3 pH

Eventhough there observed no significant spatial or seasonal variation in pH values of the surface and bottom waters, usually higher values were recorded during the post-monsoon season. The pH of bottom waters were found to be less than that of surface waters during the post-monsoon period, as a consequence of intense upwelling during the monsoon months; (Rao *et al.*, 1970, Jayaraman and Seshappa,

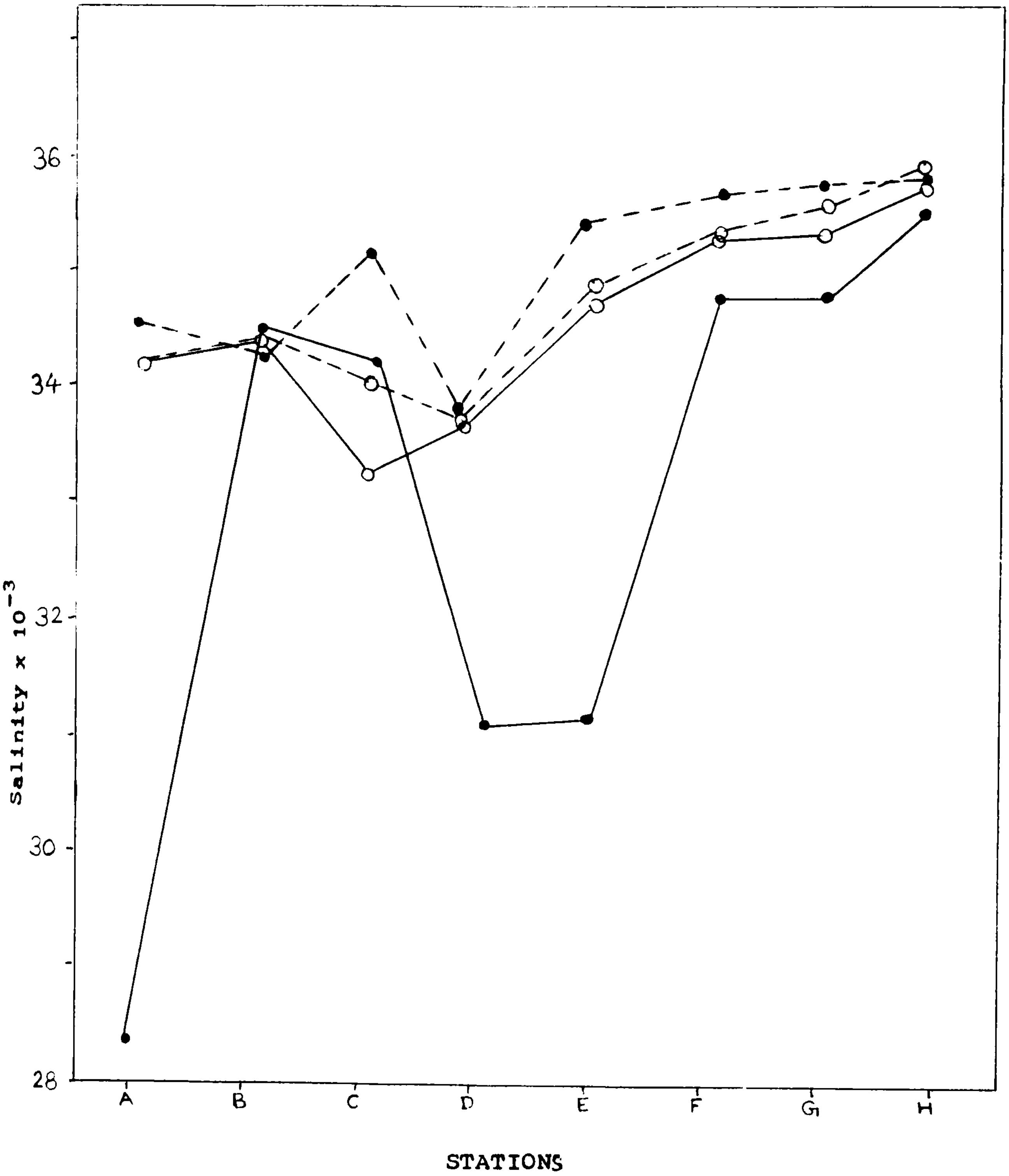

FIG.3.1.1. The seasonal and spatial distribution of salinity in the surface and bottom waters of the near shore regions of Kerala Coast. (O) Pre monsoon (●) Post monsoon,(——)surface values,(- - -)Bottom values

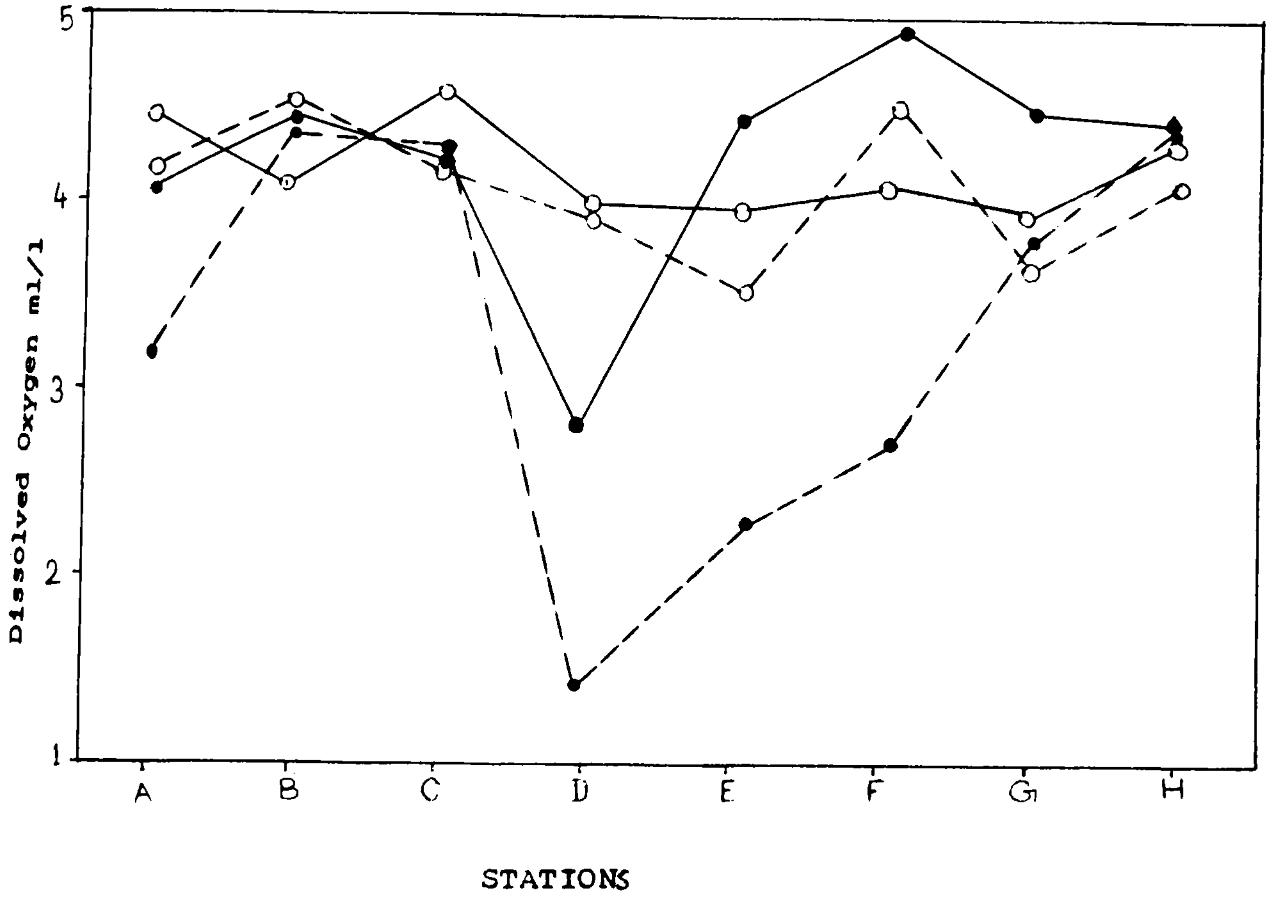

FIG.3.1.2. The seasonal and spatial distribution of dissolved oxygen in the surface and bottom waters of the near shore regions of Kerala Coast. (O) Pre monsoon, (●) Post monsoon, (——) surface values, (- - -) Bottom values

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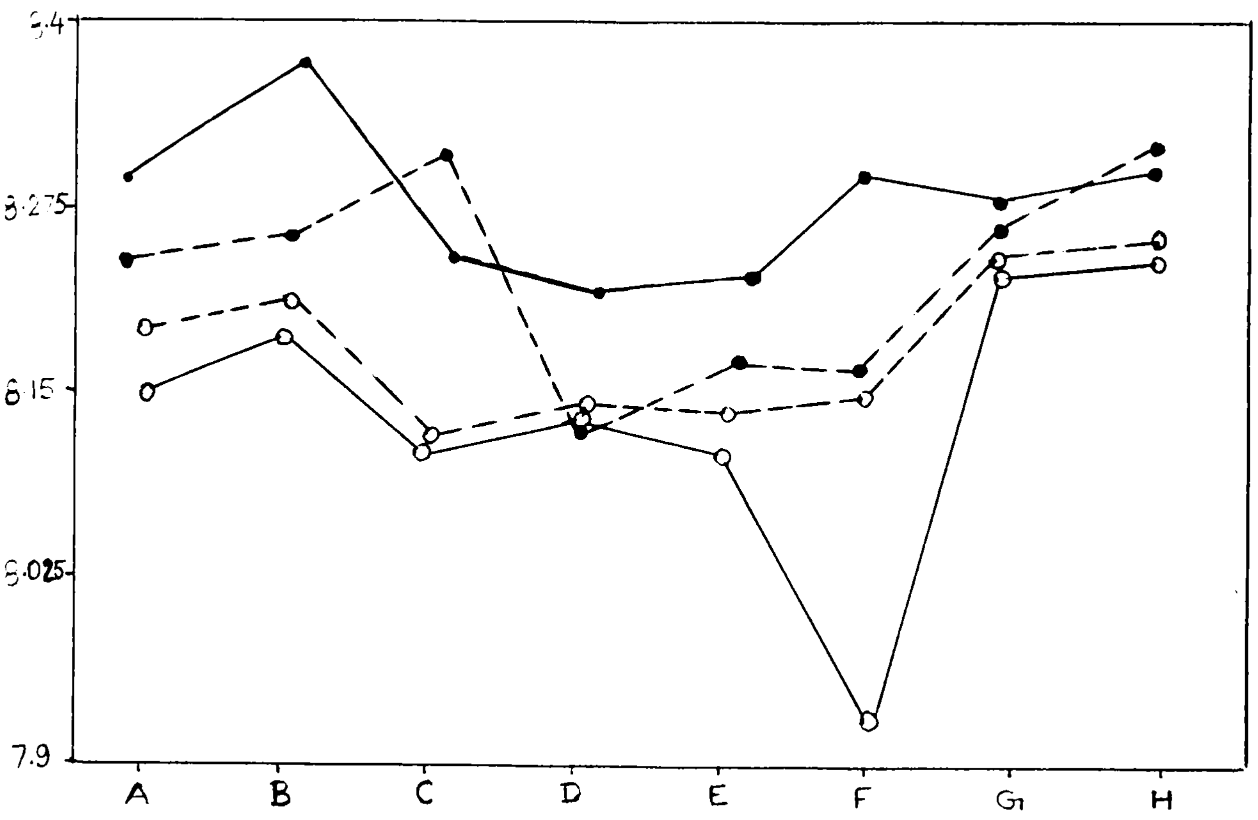


STATIONS

FIG.3.1.3. The seasonal and spatial distribution of P^H in the surface and bottom waters of the nearshore regions of Kerala Coast.
(O) Pre monsoon, (●) Post monsoon, (——) surface values
(---) Bottom values

1957) while a reverse trend was noted during the pre-monsoon season.

3.2 Hydrographical features of Cochin Estuary

3.2.1 salinity

The seasonal and spatial distribution of salinity in the Cochin estuary is depicted in fig 3.2.1. The premonsoon period exhibited relatively stabler environment in the estuary. The influence of the sea water was very much pronounced as the intrusion of saline water was traceable up to the head of the estuary. During monsoon season, the entire estuarine water is flushed out and replaced by fresh water. During the post monsoon period, the estuary behaves as partially mixed one. During the monsoon-post monsoon span, the salinity varied from 0.7×10^{-3} to 32×10^{-3} at the surface and from 8.2×10^{-3} to 35.05×10^{-3} at the bottom at the bar mouth. Salinity during the end of premonsoon varied from 29.8×10^{-3} (surface to 32.95×10^{-3} (bottom) at the bar mouth. The salinity distribution exhibited a well defined horizontal gradient throughout the entire period of investigation while the vertical stratification was pronounced only during the monsoon season.

3.2.2. Dissolved oxygen

Dissolved oxygen values of both the surface and bottom showed an increasing trend towards the upstream during the entire period of study. This could be attributed to the shallowness and the high photosynthentic activity in the upper reaches of the estuary. Joseph and Pillai(1975) also has recorded a high phytoplankton production in this region. The vertical gradient was also less in the riverine region. The distribution pattern of dissolved oxygen values (fig.3.2.2.) revealed significant spatial and seasonal variation as was observed by Sarala Devi *et al.* (1979) and Anirudhan (1988). Generally the surface values were found to be higher than at the bottom except for premonsoon season when the surface values of certain stations were even lower than the bottom ones. This might occur due to the decreased solubility of atmospheric oxygen in the surface waters at higher temperatures. Though the dissolved values were higher during the monsoon season, very low values were noted in the bottom waters of the barmouth (1.58 ml/l). The intrusion of upwelled water in the south west coast might be the reason for this depletion. (Sankaranarayanan and Jayaraman; 1972; Rao *et al.*, 1970). The depletion in values during the post monsoon season could be attributed to the degradative oxidation of organic matter.

3.2.3 pH

The pH distribution did not exhibit any significant seasonal or spatial variation. In general the pH values showed a decreasing trend towards upstream. Not much variation was observed between surface and bottom values except in certain months during post monsoon season which might be due to the degradation of organic matter at the

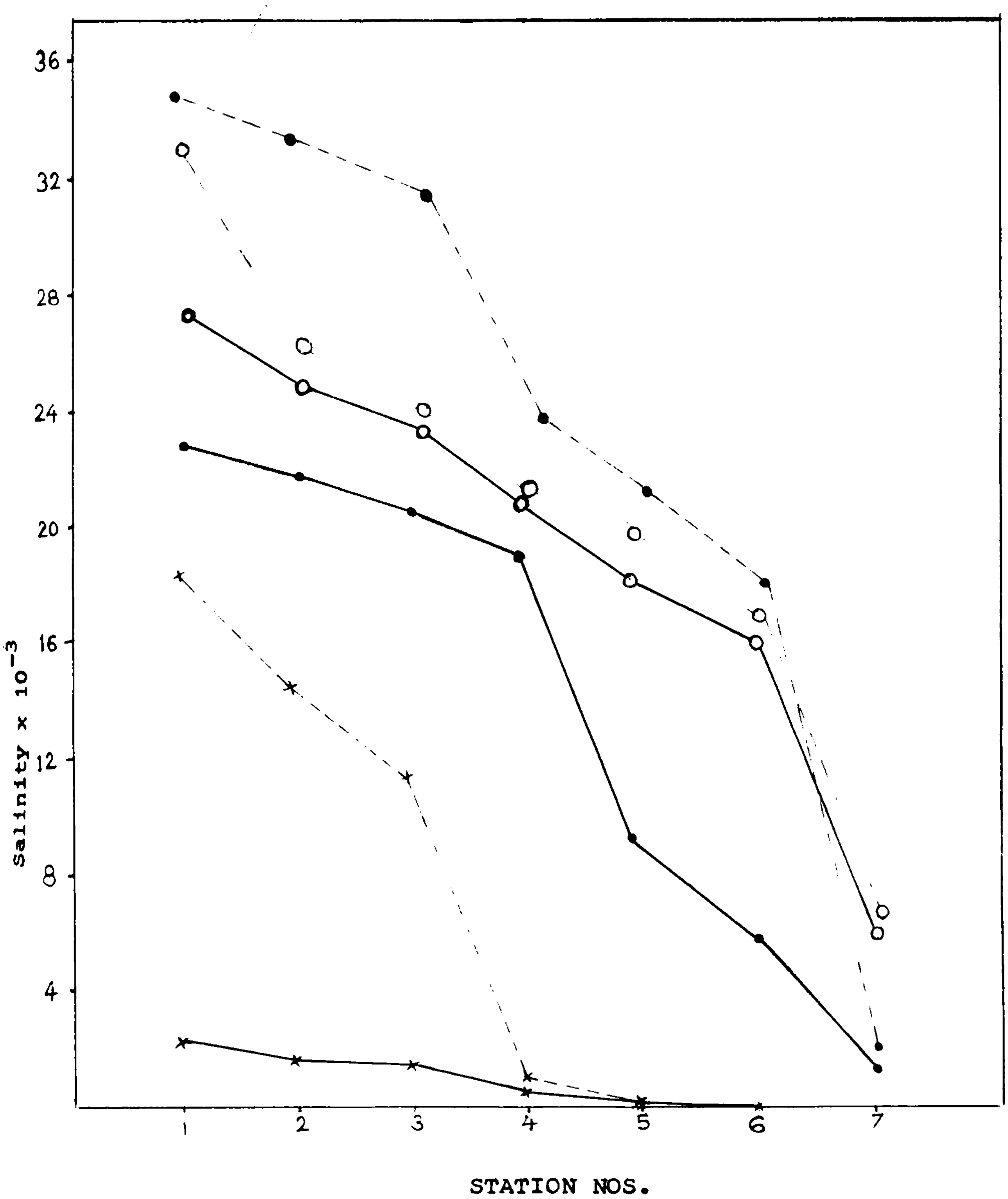


FIG.3.2.1. The seasonal and spatial distribution of salinity in the surface and bottom waters of Cochin estuary.(O) Pre monsoon, (●) Post monsoon, (X) monsoon, (——)surface values,(- - -)bottom values.

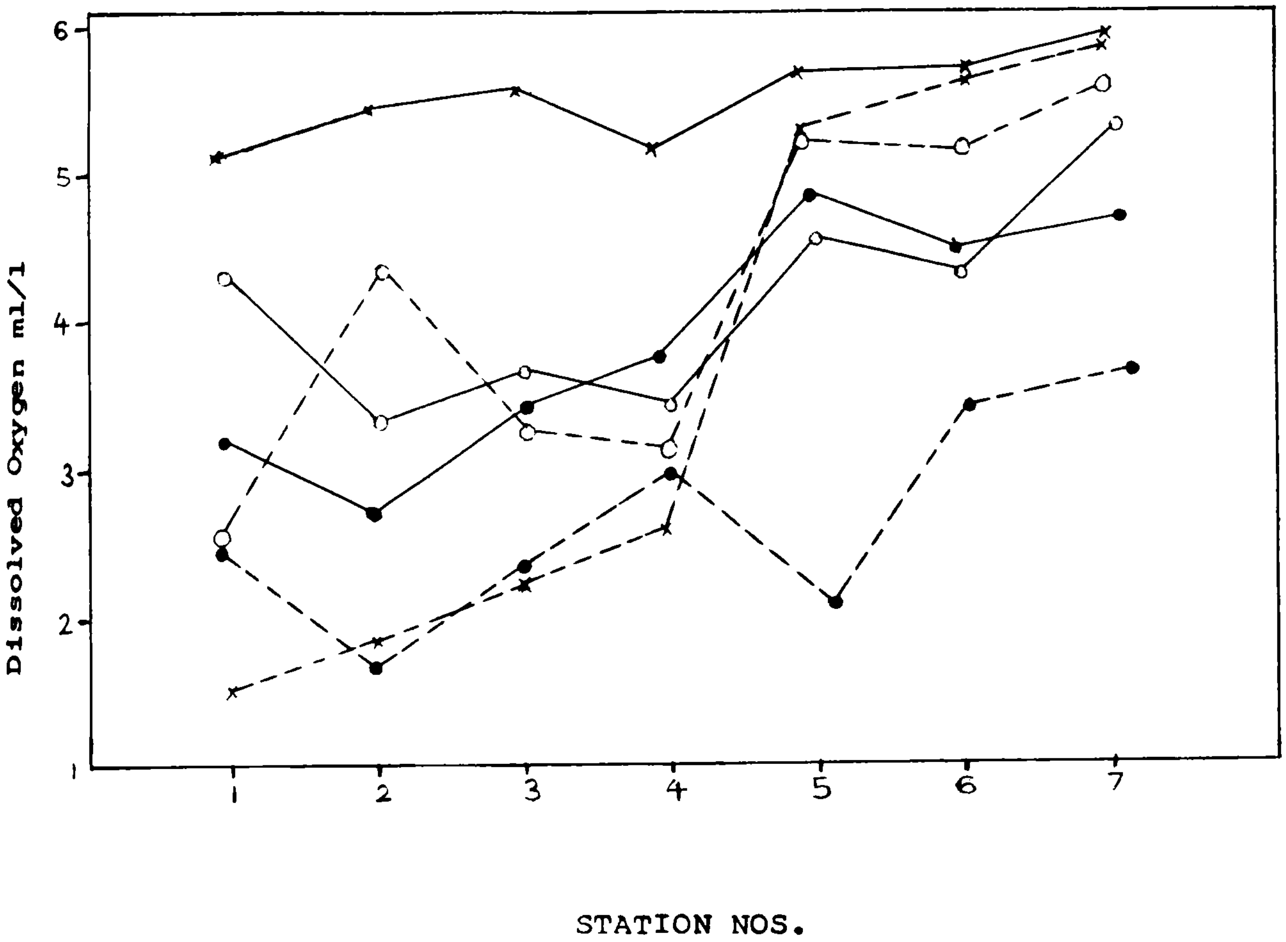


FIG.3.2.2. The seasonal and spatial distribution of dissolved oxygen in the surface and bottom waters of Cochin estuary. (O) Pre monsoon, (●) Post monsoon, (X) monsoon, (—) surface values, (- -) bottom values.

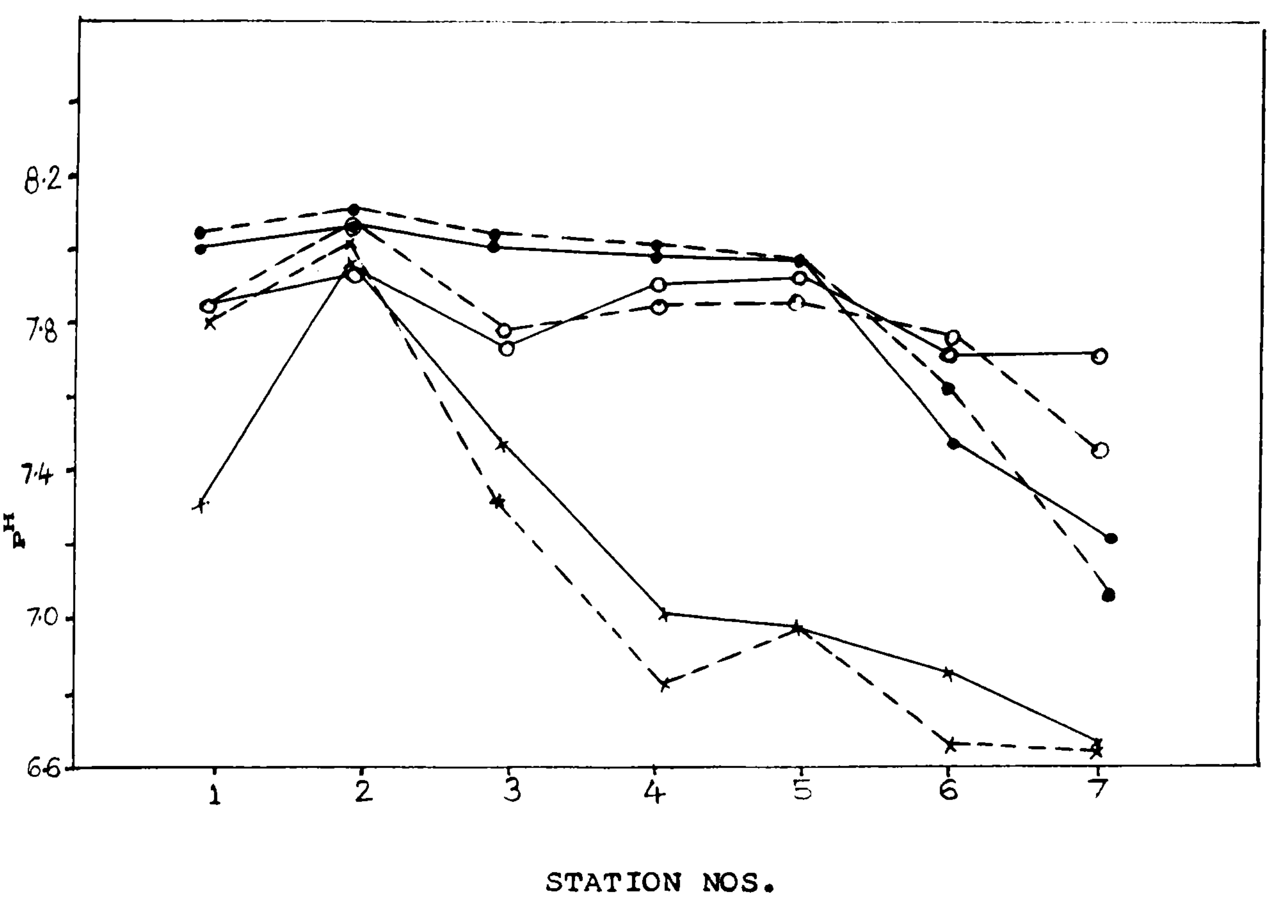


FIG.3.2.3. The seasonal and spatial distribution of P^H in the surface and bottom waters of Cochin estuary. (O) Pre monsoon, (●) Post monsoon, (X) monsoon, (——) surface values, (- - -) bottom values.

sediment/water interface causing a decrease in pH values. Comparatively the pH values were low during the monsoon season. The seasonal spatial distribution of pH is depicted in Fig. 3.2.3.

3.3 General Hydrography of Chaliyar estuary.

3.3.1 Salinity

Fig. 3.3.1 depicts the seasonal and spatial distribution pattern of salinity in the Chaliyar estuary. The salinity distribution pattern observed in the present studies is similar to that for a typical positive tropical estuary with the surface salinity values ranging from nearly zero during monsoon season to almost marine condition with high and uniform salinity ($>34\text{x}10^{-3}$) during the pre monsoon season as have been reported by several previous workers (Haridas *et al.*, 1973, Cherian *et al.*, 1975, Balakrishnan and Shynamma, 1976, Saraladevi, 1986, and Nair, *et al.*, 1983). Eventhough Premchand *et al.* (1987) reported the absence of saline water in Chaliyar river estuary during June and July ,the present observations indicate the presence of saline water at the bottom even up to 5 km from the river mouth during June-July at the time of high tide. During heavy monsoon months salinity was limited to 5 km from the river mouth as noticed by Nambudirippad and James (1987) and Natraj *et al.*(1987). Intrusion of sea water was found even up to 28 km from the river mouth during the premonsoon period (James and

Sreedharan, 1983). During the post monsoon the high saline water extends upto 10 km. upstream.

The absence of vertical salinity gradient during premonsoon season showed the prevalence of well mixed condition probably enhanced by strong tidal currents as stated by Bowden (1967). In the post monsoon season significant variations in salinity from surface to bottom was observed through out the estuary with comparatively smaller vertical gradients in the lower reaches ($2 - 6 \times 10^{-3}$) and the upstream station showed vertical gradients up to 15×10^{-3} Thus the estuary varies from a salt wedge type during monsoon to an intermediate partially mixed type during post monsoon and to a well mixed type during premonsoon season.

3.3.2. Dissolved Oxygen

The seasonal and spatial distribution of dissolved oxygen in the surface and spatial distribution of dissolved oxygen in the surface and bottom waters of Chaliyar estuary is depicted in Fig. 3.3.2. Dissolved oxygen content of the surface waters were found to be slightly higher than that of bottom water. Comparatively higher values of dissolved oxygen content was observed during the monsoon season than in post monsoon and pre monsoon periods. The depletion was more pronounced in the post monsoon season, which could be attributed to the oxidative degradation of organic matter. Lower oxygen values observed in the bottom waters (DO <3ml/l) during certain months of monsoon period were due to the incursion of high saline low oxygenated upwelled water from the coastal region during these months (Ramamirthm and Rao, 1973; Sharma, 1978; Jayaraman and Gogate, 1957; Banse, 1959). Premchand *et al.* (1987) have also reported low oxygen values (2.52 ml/l) during the month of August.

3.3.3. pH

In general, monsoon months recorded low pH values and pre monsoon high values especially in the lower reaches of the river. The pH values decreased towards the upstream and the values varied between 7.5 to 8.4. Eventhough the variation between the surface and bottom values were not so significant, surface values were found to be lower than the bottom values during monsoon period which is attributed to the heavy fresh water discharge. The gradual decrease in pH values towards the upstream and the increased pH values observed during the non-monsoon months showed the influence of incursion of sea water on pH. The relatively higher pH values recorded during the pre and post monsoon months may also be due to the increased photosynthetic activity during these periods (Gnaiger *et al.* 1978). Saraladevi *et al.* (1983) have reported for Beypore estuary an average pH value of 7.66 and 7.75 during pre-monsoon. 6.35 and 6.53 during monsoon and 6.68 and 7.63 during monsoon for the surface and bottom waters respectively. Fig. 3.3.3. depicts the distribution patterns.

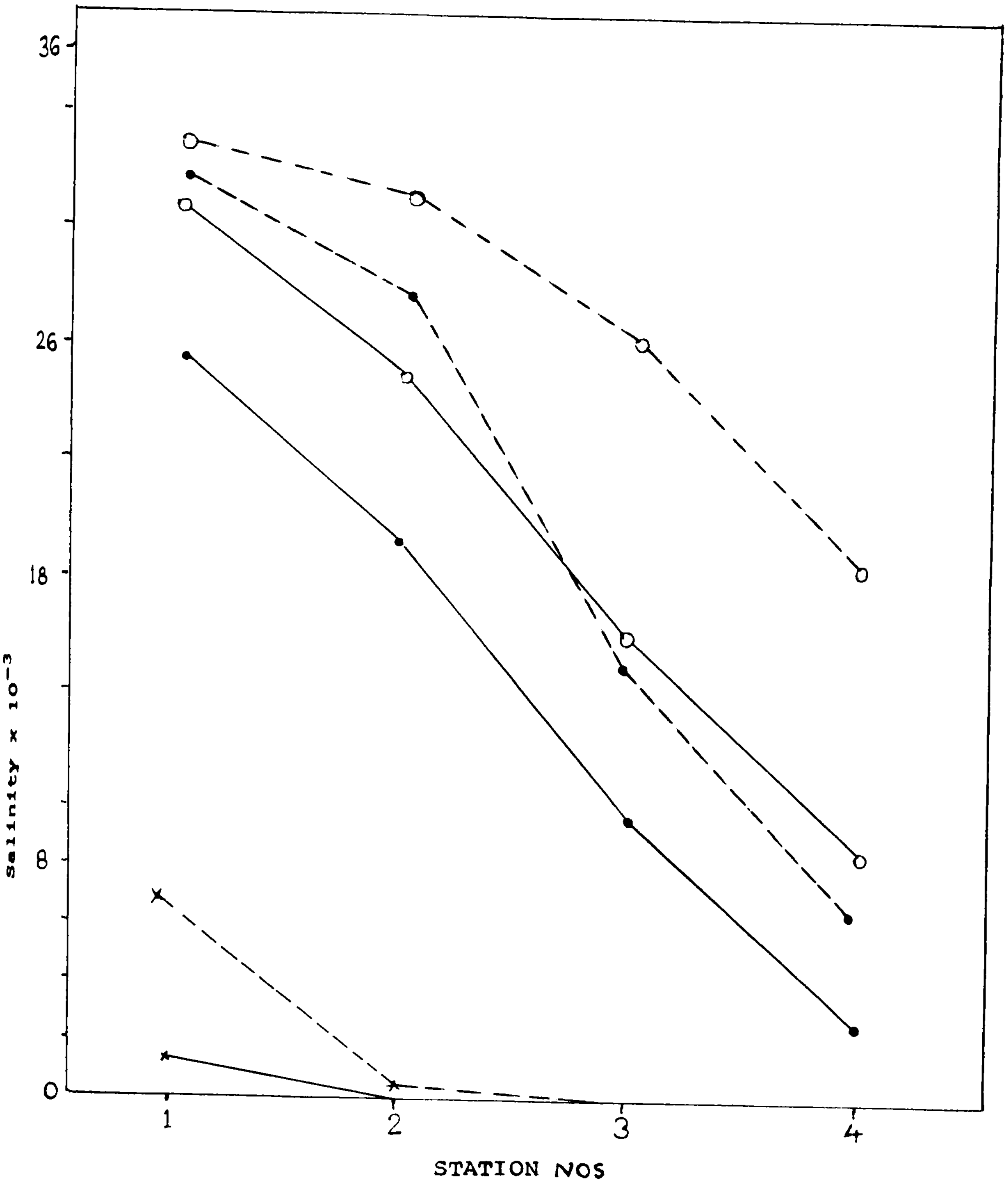


FIG. 3.3.1. **The seasonal and spatial distribution of salinity in the surface and bottom waters** of Chaliyar estuary (O) Pre monsoon, (●) Post monsoon, (x) monsoon, (—) surface values, (- - -) - bottom values.

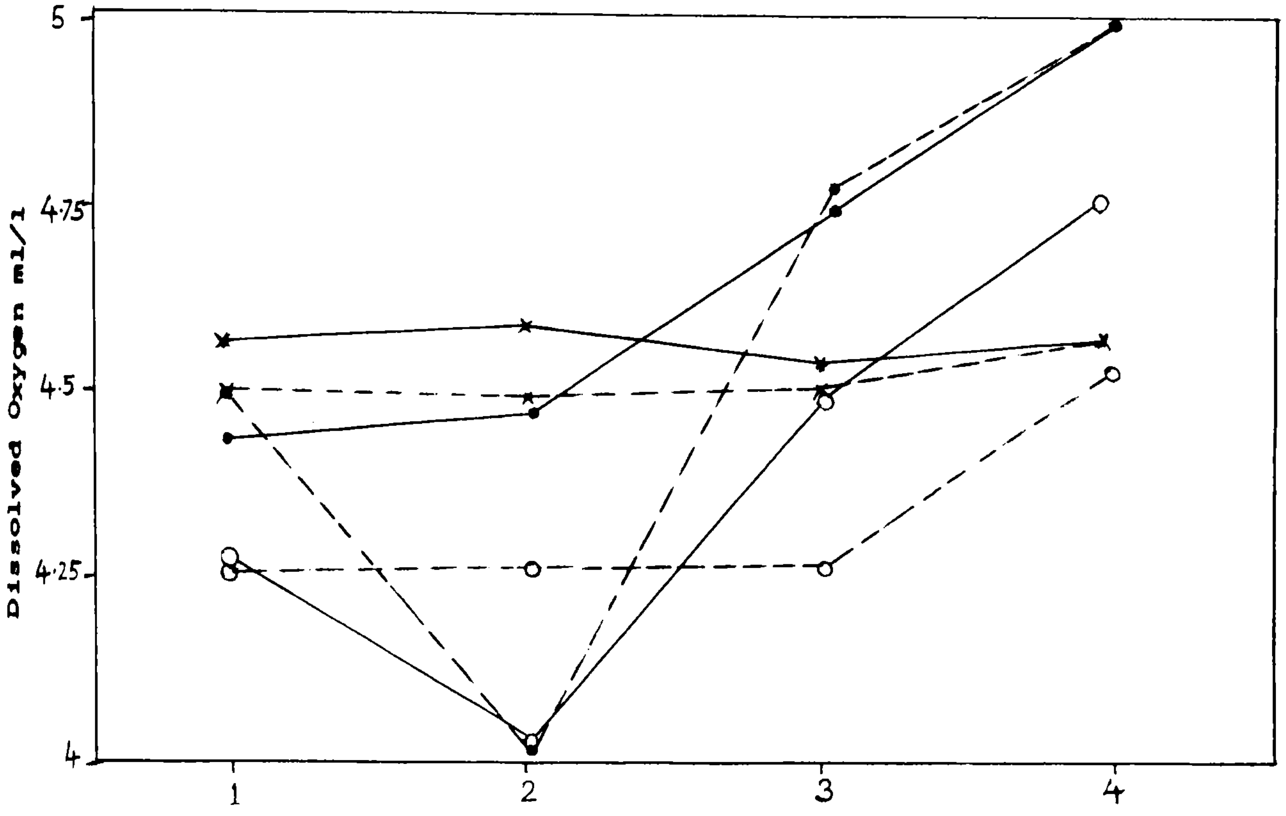


FIG.3.3.2. The seasonal and spatial distribution of dissolved oxygen in the surface and bottom waters of Chaliyar estuary(O) Pre monsoon, (●) Post monsoon, (X) monsoon, (—)surface values(---)bottom values.

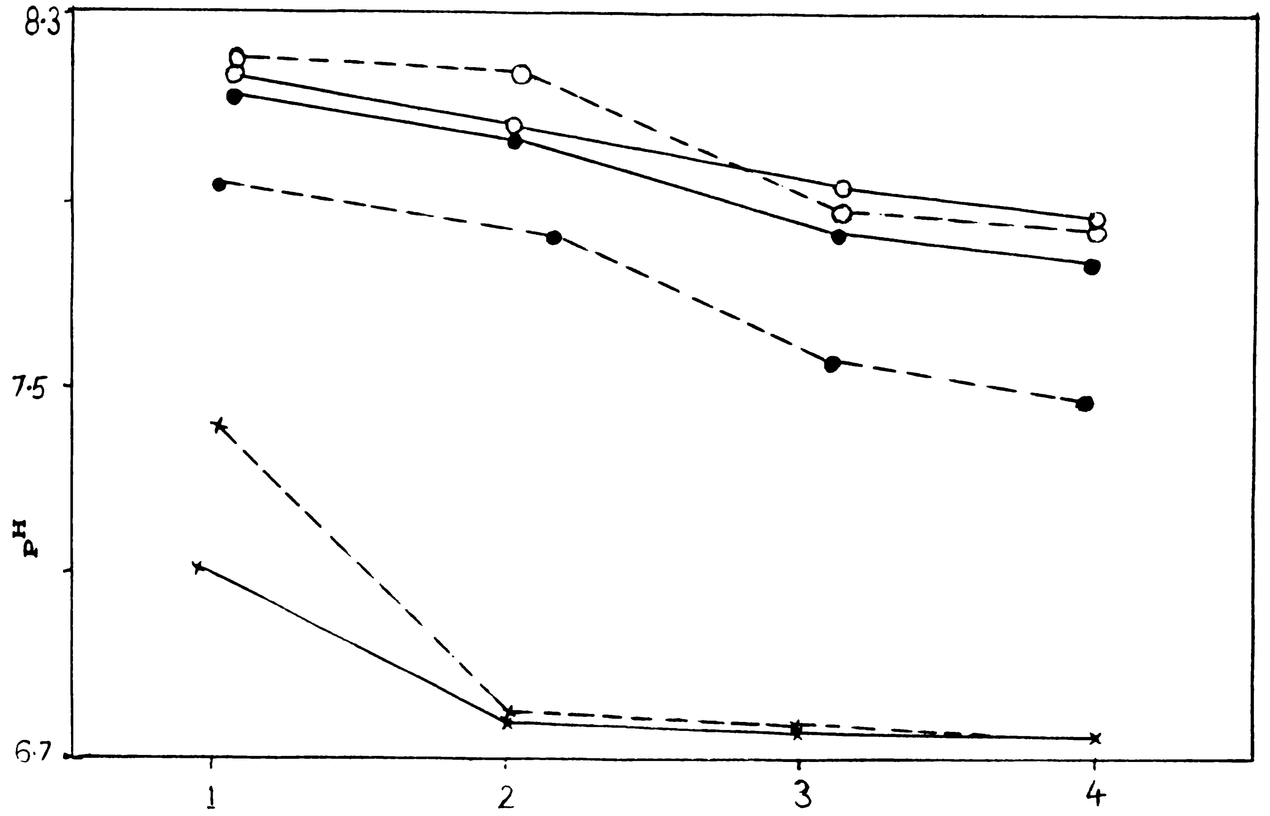


FIG.3.3.3. The seasonal and spatial distribution of P^H in the surface and bottom waters of Chaliyar estuary (O) Pre monsoon, (●) Post monsoon, (X) monsoon, (—) surface values (- - -) bottom values.

3.4 Mineralogy of the Sediments.

The sediment composition and texture are related to geology, bathymetry and physical factors of the aquatic environment. The major rock types of the study area belong to crystalline rocks of Archaen age, sediments of Tertiary age, and laterite cappings on crystallines and sediments of sub-recent to Recent age (Mallik *et al.*, 1987). The crystallines include charnockite and Khondalite, granite gneisses and granites traversed by basic rocks. Charnockite is widespread in the hill ranges of the Western Ghats, where from the rivers of Kerala originate. The geology of Kerala is depicted in fig (3.4.1). Mallik *et al.*, (1987) have demonstrated that the minerals both in coastal sediments and river sediments of Kerala are derived mainly from the crystallines of the Western Ghat mountains.

The heavy-mineral suite of the coastal and river sediments of Kerala consists of opaques, horn-blende, hypersthene, tremolite/ actinolite, pyroxene, garnet, silimanite, Kyanite, staurolite, andalusite, epidote, zircon, monazite, rutile, sphene, apatite and tourmaline. The light minerals consists of quartz, feldspar and some mica. The opaque heavy minerals include ilmenite, a little magnetite, rutile, spinel and leucoxene (Mallik *et al.*, 1987).

Veerayya and Murthy (1974) have discussed the distribution of the bottom sediments of Vembanad lake. The minerals of the lake were grouped into allogenic, endogenic and authigenic by Mallik and Suchindan (1984). The clay mineralogy of innershelf sediments off Cochin was described by Reddy *et al.* (1992). The major minerals in the sediments of Muvattupuzha was reported to be opaques (39.72%), hornblende (28.92%) and hypersthene (24.1%) (Mallik *et al.*, 1987). They noted high garnet values (7.8%) in the sediments off Calicut. 14.4% of epidote and 5.2% of staurolite was reported in the sediments of Bharathapuzha, which debounches in Arabian Sea at Ponnani. High amounts of Hornblende was reported in the coastal sediments of the northern Kerala (Mallik *et al.*, 1987.)

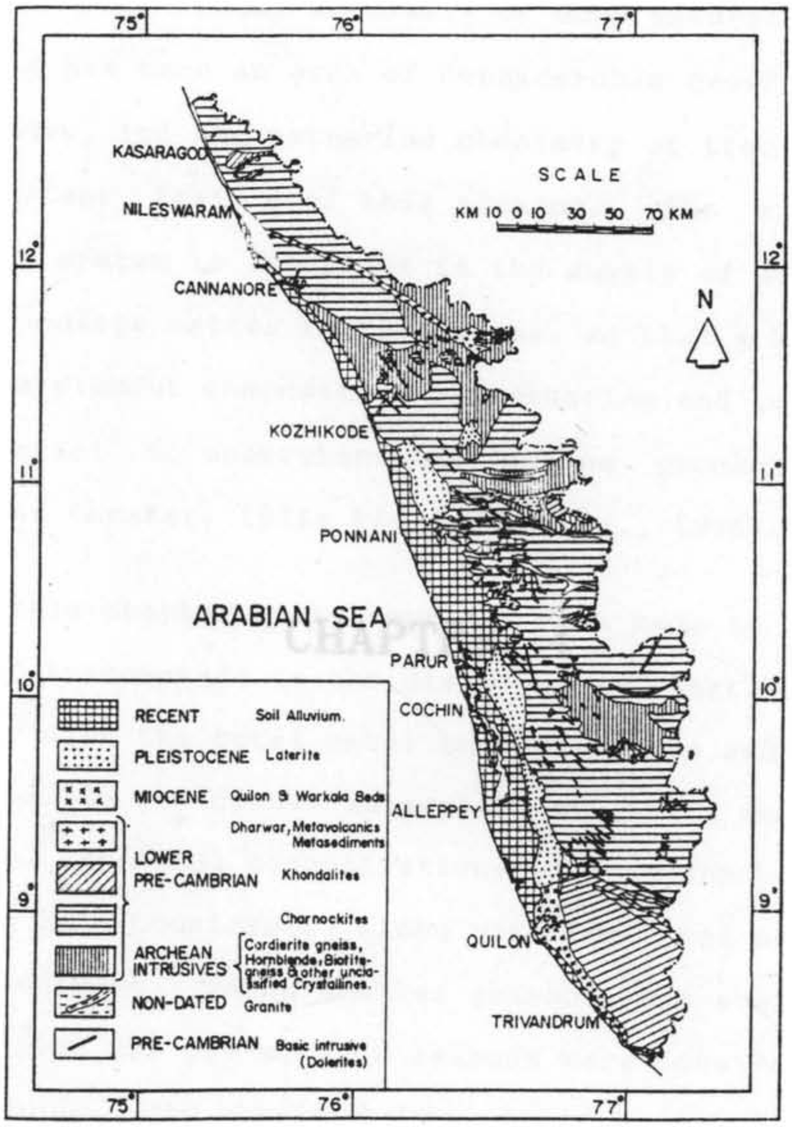


Fig. 3.4.1 GEOLOGY OF KERALA

CHAPTER - 4

Distribution of tracemetals in the water and sediments and sedimentological aspects of the study area.

The trace metal chemistry of both natural waters and sediments has been an area of considerable growth in the past two decades, and the estuarine chemistry of trace elements is an important feature of this advance. The river estuary transport system is important in the supply of both dissolved and particulate matter to the oceans, so that a knowledge of the trace element composition of estuarine and coastal waters is essential to understand the marine geochemical budget (Riley and Chester, 1971; Florence *et al.*, 1976).

In this chapter an attempt has been made to compare the levels of tracemetals in the dissolved and particulate forms in water with the total metal content of the sediments. As there exists a close interplay at the sediment/water interface, the metal concentrations of only the bottom waters are taken into cognizence, along with the total metal content of the sediment. Being stabler seasons, the average values of only post and pre-monsoon seasons were considered in the present study. The observed data showed a large variability in the distribution of metals among the dissolved phase, suspended particulate and in sediments. The results of each metal is discussed separately. The data collected on the sediment characteristics like the grain size distribution and organic carbon are also discussed in this chapter.

4.1 Iron

Very low concentration of Fe was observed in the dissolved fraction in bottom waters of the coastal region, ranging from 0.1 to 306 µg/l. However, comparatively higher values of dissolved Fe was observed off Kasargode, Canannore, Calicut and Quilon coasts. This might be due to the dissolution of desorbed Fe from the surface sediments. Fe concentration in suspended particulates of coastl waters varied from 2.85 to 25.2 mg/g in bottom waters, while the total Fe content of sediments varied from 5.6 to 49.76 mg/g. Highest value for Fe in suspended particles (25.2 mg/g) was observed off Quilon coast where the total Fe content of the sediment is only 5.6 mg/g. For all the other coastal stations the order of Fe content decreased as sediment > suspended particles > water.

It is obvious from the above sequence that the sediments are the major repository for Fe in coastal environment. The results are comparable with those observed by previous investigators (Murthy *et al.*, 1973, Subrahmanyam and Kumari, 1990, Mohanachandran and Subramanian, 1990). In Cochin estuary, the dissolved fraction of iron in bottom waters ranged from < 0.1 to 64 µg/l whereas the average value for particulate iron varied between 11.5 and 35.7 mg/g. Higher values for dissolved Fe observed at station No.2 and station No.4 can be attributed to the desorption occuring at the sediment/water interface under reducing conditions. The

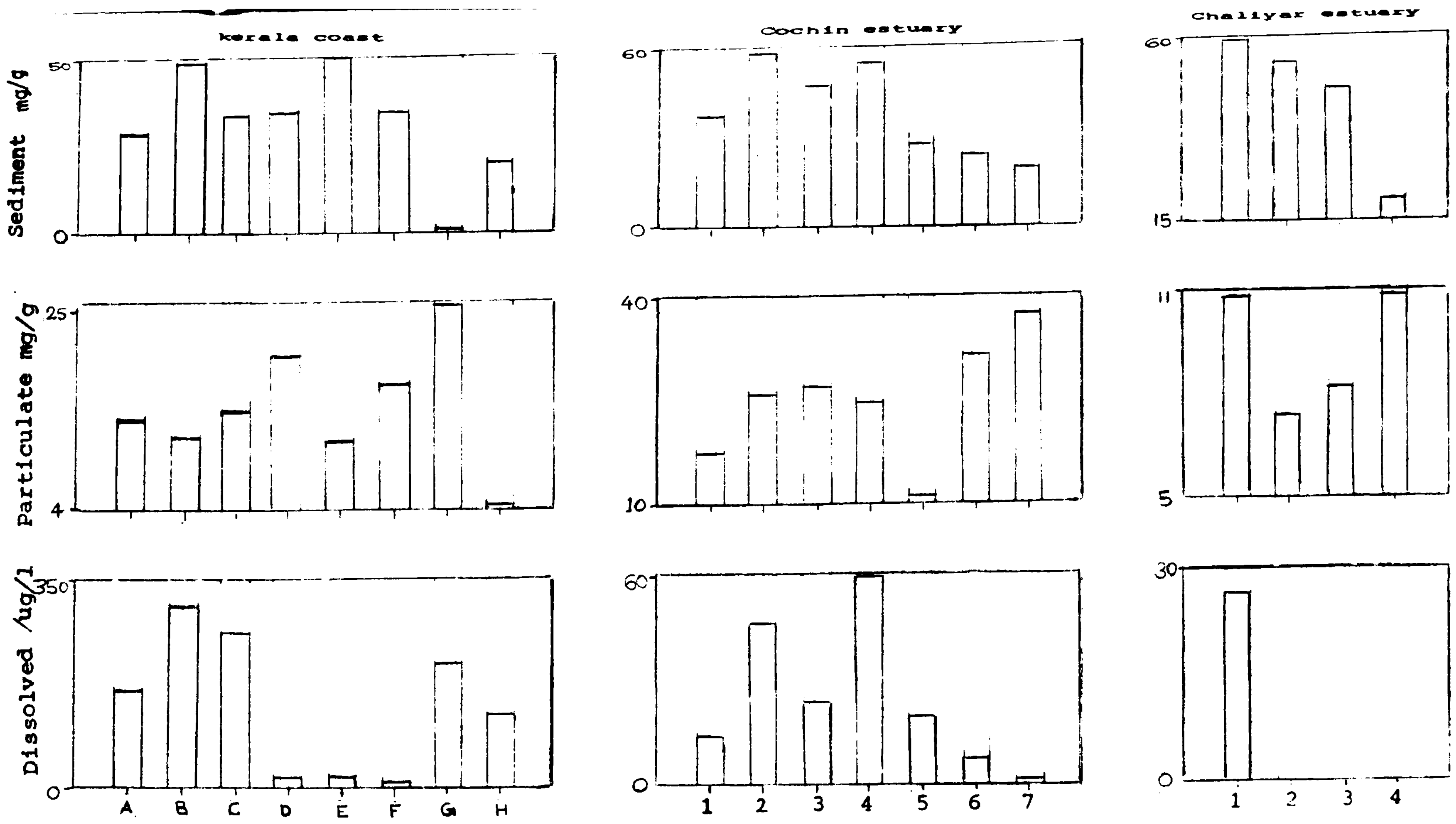


FIG. 4.1. Spatial distribution pattern of Fe in the bottom waters (dissolved and particulate) and in sediments of the coastal and estuarine regions.

total Fe content in the sediments varied from 15.2 to 58.91mg/g with a decreasing trend towards upstream whereas the particulate Fe showed an increasing trend towards upstream ie: in the upper reaches or in the brackish water region more Fe was found to be accumulated in the suspended particles while in estuarine region sediment acts as the major sink for Fe. The values are comparable with those reported by Nair *et al.*(1990).

In Chaliyar estuary the dissolved Fe was observed only in the barmouth region (26.6 µg/l). The dissolved oxygen saturation and the shallow nature of the upper regions of the estuary helps the oxidation of dissolved Fe to colloidal hydrous oxides of iron (Stumm and Lee, 1960). This might be the reason for the depletion of dissolved Fe in the bottom waters of the estuary. 7.0 to 10.9 mg/g of Fe was found to be associated with the suspended particles of Chaliyar estuary. The iron content of the sediments varied from 18.0 to 60.0 mg/g. In the Chaliyar estuary also sediments are the major sinks for the heavy metal iron.

The distribution pattern of Fe in waters and sediments of estuarine and coastal regions are depicted in Fig.4.1.

4.2 Manganese

The distribution of Mn in sediments and suspended particles in the bottom waters are depicted in Fig. 4.2. Dissolved Mn fraction could not be discussed here as the concentrations were below detectable limit. It is obvious

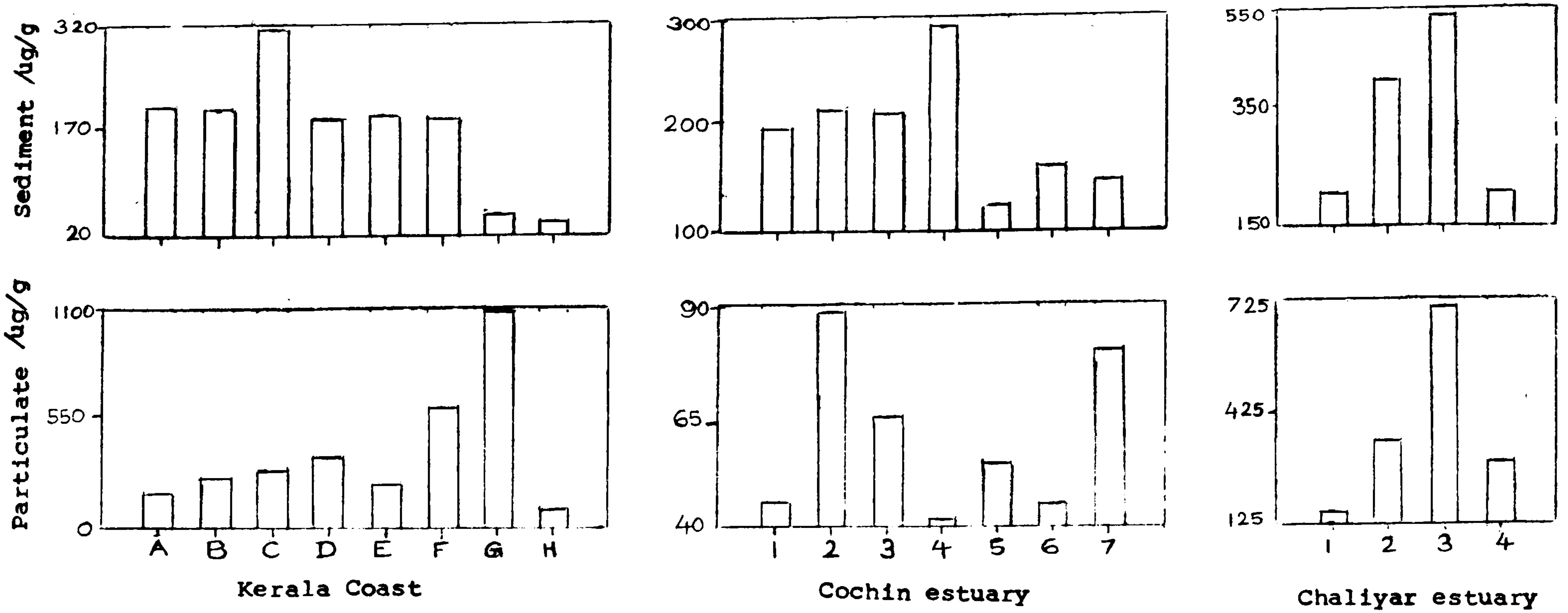


FIG. 4.2. The distribution pattern of Mn in the sediment and in the suspended matter of the bottom waters of the coastal and estuarine regions.

from the distribution pattern that the a major quantity of Mn in the coastal region and chaliyar estuary is associated with the suspended particles, while in the Cochin etuary the sediment is the major sink for Mn. Particulate Mn values varied from 74.19 to 1103.8 µg/g in the coastal waters, 35.78 to 89.47 µg/g in Cochin estuary and from 133.96 to 724.11 µg/g in the bottom waters of Chaliyar estuary. Total Mn in the sediments of Cochin estuary ranged from 123.65 to 280.53 µg/g ie: a three fold enrichment was observed in sediments.

4.3 Copper

Fig. 4.3 depicts the spatial distribution of dissolved and particulate Cu in the bottom waters along with the total Cu content of the sediments. Dissolved copper was found to be very low < 1 µg/l in the coastal waters, while the concentrations were from 0.1 to 6.0 µg/l in the bottom waters of Cochin estuary and 0.36 to 1.8 µg/l in Chaliyar estuary. There observed very little spatial variation in the distribution of dissolved Cu in estuarine and coastal waters during the pre and post-monsoon periods. Particulate Cu values varied from 23.61 to 168.13 µg/g in the coastal waters, 31.87 to 333.78 µg/g in Cochin estuary and from 10.35 to 19.65 µg/g in the bottom waters of Chaliyar estuary. Compared to total Cu values in the sediments, higher concentration of Cu was found to be associated with the suspended matter of the coastal region and in the Cochin estuary,while in Chaliyar estuary a two fold enrichment was

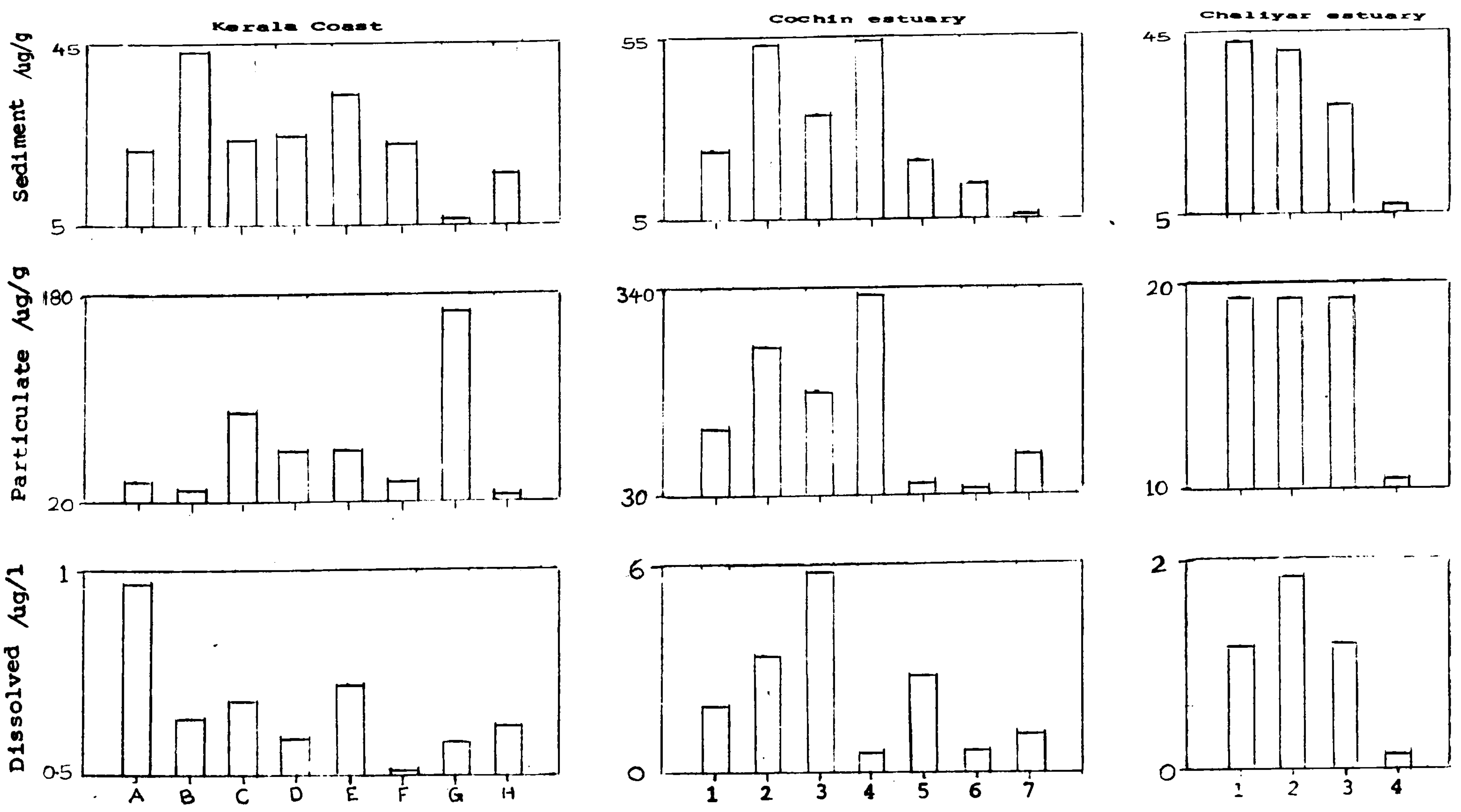


FIG. 4.3. Spatial distribution pattern of Cu in the bottom waters (dissolved and particulate) and in sediments of the coastal and estuarine regions.

observed in sediments. Danielsson (1980) has reported 0.08 to 0.35 µg/l of dissolved Cu for the waters of the Indian Ocean. Shibu *et al.* (1990) have reported 1.4 to 6.4 µg/l dissolved Cu and 20.0 to 30.0 µg/g particulate Cu in periyar and Muvattupuzha rivers and Cochin estuary. Present values are comparable with the above values.

4.4 Zinc

Dissolved Zn in the coastal waters of Kerala varied from 0.26 to 34.64 µg/l, whereas the concentration varied from 1.25 to 9.53 µg/l in the bottom waters of Chaliyar estuary. High concentration of dissolved zinc observed at off Ponnani (34.64 µg/l) and off Alleppey (17.71 µg/l) indicated the presence of some point discharges at these sites. Higher values of dissolved Zn was encountered in the bottom waters of cochin estuary, and the values were 89.01 µg/l at station No.2 and 78.03 µg/l at station No.4. The dissolved Zn decreased towards upstream in both the estuaries. In the Chaliyar estuary the particulate Zn values varied from 34.81 to 64.34 µg/g and the total Zn in sediments ranged from 25.37 to 75.06 µg/g. However in the coastal region a major portion of Zn was found to be associated with the suspended particles and the values of particulate Zn ranged from 11.18 to 954 µg/g. Both the sediment and the suspend matter of Cochin estuary had very high content of Zn (654 to 1748 µg/g in suspended matter and 29.29 to 290.5 µg/g in sediments). The values agreed with those obtained by previous investigators (Nair *et al.*, 1990; Shibu *et al.*, 1990; Mohanchandran and

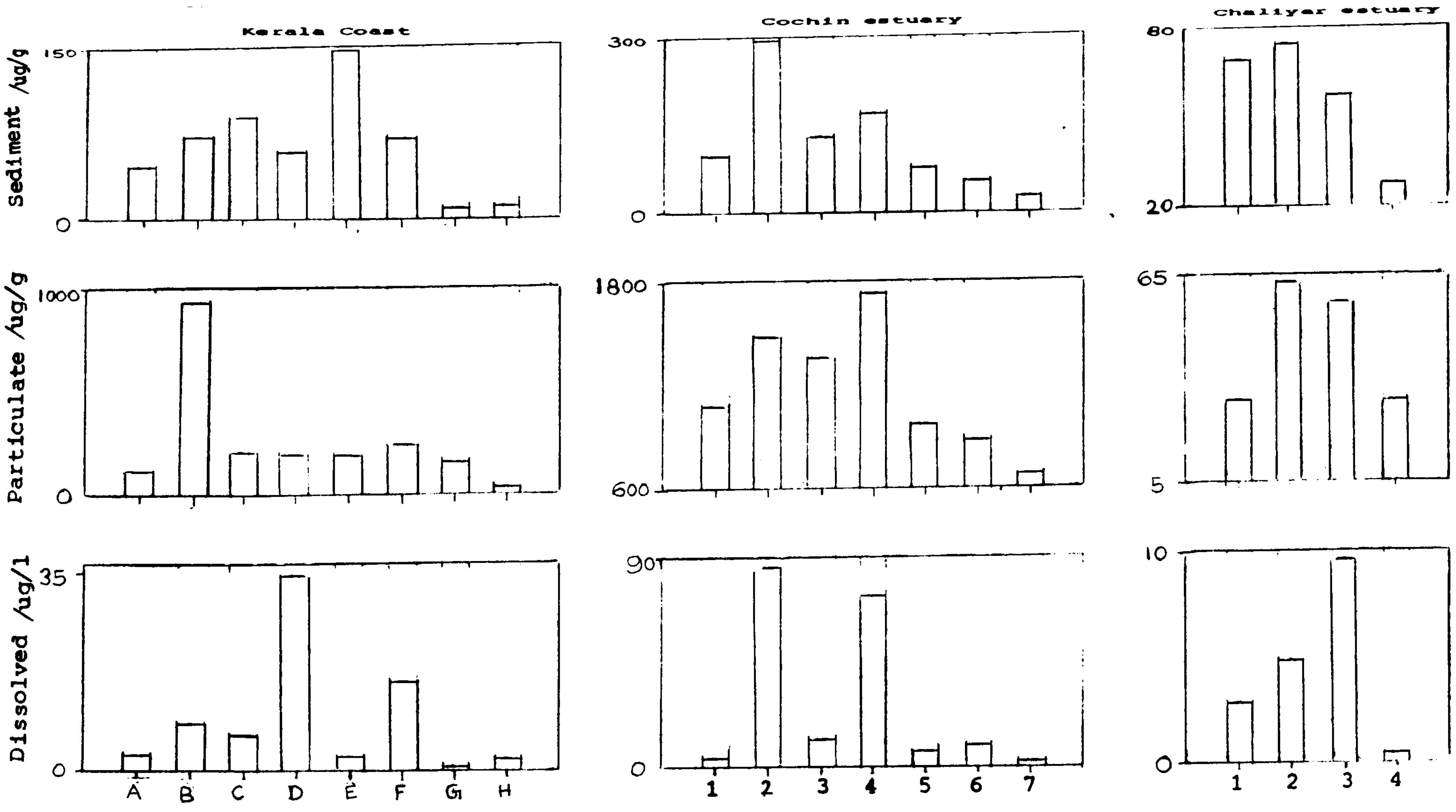


FIG. 4.4. Spatial distribution pattern of Zn in the bottom waters (dissolved and particulate) and in sediments of the coastal and estuarine regions.

Subramanian, 1990 ; Mallik and Suchindan, 1984). The distribution pattern of Zn in waters and sediments of coastal and estuarine regions are shown in fig. 4.4.

4.5 Lead

The spatial distribution of dissolved particulate and total lead in sediments are shown in fig.4.5. A very high enrichment of Pb was observed in the particulate fraction. Dissolved lead in the bottom waters of the estuaries and coastal region were found to be very low. Precipitation of lead chloride ($PbCl_2$) due to its very low solubility product of $1.7x10^{-5}$ might be the reason for the low lead concentrations observed in the bottom waters.

4.6 Cadmium

Very low Cd values were observed for the dissolved fraction of Cd in Cochin estuary. However comparatively higer values were encountered in the coastal waters and values ranged from 0.14 to 8.46 µg/l. In the Chaliyar estuary, the values varied from 0.27 to 2.16 µg/l. In the estuarine waters the values of particulate Cd was found to be higher compared to that of sediments. For most of the coastal stations the particulate Cd values were below detectable limit. Fig. 4.6 depicts the distribution of cadmium.

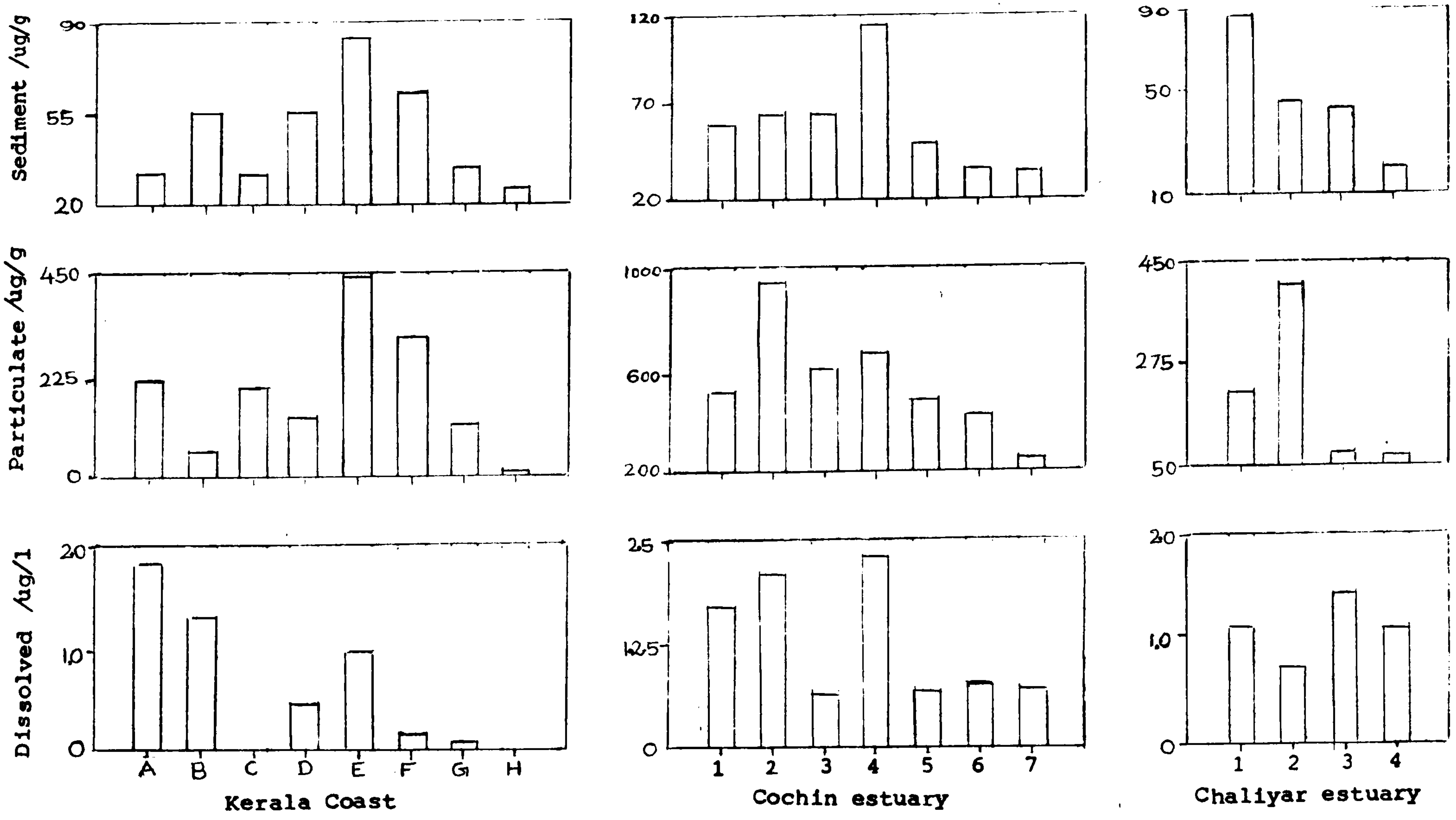


FIG. 4.5. Spatial distribution pattern of Pb in the bottom waters (dissolved and particulate) and in sediments of the coastal and estuarine regions.

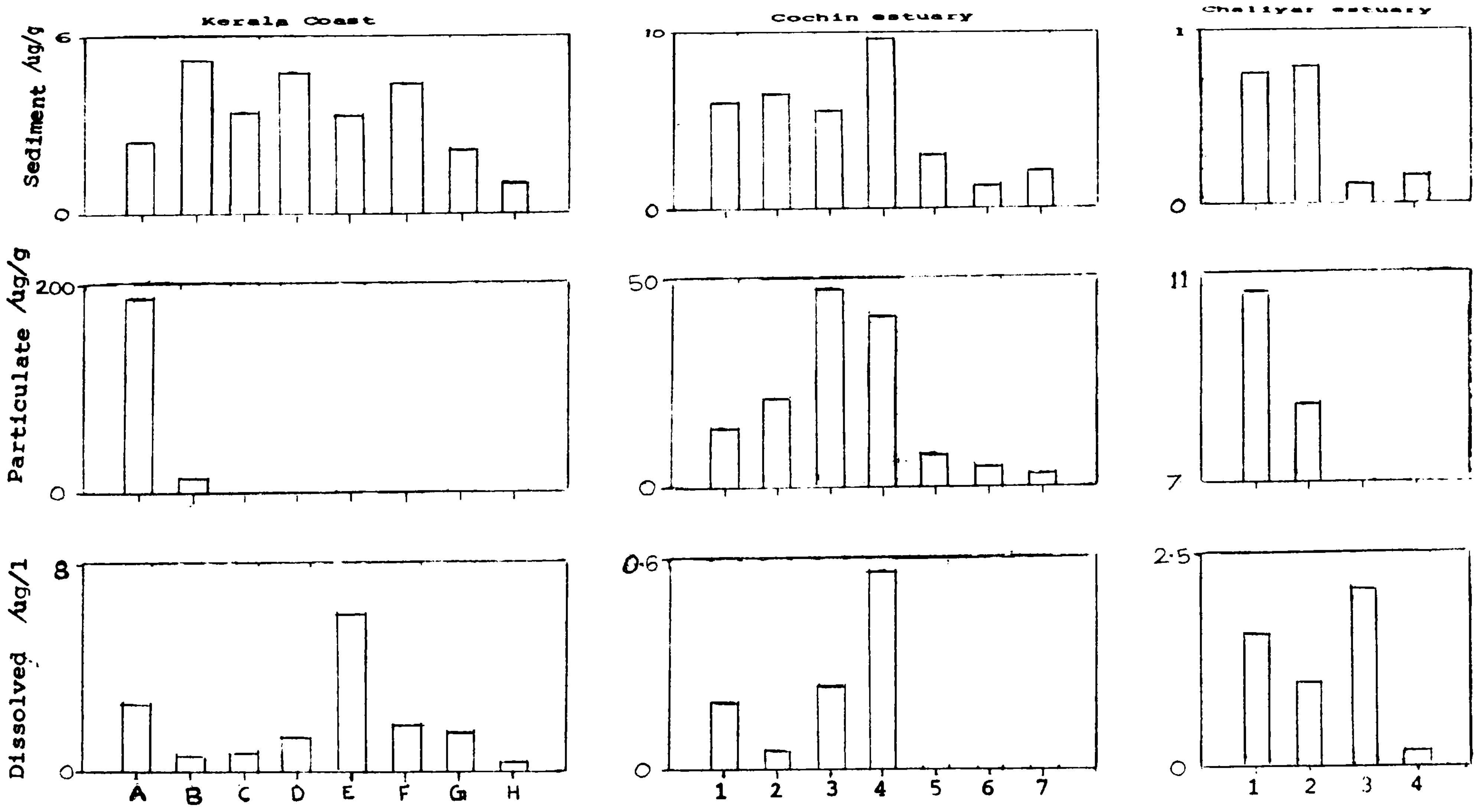


FIG. 4.6. Spatial distribution pattern of Cd in the bottom waters (dissolved and particulate) and in sediments of the coastal and estuarine regions.

4.7 Sedimentological Aspects

Organic matter content and the sediment texture are the two main factors controlling the distribution of trace metals among various phases in the aquatic system.

The average values for the organic carbon content and the grain size distribution of the sediment samples are given in Tab. 4.7. Highest organic carbon was obtained for the near-shore sediments of Alleppey coast and for the barmouth samples of both the estuaries.

Correlation studies revealed that there existed a strong correlation between the organic carbon content and the metals Fe, Cu and Zn in the sediments.

STATION		Org. C mg/g	% Clay	% Silt	% Sand
Kasargode	1	6.34	15.05	7.56	77.39
	2	26.26	53.25	44.74	2.009
Canannore	1	29.0	44.1	54.583	1.317
	2	30.57	42.05	56.01	1.934
Calicut	1	11.77	20.95	18.91	60.14
	2	32.61	47.1	49.53	3.37
Ponnani	1	16.76	26.6	41.22	32.18
	2	31.03	52.65	45.67	1.68
Cochin	1	25.14	44.35	38.95	16.70
	2	26.97	64.75	24.91	0.34
Alleppey	1	33.30	48.25	47.17	4.58
	2	32.38	34.20	56.75	9.05
Quilon	1	1.812	0.75	5.3	93.95
	2	15.86	32.45	57.52	10.03
Cochin estuary	1	21.19	54.13	39.2	6.67
	2	28.28	67.2	23.02	9.779
	3	27.95	87.23	9.32	3.45
	4	28.45	66.91	16.7	16.39
	5	19.91	53.5	29.34	17.16
	6	4.75	2.62	11.53	85.85
	7	2.49	0.2	0.79	99.01
Chaliyar estuary	1	22.08	37.1	20.1	42.8
	2	21.50	46.0	30.32	23.48
	3	13.36	4.56	40.76	54.68
	4	2.03	1.28	2.99	95.73

Table 4.7.1

CHAPTER - 5

RESULTS AND DISCUSSION ON GEOCHEMICAL PARTITIONING OF TRACE METALS.

The interpretation of the enrichment of chemical elements in sediments by anthropogenic influence must take into account geological, mineralogical, hydrological and biological processes controlled both by internal and external factors namely 'allochthonous' influences comprising of natural and civilizational effects and 'autochthonous' influences such as precipitation, sorption, enrichemnt in organisms and organo-metallic complexing during sedimentation as well as the post depositional effects of diagenesis. The general sequence of events leading to the ultimate dispersion of metals into sediments ie: the fate of metal ions derived from chemical weathering or by anthropogenic inputs is controlled by many factors involving atmospheric precipitation, water movement, soil movement, changes in redox and pH conditions, adsorption - desorption processes, chemical complexation, precipitation and hydrolysis, decay of vegetation and biochemical - bacterial interactions. Whether or not a specific flush load of freshly leached metal ions eventually reaches an estuarine system intact or widely dispersed, depends on the relative interplay of these factors. It is obvious from the above facts that in order to evaluate their fate in aquatic environment, a quantitative knowledge on the selective distribution of tracemetals among the specific components of the sediments is required.

However, direct methods are not presently available to quantify these metal distribution. One-step extraction techniques for the characterisation of metal binding in well defined media to specific well defined surfaces such as organic and mineral sediments (Chester and Hughes, 1967; James and Healy, 1972; Hohl and Stumn, 1976; Malo, 1977; Davis and Leckie, 1978) is found to be inadequate for the natural sediments comprising of complex assemblage of multiligand, multi component, aggregated surface systems. Sequential chemical extraction and statistical correlation methods have been proved to be the most useful techniques for quantifying the various metal associations in sediments (Gupta and Chen, 1975; Engler *et al.*, 1977; Tessier *et al.*, 1979; Pickering 1981; Luoma and Bryan, 1981 & 1982; Forstner *et al.*, 1982; Luoma and Davis, 1983; Chester *et al.*, 1985; Martin *et al.*, 1987; Tessier and Campbell, 1991).

The present study was aimed at demonstrating the significance of chemical partitioning in various accumulative phases of tracemetals in the surface sediments of Kerala coast and to trace out the pathway and fate of metal ions (introduced either by chemical weathering or by anthropogenic input) entering into the coastal environment through the two major estuaine systems of Kerala namely Cochin estuary and Chaliyar river estuary. The trace metals studied were iron, manganese, zinc, copper, lead and cadmium. The first two, iron and manganese, are the most abundant and mobile heavy metals in the aquatic environment while copper, zinc, lead and cadmium are metals with a high index of relative pollution potential which are enriched by man's activities by a factor of ten or more in the sediments (Lowe, 1970; Tyler and Buckney, 1973; Klein *et al.*, 1974; Asami, 1974; Kneip *et al.*, 1974; Prater, 1975).

The seasonal distribution of the metal fractions in the sediment of a tropical estuary was discussed in detail by Kunhikrishnan Nair, (1992). As the variations in the percentage-wise seasonal distribution was found to be less and also the post and pre-monsoon were comparatively stable, the average values of only pre-monsoon and post-monsoon seasons were taken into account for the present study. Stress was given only to the spatial variation as it is an essential requisite to trace out the pathway and fate of the metal contaminants entering the aquatic environment.

The details of location of stations, sampling and methodology are furnished in chapter 2. The various steps involved in the sequential extraction scheme adopted for the present study (Gupta and Chen, 1975; Tessier *et al.*, 1979; and Forstner *et al.*, 1981) are also detailed in Chapter 2. The extraction of first four fractions were carried out under nitrogen atmosphere with deaerated (N_2 sparged) extractants inorder to eliminate any possible changes (by oxidation) to the metal fractions whih can be brought about by the oxygen present in the air as well as in solution of the extractants.

The easily reducible fraction comprises mainly of Mn - oxide bound metals while Fe-oxide bound fraction extracted with ammonium oxalate in oxalic acid is described as the moderately reducible fraction. The reduction steps were completed before the hydrogen peroxide oxidation. The various fractions extracted have been designated with numbers 1 to 6, respectively representing Exchangeable, Carbonate bound, Easily reducible, Moderately reducible, Organic + Sulphidic and Residual fractions. To simplify the computations, the sum of the six fractions was taken as the total metal concentration in sediment, indicated by the subsript 'T' to the symbol of the respective metal. For instance, a metal having symbol 'M' has the various fraction described as M1, M2, M3, M4, M5, M6 and MT as the total metal.

The results of the present investigation on the partitioning of heavy metals in the sediments are presented and discussed in this section. The metals discussed are in the order of iron, manganese, copper, zinc, lead and cadmium. An attempt has been made to compare the various metal fractions studied in different aquatic environments ie: in coastal and estuarine environment on the basis of the partition patterns of the trace metals in the sediments from Kerala Coast, Cochin estuary and from Chaliyar river estuary.

Since the estuaries and shallow coastal regions are the areas of highest organic productivity and potential source for sea food, the trace metal concentrations observed in the various parts of the body of some very common species of fish in the estuarine and near shore regions of Cochin are also discussed in this Chapter. In the following section, a brief attempt has been made to evalute the significance of geochemical partitioning in the coastal ecosystem.

5.1. Iron

As was observed from the previous section, iron is the most abundant heavy metal in the aquatic environment. The high concentration as well as the ability of hydrous oxides of iron to act both as a sink and source for other trace metals such as copper, manganese, lead etc. in the aquatic environment has assigned a paramount position to iron during the partition studies of tracemetals (Gibbs, 1973; Forstner and Wittmann 1979, ; Bowers and Huang, 1987). Perhaps iron may be the most sensitive heavy metal in aquatic system towards pH changes, formig new solid phases capable of absorbing other trace metals from solution with rise in pH during estuarine mixing (Boyle *et al.*, 1977, Aston, 1978; Mayer, 1982). The redox sensitive Fe-and Mn-hydroxides and oxides under oxidising conditions, constitute significant sinks of heavy metals in aquatic systems. These hydroxides and oxides readily sorb or coprecipitate cations and anions; even a low percentage of Fe $(OH)_3$ and MnO_2 has a controlling influence on the heavy metal distribution in an aquatic system. Under reducing conditions particularly in the presence of higher concentrations of dissolved organic matter, the sorbed beavy metals are readily mobilized; accumulations of Fe/Mn oxides can therefore act as a major source of dissolved metals in natural waters (Jenne, 1976). Fe has been suggested to be a limiting element in phytoplankton growth (Martin and Fitzwater, 1988; Martin and Gordon, 1988 and Martin, 1990).

The distribution patterns of various fractions of iron in sediments of various station under the present investigation are depicted in figs. 5.1.1, 5.1.2 and 5.1.3. The total iron values range from 5000 - 55,000 µg/g along the Kerala Coast, 15000 - 55,000 µg/g in Cochin estuary and 18,000 - 60,000 µg/g in Chaliyar estuary. The values are comparable with those obtained by the previous investigators for the study area (Mallik and Suchindan, 1984; Venugopal *et al.*, 1982; Murthy and Veerayya 1981; Murthy *et al.*, 1973).

The values are also in good agreement with those reported for similar regions from all over the world. Table 5.1 illustrates the results. Recently Kunhikrishnan Nair (1992) has reported only 2811 to 20183 mg/kg Fe in the sediments of Cochin estuary and the discrepancy was observed due to two reasons (i) unaccountability of moderately reducible fraction (Brannon *et al.*, 1977) and (ii) the acid mixture used (HNO_3 - $HClO_4$) was not capable enough to digest the silicate materials. Gibbs (1977) has reported more than 90% of the iron content in the Amazon River is transported in the grain size interval or 0.2 µm to 20 µm. It is also obvious from his studies that the transportation mode of iron in the hydrous oxide state is approximately 1-2 µm (coating mainly on clay minerals), whereas the mode in crystalline particles is located at approximately 10 µm (predominantly silicate).

The concentration of iron in the ammonium acetate extract ie: exchangeable fraction or Fel was found to vary from 0.27 to 0.89 µg/g in the sediments of Chaliyar estuary, contributing only 0.0015 to 0.0018% of the total iron content of the sediment. The range of Fel values in the sediments of Cochin estuary is 0.27 to 10.099 µg/g and the percentage wise contribtution is less than 0.005% only in the southern part of the estuary. The Fel content in the coastal sediments of Kerala varies from 0 to 19.69 µg/g and upto 0.052 % of total iron exists in the exchangeable fraction of coastal sediments.

Three stations of Kerala Coast viz. Kasargode Stn. No.1, Canannore Stn. No.2 and Calicut Stn. No.1 have Fel values below detection limit, and that was due to the desorption of Fe from the exchangeble sites into the overlying bottom waters in presence of very high concentration of Ca and Mg ions in the coastal environment supplemented by the sandy silt texture of the sediment samples. The Eh of these sediment samples (-258, -330 and -326 respectively) also reveal the prevailing reducing conditions at these sites which favours the solubilisation of Fe (II) ion into the overlying waters, supported by comparatively higher concentration of dissolved fraction of iron, observed in the bottom waters of these coastal stations.

Along Kerala coast the maximum value both in terms of absolute and percentage wise for Fel was obtained for the sediment samples from Ponnani station No. 2. (19.2 µg/g) followed by station No. 2 off Alleppey (9.09 µg/g) and station No. 1 off Cochin (8.02 µg/g). The texture of these sediments is found to be of clayey silt, which is the main factor controlling the exchange of metal ions between the interstitial water and overlying waters. Brannon *et al* (1977) has reported that interstitial water contain more dissolved iron than the overlying waters and in the present extraction procedure the exchangeable fraction comprises of the metals dissolved in interstitial water and loosely bound to the adsorbing surface of the sediment; the clayey silt nature of the sediments together with the high organic matter content which mobilises iron under mild oxidising conditions explain the higher concentration of Fel in the clayey silt sediments of Kerala coast.

The distribution of Fel in the sediments of Cochin estuary and Chaliyar estuary is also explained on the same basis ie: the clayey silt sediments of the lower estuarine regions are having higher concentrations of the exchangeable fraction of iron. Very high concentration of Fel (10.09 µg/g) obtained for station No. 2 of Cochin estuary is due to the sheltered sedimentary environment of that station even during monsoon season (Pillai, 1989).

Fe2 values varied from 2.7 to 2635.58 µg/g contributing upto 5.3% of total iron in the sediments of Kerala Coast, 45 to 1850 µg/ g in the sediments of Cochin estuary contributing 0.3 to 4.06% to total iron and from 1020-3620 µg/ g ie: 4.4 - 6.6% of total iron in the sediments of Chaliyar estuary. Comparatively high amount of Fe2 observed in the coastal sediments of Calicut was due to the riverine input as was observed from the very high values of Fe2, both in absolute and relative terms in the sediments of Chaliyar estuary.

Previous investigators have reported (Rao *et al.*, 1983) a depletion in the carbonate bound fraction of heavy metals due to sedimentological features, in the sediments of estuarine systems where the rivers drain into the lake prior to sea. The results of the present study also reflect the same ie: the Fe2 values are higher for the Chaliyar river estuarine system while lower percentage of Fe2 fractions were obtained for the sediments of Cochin estuary as the rivers drain directly to the Vembanad lake.

A progressive increase in Fe2 values towards the marine region is observed in Chaliyar estuary indicating the settling effect of suspended particulates during estuarine mixing.

The easily reducible fraction of iron, Fe3, extracted with acidified (pH-2) hydroxylamine hydrochloride, in the sediments of the coast ranged from 0.3942 to 1177.28 µg/ g in terms of absolute concentration and the percentage wise distribution was found to be 0.007 to 3.42 %. Minimum concentration was obtained for the coarser sediments of Quilon station No. 1, where the organic matter content (1.812 mg/g) and percentage of clay (0.75%) were lowest. The Fe3 values ranged between 178 and 893.94 µg/ g ie. 1.17 to 1.93% of the total iron is in the easily reducible fraction of the sediments of Cochin estuary. In Chaliyar estuary the percentage of Fe3 varied from 0.37 to 2.72 % and the absolute values from 68.18 to 1188.68 µg/g.

Brannon *et al.*, (1977) and Tessier *et al.*, (1979) observed that the extractant leached down manganese oxides (about 85%) more easily than the iron oxide. So both the concentration and the chemistry of iron in the easily reducible fraction is controlled by the levels of manganese oxide and organic matter in the sediment samples.

The moderately reducible fraction (Fe4) comprising mainly of hydrous oxides of iron (Forstner *et al.*, 1981) extracted with ammonium oxalate in oxalic acid extractant ranged from 2878 to 27751 µg/ g along Kerala Coast, 4728 to 22717 in Cochin estuary and from 5324 to 35,010 in Chaliyar estuary contributing 30 to 60%, 31 to 53% and 30 to 60% respectively. The values (in absolute and relative terms) declined towards upstream in both the estuaries with a small depletion in values in and around the barmouth area of Cochin due to the presence of less oxygenated bottom waters during the post and premonsoon seasons (average 1.74 ml/l). The values of Fe4 in Chaliyar estuary was found to be higher compared to Cochin estuary which is attributed to the high dissolved oxygen levels of the bottom waters of Chaliyar during post and premonsoon seasons. In alkaline pH range iron is readily oxidised to ferric form by dissolved oxygen within a few minutes (Stumm and Lee, 1960). Hydroxide ions often posses a greater affinity to Fe^{3+}, thus forming hydrous oxides of iron (Stumm and Morgan, 1970). Brannon *et al.* (1977) have reported that 68.54 to 72.75% of total Fe in the sediments of Mobile bay was present as the moderately reducible fraction and Patchineelam and Forstner (1983) have reported 14 and 69.4% of total Fe as Fe4 in the sediments from the unpolluted and polluted regions of Subae river. Results of the present study are comparable with the above values.

The organic and sulphide bound fractions of iron Fe5 in the coastal sediments of Kerala varied from 5.13 to 18581.5 µg/ g contributing 0.09 to 36.49% of total iron. The minimum value was registered for Quilon station No. 1 with coarser sandy sediment texture and very low content of organic C (1.812 mg/g). Higher percentage of Fe5 was obtained for stations off Kasargod station No.2, Calicut station No.2 and Alleppey station No.1, clayey silt sediments which is rich in organic matter. The total sulphide content was also found to be high off Kasargod stations compared to other coastal stations of Kerala.

The Fe5 values of Cochin estuary ranged from 2627 to 21469 µg/ g with very high values of 21,469 (36.4%) and 18,924 µg/ g (34.05%) for station Nos. 2 and 4 which are located near the drainage sites of sewage effluents from the heavily populated urban areas of the Cochin City. Percentage wise distribution of Fe5 in the Cochin estuary varied from 17.33 to 36.44%. The Fe5 values were found to decline towards upstream from station 4 onwards. The enhanced values of Fe5 even in the upstream regions could be explained by the biological productivity of these regions as was reported by Joseph and Pillai (1975) and Joseph and Nair (1975).

The maximum contribution of Fe5 in the sediments of Chaliyar estuary is only 14.34% and a progressive increase towards the lower estuary was observed. The distribution pattern of Fe5 in the sediments of Chaliyar estuary is more or less similar to the distribution of organic C content of the sediments, revealing that the concentration as well as the chemistry of Fe5 fraction in the Chaliyar estuary is mainly controlled by the organic matter load of the estuary.

The Fe6 values ranged from 2671.28 to 16258.8 µg/g contributing 9.7 to 48.09% of the total Fe concentrations in the sediments of Kerala Coast. The mud bank forming clayey silt sediments off Alleppey coast with high content of organic matter and inorganic phosphate (Jacob and Qasim, 1974) have the least percentage wise contribution of Fe6. The highest percentage contribution of Fe6 (48.09% of FeT) was obtained for the sediments at Station No.1 of Quilon coast with coarser sediment particles composed of silicate minerals.

In the Cochin estuary the absolute values of Fe6 was found to be around 7000 µg/g except for station Nos. 2 and 4, both receiving sewage effluents. It is obvious from the distribution pattern of Fe6 in the Cochin estuary that the mineral held iron fraction brought to the estuary by the sewage effluent is retained in and around the site of discharge itself without being flushed out of the area. The percentage wise contribution of the residual fraction of iron was found to decrease towards the lower reaches of the estuary (16-50%) without any decrease in the absolute values due to the dilution taking place to the mineral rich riverine sediment load brought into the estuary by the settling of organic matter in the fine clayey fraction of suspended particulates of the overlying waters as a result of estuarine mixing.

The Fe6 values ranged from 11064.76 to 18645.73 µg/g contributing 19.75 to 60.55% of total iron, in the sediments of Chaliyar estuary. A progressive increase in percentage wise values was observed towards upstream. Higher values of Fe6 observed at station Nos.2 and 3 are due to the settling of suspended particulates of the overlying waters as a result of the enhanced ionic concentration by sea water intrusion.

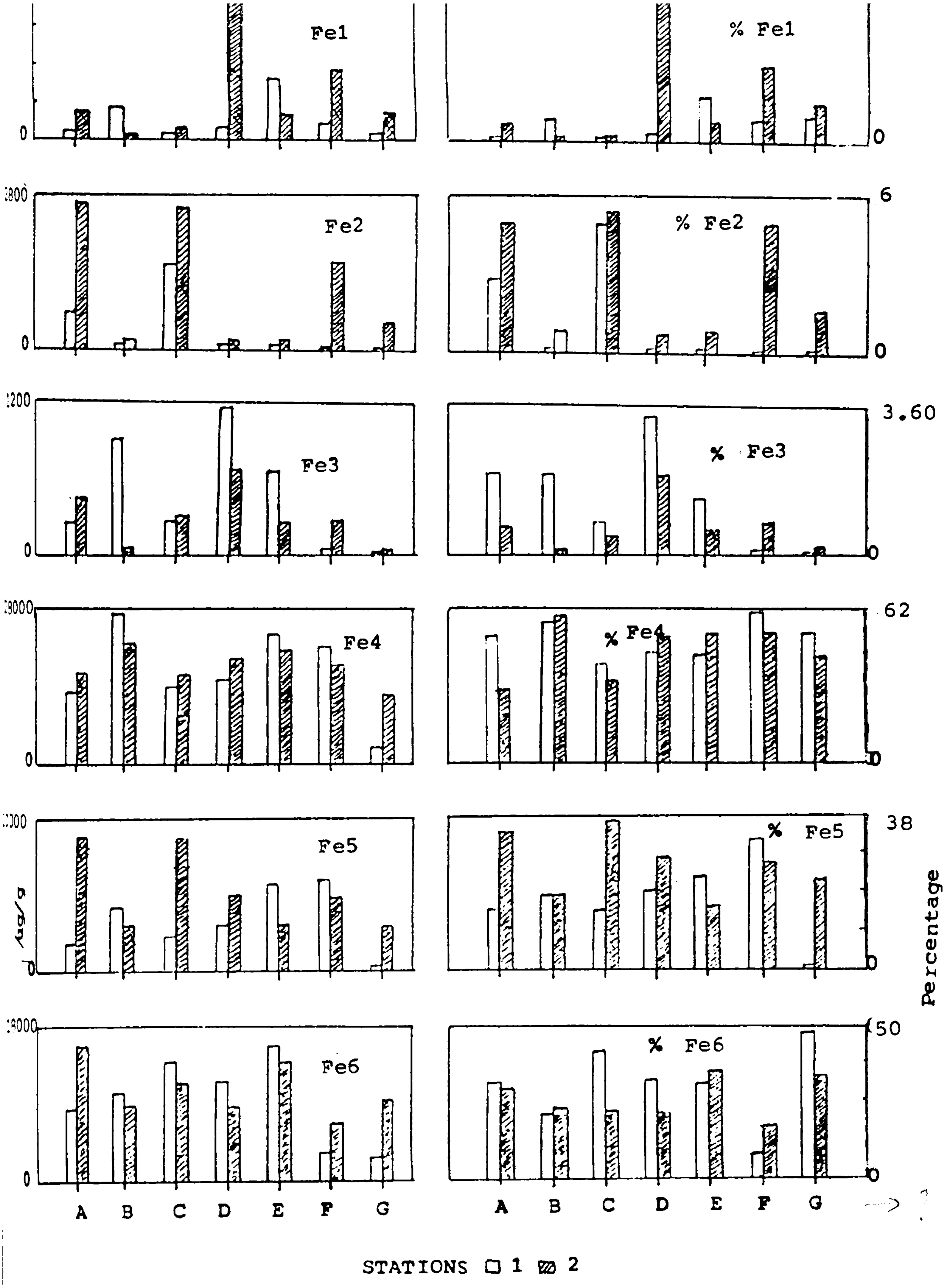


FIG.5.1.1. The distribution pattern of various fractions of Fe in the sediments of Kerala Coast.

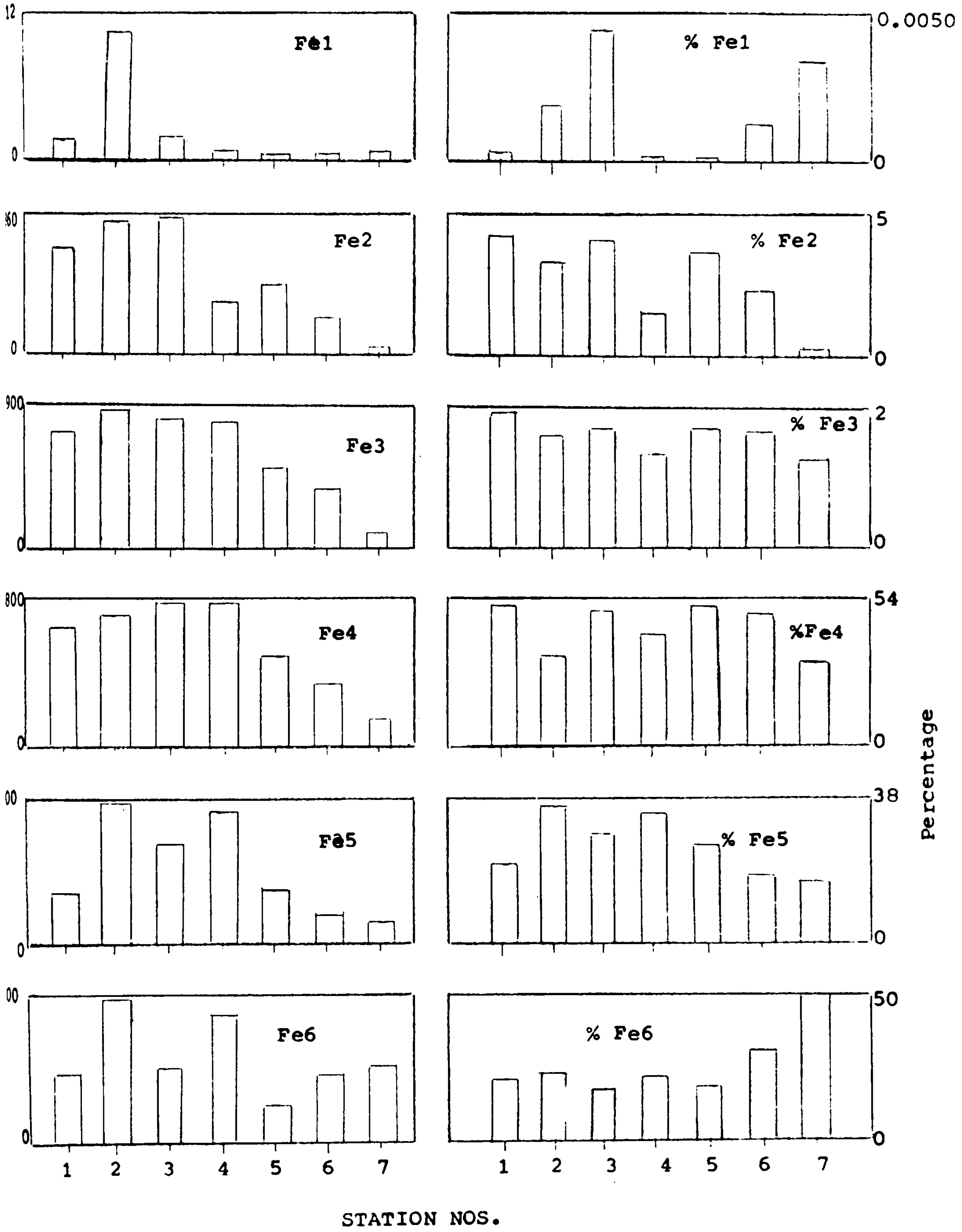


FIG.5.1.2. The distribution pattern of various fractions of Fe in the sediments of Cochin estuary.

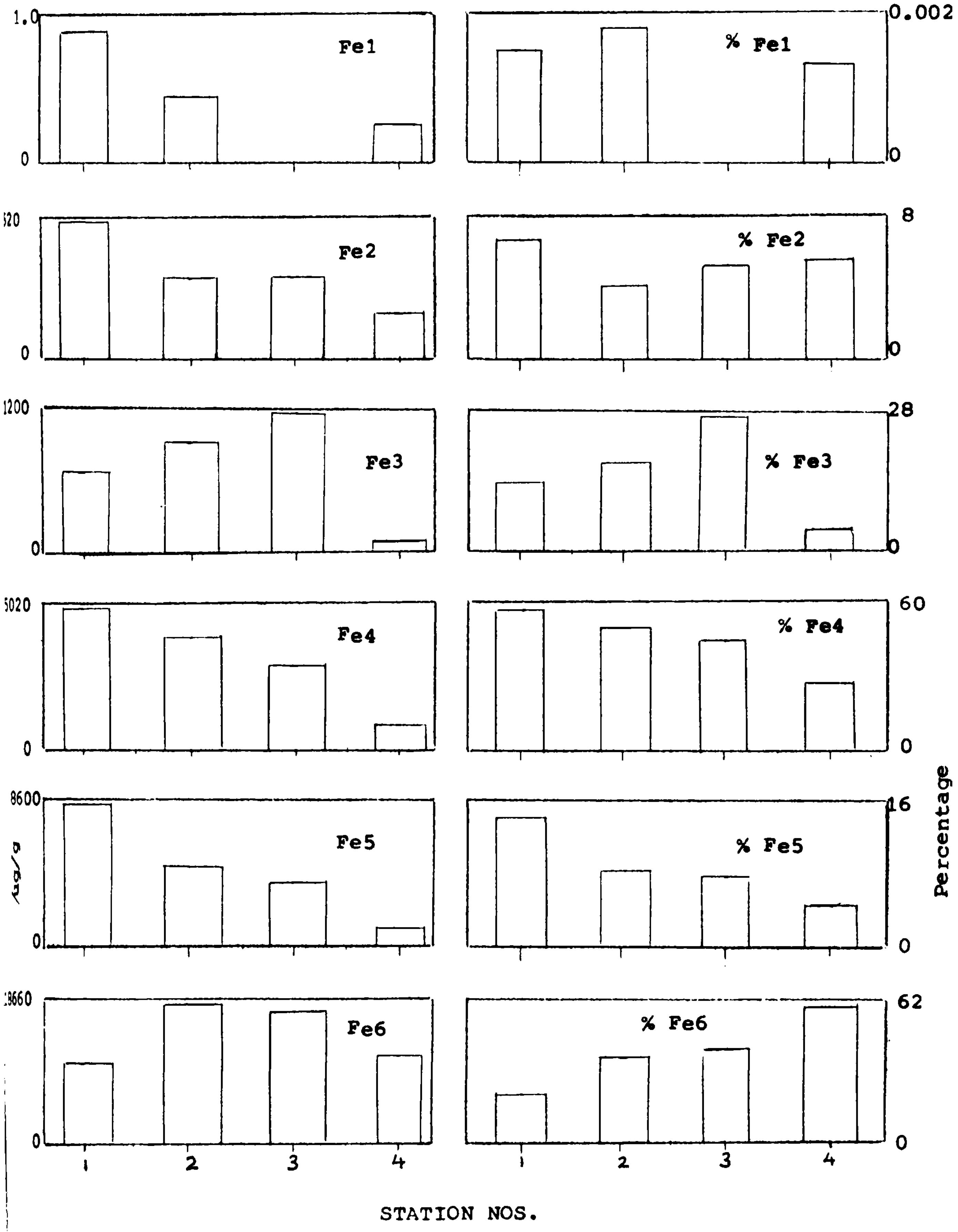


FIG.5.1.3. The distribution pattern of various fractions of Fe in the sediments of Chaliyar estuary.

Location	E.F.	C.F.	E.R.F.	M.R.F.	O & S.F.	R.F.	Total /ug/g	Reference
Yukon-SPM	0.01		40.60		11.00	48.20	63000	Gibbs, 1973
Mobile bay, Site 1	1.35		4.10	72.75	12.67	9.11	28000	Brannon et al.1977
Site 2	0.97		2.28	68.54	19.41	8.79	30700	-do-
Yamaska river-SPM	0.01	2.10	32.00		4.80	61.00	43000	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	14.00		83.00	26161	Patchineelam and Forstner, 1983
- Polluted			3.60	69.40	0.20	26.80	48540	-do-
Yellow river	0.10	1.00	1.00	26.00	7.00	65.00	14198	Hong and Forstner, 1983
Cochin Estuary-MEAN	0.06	0.07	1.27		1.16	97.44	8323	Kunhikrishnan Nair 1992
Kerala Coast Range	<0.052	0.01-5.3	0.007-3.42	30-60	0.09-36.49	9.7-48.09	5000-55000	Present study
Cochin Estuary Range	<0.005	0.3-4.06	1.17-1.93	31-53	17.33-36.44	16.50	15000-55000	-do-
Chaliyar Estuary Range	0.0015-0.0018	4.4-6.6	0.37-2.72	30-60	1-14.34	19.75-60.55	18000-60000	-do-

Table 5.1 Percentage of iron fractions reported in sediments from different geographical locations.

5.2. Manganese

Manganese is an essential micro nutrient element in biological system. Manganese is not normally in limiting supply for estuarine biological processes, its interest lies in its reactivity, its response to environmental conditions, and its speciation (Evans *et al.*, 1977). Knowledge of its behaviour in a complex aquatic system can lead to a general understanding of the chemistry of other metals and yield information on circulation and recycling within the aquatic system (Evans *et al.*, 1977). The chemistry of manganese in oceanic, freshwater, and nearshore environments has been reviewed by Glasby (1984). Reactivity of manganese in aquatic system exhibits a complex behaviour with conservative and non-conservative nature depending upon a number of factors such as the concentration in sediment, water and suspended particulates, ionic strength. pH, Eh etc. (Burton and Liss, 1976; Duinker *et al.*, 1979; Wollast *et al.*, 1979; Yeats *et al.*, 1979, Wilke and Dayal, 1982; Callaway *et al.*, 1988).

The internal supply of dissolved Mn to an estuary has been attributed to (1) desorption from suspended particles; (2) reductive solubilization and (3) sediment pore water flux (Elderfield and Hepworth, 1975; Graham *et al.*, 1976; Sanders, 1978; Morris and Bale, 1979; Knox *et al.*, 1981; Morris *et al.*, 1982). Demonstrable losses of dissolved manganese have been attributed to adsorption on to suspended particles (Bewers and Yeats, 1978) coupled with catalytic oxidation

(Morris and Bale, 1979), to flocculation of fine colloids (Sholkovitz, 1976) and to direct or oxidative precipitation (Graham *et al.*, 1976; Evans *et al.*, 1977; Duinker and Nolting, 1978; Duinker *et al.*, 1979, Wollast *et al.*, 1979).

Manganese can exist in two oxidation states as Mn(II) under reducing conditions and as Mn(IV) under oxidising environments.

The distribution patterns of various fractions of manganese are shown in Figs. 5.2.1, 5.2.2. and 5.2.3. The MnT values varied from 44.1 to 318.5 µg/ g in the sediments of Kerala Coast, 123.6 to 280.5 µg/g in the Cochin estuary and from 196.9 to 545.09 µg/ g in the sediments of Chaliyar river estuary. More than 50% of Mn in sediments was found to be in the non-lithogenous fraction indicating the high chemical reactivity of Mn in aquatic environments. This has also being reported by various investigators for estuaries and shallow coastal waters (Jacobs *et al.*, 1985; Prohic and Kniewald, 1987; Samanidou and Fytianos, 1987).

The values for Mnl fraction ranged from 0.37 to 11.2 µg/g in terms of absolute values while the percentage wise contribution was found to be from 0.34 to 5.3% in the coastal sediments with maximum values recorded both in absolute and relative terms for the sediments off Cochin coast. The enrichment of Mnl in the sediments of Cochin coast was attributed to the remobilization of Mn dissolved in interstitial waters of the sediment during ammonium acetate leaching step due to the high dissolved Mn content of the interstial waters of the sediments with Eh below the oxidation limit, in accordance with the redox geochemistry of this element (Bonatti *et al.*, 1971), details of which are given in the following section (5.7).

In the surficial sediments of Cochin estuary the Mn1 values ranged from 1.79 to 6.25 µg/ g in the estuarine region with below detection limit in the sediments of station No. 7. The sediments of station No. 7 are having only very low percentage of clay as well as organic matter content corresponding to which the exchangeable sites are also very little and due to the high mobility Mn is not at all competent enough to occupy any such sites under the prevailing conditions (Morris *et al.*, 1982). The percentage wise contribution of Mn1 in Cochin estuary was found to be ranging from 0.63 to 4.3 %. The Mn1 values varied between 5.16 and 135.83 µg/ g in the surficial sediments of Chaliyar estuary contributing 2.6 to 24.9 %. The very high concentration of exchangeable and carbonate fractions of Mn determined at station No. 3 indicated the input of Mn into the Chaliyar estuary through some point source.

In the surficial sediments of Kerala Coast Mn2 fractions varied from 0.37 to 89.77 µg/ g with a relative contribution of 0.85 to 29.13%.

The Mn2 values in the surface sediments of Cochin estuary and Chaliyar estuary ranged from 23 to 26% and 28 to

38% in terms of relative concentrations, excluding the upstream freshwater sediments having comparatively low percentage of carbonate fractions (3.3% in Cochin estuary and 8.03% in Chaliyar estuary). A unique feature observed in the case of Mn2 distribution was its more or less equitable percentage wise concentration in sediments, differing in their texture and organic matter contents, from various stations of both the estuaries. A little bit higher percentage of Mn2 was observed in Chaliyar estuary.

The higher percentage of carbonate bound manganese as well as the uniform distribution of Mn2 in estuarine sediments can be explained on the basis of the substitution of Mn^{2+} to Ca^{2+} ions in the crystal lattices of calcium carbonate. The ionic radii of the Mn^{2+} and Ca^{2+} ions are 0.80 and 0.99 A^{o}, respectively. According to Pingitore (1978) the Mn^{2+} ions can substitute the Ca^{2+} ions in the crystal lattice of calcium carbonate (calcite) giving upto 40% (by wt.) of $MnCO_3$. Studies of various trace metals associated with the carbonate fraction have shown that there is an average increase in Mn content in sediments with a higher percentage of the carbonate fraction (Deurer *et al.*, 1978).

The percentage of Mn in the easily reducible fraction Mn3 is low as expected, the range being 0.94 to 8.3% in the coastal sediments of Kerala, 1.02 to 12% in Cochin estuary and 0.42 to 4.7% in Chaliyar estuary, since iron is readily oxidised by dissolved oxygen to the ferric form, in the alkaline, neutral to slightly acidic pH range, while manganese requires a much higher pH for equivalent rates of oxidation (Stumm and Lee, 1960). Moreover the chemical oxidation of manganese is influenced by inorganic ions such as HCO^-_3 or SO^{2-}_4 (Hem, 1964). Experiments by Schweisfurth (1972) indicate that ortho-phosphates in concentrations above 50 mg/l inhibit the oxidation of manganese, whereas pyrophosphates upto 50mg/l catalyze such processes. Polyphosphates in small amounts also have a positive effect on the manganese oxidation. Spratt and Hodson (1994) has reported that 20% of Mn oxidation in the aquatic environment occured by microbial activity

The very low percentage of Mn3 at Calicut station No. 1 is attributed to the inhibition of Mn oxidation at the surface of ortho phosphate rich mud bank forming sediments of malabar coast (Seshappa, 1953, Schweisfurth, 1972). Both in Chaliyar estuary and Cochin estuary a mid-estuarine maxima was obtained for Mn3 values.

Comparatively higher percentage of Mn was found to be present in the moderately reducible fraction ie: coprecipitated with hydrous oxide of iron. The Mn4 values ranged between 3 and 205 µg/g in the coastal sediments contributing 2.95 to 11.41%. The nearshore coastal stations ie: station No:1 is having higher values for the releative concentrations of Mn4 except for Alleppey. The increased ionic concentration in marine waters causes a remobilization of Mn coprecipitated with hydrous iron oxide resulting in higher concentration in the nearshore region. A reverse trend observed in the precentage wise distribution of carbonate fraction supported the depletion of Mn4 towards the offshore region.

The Mn4 values ranged from 21 to 38.1 µg/g in the sediments of Cochin estuary contributing 11.9 to 18.8% of the total Mn. The distribution pattern of moderately reducible fraction of manganese in the Cochin estuary did not show any peculiar trend, but only resembled that of carbonate bound fraction, whereas in the chaliyar estuary the distribution of Mn4 in terms of relative values was found to increase progressively from 5.26 to 19.3% towards barmouth similar to the distribution pattern of Fe4, indicating the association of manganese with the hydrous oxides of iron.

The organic and sulphidic fractions of Mn in the coastal sediments of Kerala ranged from 5.1 to 122.5 µg/g contributing 11.5 to 42.9% towards MnT. The strong positive correlation of Mn5 with organic C revealed that the major portion of Mn5 was bound to organic matter. The elevated percentage of Mn5 in the sediments of Cochin coast was attributed to high sulphide content.

In the sediments of Cochin estuary, Mn5 values ranged from 23.3 to 99.7 µg/g contributing 14.8 to 38.3% and in Chaliyar estuary the absolute values ranged from 4.7 to 36.0 µg/g with rather low percentage wise contribution, ranging from 2.3 to 4.5% except for station No.1 where it was determined to be 18.3%. The enhanced concentration of Mn5 at station No.1 of Chaliyar estuary was attributed to the contribution from sulphide bound Mn precipitated under the influence of relatively more alkaline overlying bottom waters (pH = 8.21). In Chaliyar estuary Mn5 values declined towards upstream, while no such trend was observed in Cochin estuary.

The relative contribution of residual fraction of manganeses in the sediments of Kerala Coast were found to be varying from 22.9 to 76.36% of total manganese, the high percentages being recorded for the sediments of Quilon coast as was expected from the sedimentological characteristics. The nearshore surface sediments of Calicut coast also showed an enrichment of Mn6 fraction as a result of settling of heavier sandy particles by which the surface sediments got concentrated with sand grains due to intense fishing activity in this shallow region. The grain size analysis also revealed that an average of 60.14% of sand particles with only 20.95% of clayey grains in the nearshore surface sediments of the calicut coast.

In the surface sediments of Cochin estuary, the lithogenous fraction of manganese was found to vary from 6.0 to 104.3 µg/g contributing 4.8 to 66.5% of the total manganese.

The minimum concentration of Mn6 both in absolute and in relative terms was obtained for station No.5 which receives effluents from a mini industrial estate, fish processing centres and sewage. The prevailing reducing condition at the surface of sediments as is evidenced by Eh value of -316 causes remobilization of Mn to more labile exchangeable sites along with the dilution occuring to the surface sediments by the settling of very fine fraction of suspended particulates under the influence of estuarine mixing acted together to reduce the Mn6 values in the sediments of station no.5 in Cochin estuary.

The Mn6 values ranged from 52.0 to 178.7 µg/g contributing 23.9 to 80.2% to the total manganese concentrations in the surficial sediments of Chaliyar estuary. The observed data showed that a major portion of the anthropogenic input of manganese entering the estuary via station No.3 as the most labile exchangeable fraction was partly converted into non-labile form and retained in the estuary itself without being flushed out into the sea as was evidenced from a decrease in the value of exchangeable fraction from 135.8 to 19.1 µg/g (ie: 24.9 to 4.6%) and an increase both in absolute and relative terms in the values of residual fraction from 130.4 to 178.7 µg/g (ie 23.9 -42.8%) towards station No.2 and from the very high values of total manganese in the sediments of station No.2 and 3, in comparison with the upstream or coastal sediments.

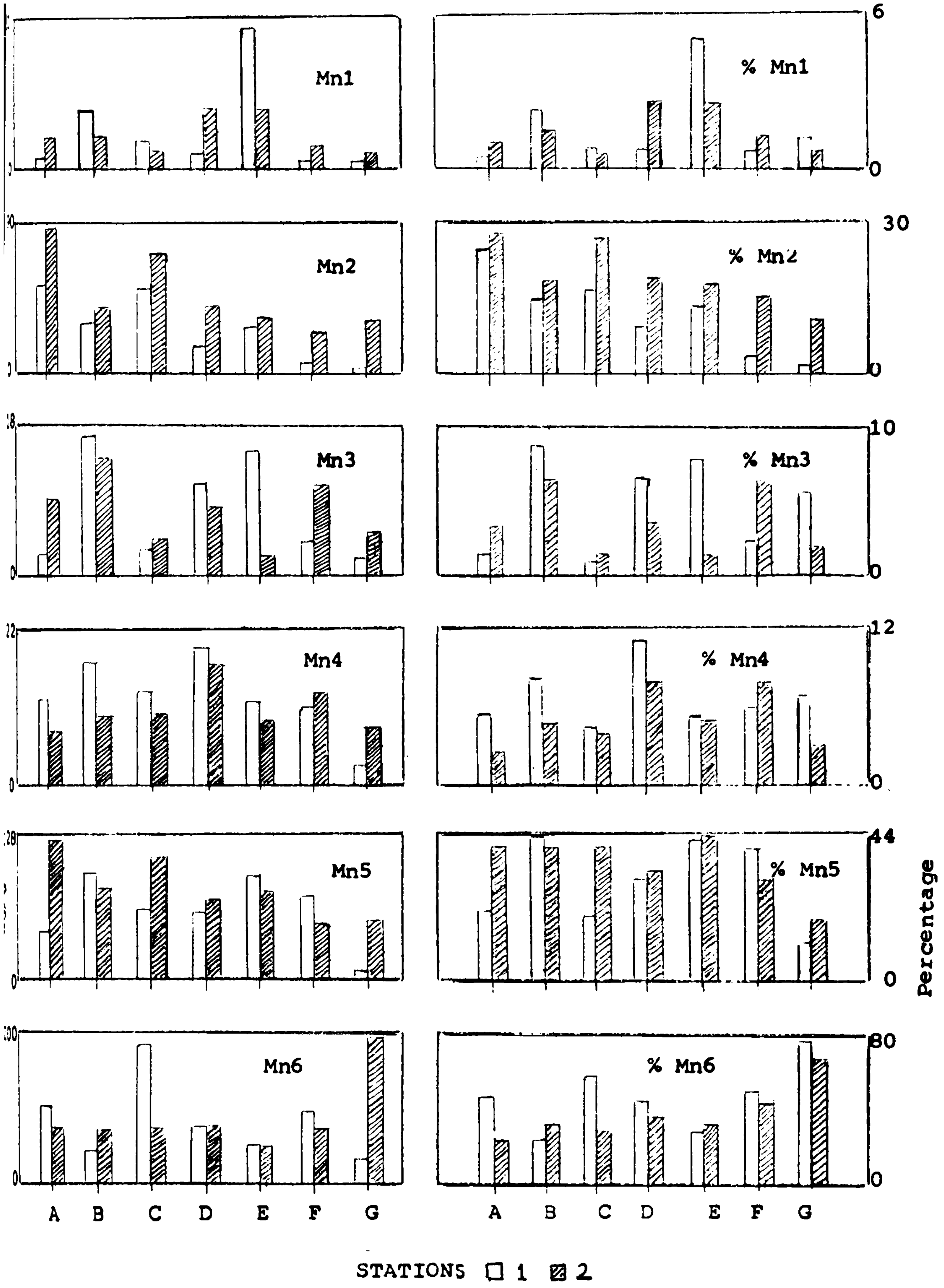


FIG.5.2.1. The distribution pattern of various fractions of Mn in the sediments of Kerala Coast.

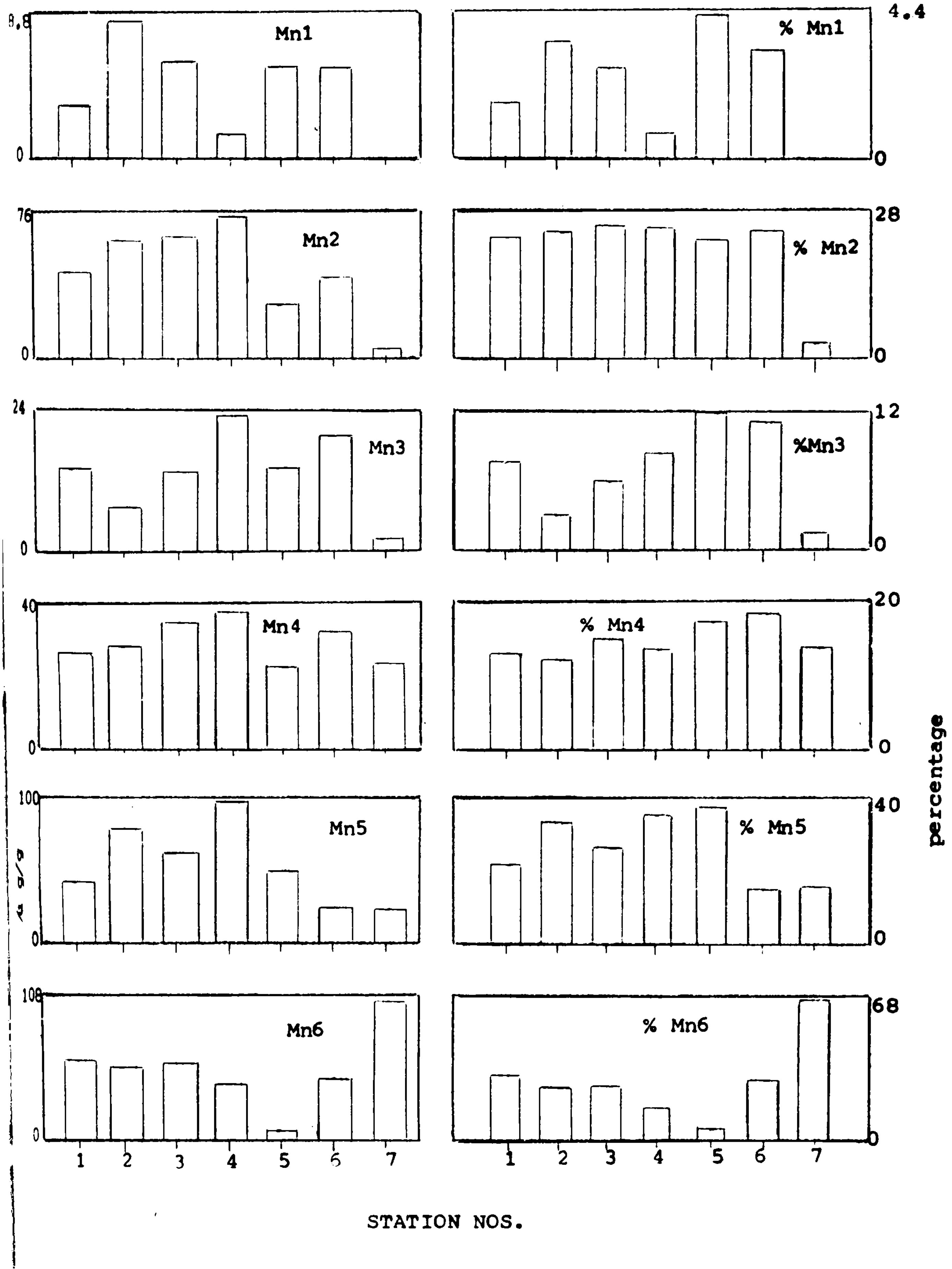
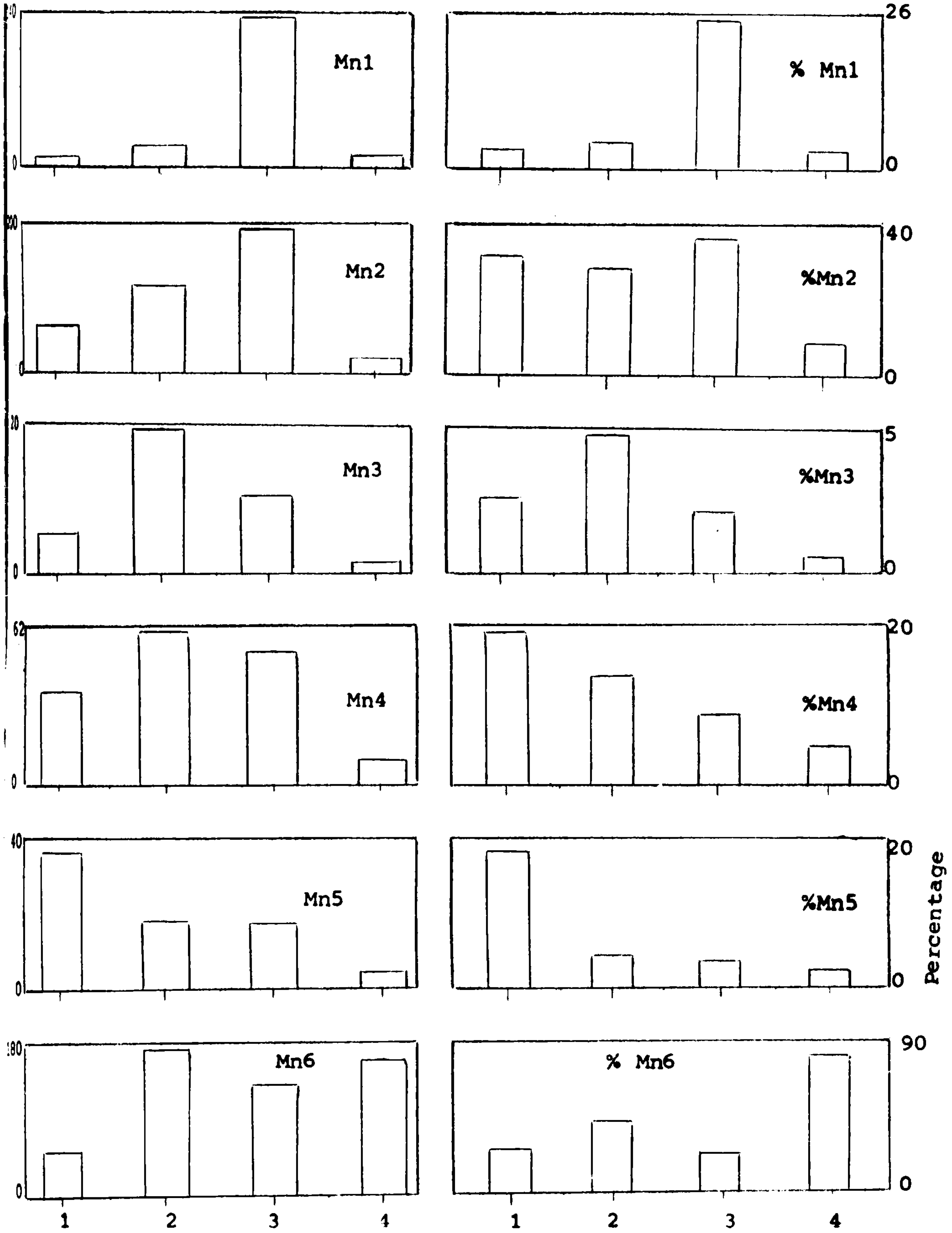


FIG.5.2.2. The distribution pattern of various fractions of Mn in the sediments of Cochin estuary.



STATION NOS.

FIG.5.2.3. The distribution pattern of various fractions of Mn in the sediments of Chaliyar estuary.

Location	E.F.	C.F.	E.R.F.	M.R.F.	O & S.F.	R.F.	Total Mn /ug/g	Reference
Yukon-SPM	0.50		45.70		6.60	37.10	1270	Gibbs, 1973
Mobile bay, Site 1	14.93		35.50	5.97	35.53	8.07	1069	Brannon et al. 1977
Site 2	7.88		14.92	10.74	44.36	22.12	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	38.1	3.8	17.2	583	Forstner, 1982
Subae river-unpolluted			45.8	7.1		47.1		Patchineelam and Forstner, 1983
-polluted			58.8	34.40	0.38	3		-do-
Yellow river	6.5	31.0	8.0	11.0	17.0	27.0	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 Knieweld, 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	Kunhikrishnan Nair, 1992
Kerala Coast Range	0.34- 5.3	0.85- 29.13	0.94- 8.3	3-11.41	11.5-43	30- 76.36	44.1- 318.5	Present study
Cochin Estuary Range	0.63- 4.3	23-26	1.02- 12.03	12-19	14.8- 38.3	4.8- 66.5	123.6- 280.5	-do-
Chaliyar Estuary Range	2.6- 24.9	28-38	0.42- 4.7	5.26- 19.3	2.3- 18.3	24-80.2 80.2	196.9- 545.05	-do-

Table 5.2 Percentage of manganese fractions reported in sediments from different geographical locations.

bdl = Below detection limit.

The relative abundance of Mn in various fractions of the surficial sediments was found to be in the sequence Mn6 > Mn5 > MN2 > Mn4 > MN3 > Mnl in coastal sediments, Mn6 > Mn5 > Mn2 > Mn4 > Mn3 > Mnl in Cochin estuary and Mn6 > Mn2 > Mn4 > Mnl > Mn5 > Mn3 > in the sediments of Chaliyar estuary. In the case of iron Fe4 was found to be the most abundant fraction and there observed no resemblance between the distribution of partition patterns of Fe and Mn in various geochemical fractions of sediments. The results of the present study are comparable with those reported from various parts of the globe. (Table 5.2).

5.3 Copper

The prsence of copper in plant and animal tissues was recognized more than 150 years ago. Long before it was recognized as an essential element in the diets of birds and mammals, it was detected as a component of blood proteins of snails. Copper is an essential metal in a number of enzymes. Thus copper is an essential trace element in the nutrition of plants and animals including man. It is required for the function of several enzymes and is necessary in the biosynthesis of chlorophyll. Higher levels are toxic to organisms. Copper in aquatic systems received attention mostly because of its toxic effects on biota. Algae and molluscs are particularly sensitive to copper. An excellent review on the toxicity and chemistry of copper in the environment was presented by Flemming and Trevors (1989) and they summarised that the chemical form of copper was important in controlling its geochemical and biological behaviour. Tests showed that copper toxicity was apparently related to the soluble form of copper ion occuring in the presence of carbonate ion (Gray and Ventilla, 1973). In the aquatic environment the behaviour of copper differs from that of iron and manganese. Jacobs and Emerson (1982) revealed the solubility behaviour of heavy metals in O_2/H_2S interface; Cu and Cd showed solubility decrease across the interface due to formation of insoluble sulphides while Fe and Mn showed an increase in solubility due to the reductive dissolution of metal oxides and subsequent formation of a more soluble metal sulphide solid phase. In waters containing high concentration of sulphides the solubility trend is reversed due to the equilibrium relationships betwen the metal sulphide and the dissolved species. The solubility of Cu and Cd increases due to metal-sulphide ligand complexation while Fe and Mn would decrease in solubility because of increasing sulphide concentration.

In aquatic environment copper exists as sulphides, sulphates, carbonates and other compounds, and also associated with organic matter, co-precipitated with hydrous oxides of Fe and Mn and as adsorbed on the exchangeable sites of clayey and silicate particles or in mineral form. Copper is not only coprecipitated with hydrous oxides of Fe but also catalyse the oxidation of ferrous sulphate by dissolved oxygen (Stumm and Lee, 1961). This has also been confirmed for the oxidation of manganese during water treatment (Jenne, 1968). Copper forms stable, soluble complexes with organic and sulphide ligands (Nelson and Lund 1982, Windom *et al.*, 1983). Cocoran and Alexander (1964), Lee and Hoadley (1967), and slowey *et al.* (1967) found that the major portion of copper in tropical sea water is associated with organic matter. Rashid (1974) has shown that copper is preferentially sorbed (53%) on to the organic materials. Leaching experiments have demonstrated that copper is more firmly associated with organic material than other metals (Jonasson, 1977). Paulson *et al.* (1991) showed that the behaviour of copper in estuaries was linked to that of organic matter mineralisation. Slauenwhit and Wangersky (1991) have shown that the increase in biogenic particles associated with a phytoplankton bloom is an important factor in controlling the dissolved concentration and speciation of copper.

Sankaranarayanan *et al.* (1973) carried out studies on copper content in the inshore and estuarine waters along the central west coast of India. Nair *et al.* (1990) has reported a wide variability in the spatial and seasonal distribution of copper in the surface sediments of Cochin estuary.

The total amount of copper in the surficial sediments of Kerala coast varied from 5.1 to 48.1 µg/g. In the surficial sediments of Cochin estuary it varied from 5.52 to 51.3 µg/g and from 5.9 to 39.6 µg/g in the sediments of Chaliyar estuary. The distribution of various fractions of Cu is shown in Figs. 5.3.1, 5.3.2 and 5.3.3.

The concentration of Cu in the exchangeable fraction of coastal sediments were found to be below the detection limit except for the surficial sediments of Alleppey. This is mainly due to the fact that with an increase in ionic strength the adsorption density of Cu^{2+} ions on particle surfaces decreases on account of the competitive exchange by Ca^{2+} and Mg^{2+} ions. Moreover, Sibley and Morgan (1975) have reported that in the sea water environment, chloro-complexes would be the dominant species for Cu, most of which are water soluble in nature. Comparatively higher values for Cul in the sediments of Alleppey was due to the silty-clay texture of sediments having very high organic matter content providing ample sites for absorption.

The Cul values varied between 0.06 to 0.98 µg/g in the surfical sediments of Cochin estury contributing 1.08 to 1.98% of the total Cu content, while in the sediments of Chaliyar estuary, Cul level were found to be below detection limit. Gupta and Chen (1975) also reported very low values for Cu in the exchangeable fraction of sediiments. Comparatively higher percentage of Cul in the sediments of station Nos. 2, 3, & 4 were attributed to the dredging operations at station No.3 causing resuspension of surface sediments and the sewage sludge discharge at station Nos.2 and 4.

The distribution of Cu2 in the coastal sediments was also in low amounts ranging from below detection limit to 2.01 µg/g with relative contributions up to 9.07%. The distribution of Cu2 in the sediments of both the estuaries were also found to be low varying form < 0.1 to 1.07 µg/g in Cochin estuary and from 0.39 to 1.49 µg/g in the Chaliyar estuary. The highest percentage of this fraction at the upstream stations of the both estuaries indicated the land derived source of this form of copper probably associated with the phosphatic fertilizers used in the Agricultural land.

The amount of copper in the easily reducible fraction Cu3 was found to be the minimum and the values ranged from below detection limits to 0.96 µg/g in the coastal sediments, up to 0.14 µg/g in the sedmiments of Cochin estuary and up to 0.42 µg/g in the sediments of Chaliyar. A notable feature observed in the distribution of Cu3 in costal sediments was its detectable amounts in sediments samples with very low values for either Cul and Cu2 or both. The very low values detected in most of the samples coupled with the lack of any trend rendered limitations to any discussion of the distribution of this fraction of copper. Even though the values of Cu3 obtained from the present study are not in conformity with those recorded by previous investigators, the low values observed for Cu3 in the coastal and estuarine sediments of Kerala can be attributed to the greater association of copper with iron oxides than with manganese oxides, since hydroxylamine hydrochloride could leach out a greater percentage of manganese oxide only (85%, Brannon *et al.*, 1977). Very high concentration of copper determined in the moderately reducible fraction observed in the present study also supports the above fact.

Appreciable amount of copper was found to be present in the moderately reducible fraction Cu4, in association with hydrous oxides of iron. In the coastal sediments the absolute values ranged between 0.49 and 11.01 µg/g with a contribution of 5.4 to 35.7% to the total Cu content of the sediments. An increase in the value of Cu4 both in absolute and relative terms was observed towards the nearshore region in the northern sector whereas a reverse trend was observed in the sediments of the southern sector.

The Cu4 values in the surfical sediments of Cochin estuary varied from 0.74 to 17.74 µg/g with a relative contribution of 13.48 to 34.13% to CuT. The distribution pattern showed a close resemblance to the distribution pattern of Fe4 in the Cochin estuary. The values are comparable with those reported by previous workers from different parts of the world (Brannon *et al.*, 1977; Forstner, *et al.*, 1982; Calmano and Forstner, 1983; Hong and Forstner, 1983; Elliot *et al.*, 1990)

The Cu4 values in the surficial sediments of Chaliyar estuary was found to vary from 2.2 to 18.29 µg/g with more or less equitable percentage-wise distribution, throughout the estuary. Cu4 was found to be the most abundant fraction of copper in the sediments of Chaliyar estuary. The order of abundance of various fractions of Cu in the sediments of Chaliyar estuary decreases in the sequence Cu4 > Cu6 > Cu5 > Cu2 > Cu3 > Cu1

16.49 to 55.1 % of total copper was found to be in the organic and sulphidic fraction in the surficial sediments of Kerala coast. The absolute values ranged from 1.95 to 25.24 µg/g. The distribution pattern of Cu5 which resembled that of CuT, revealed that the organic and sulphidic fraction of Cu is having an appreciable contribution towards the total metal.

The most abundant fraction of copper in the surficial sediments of Cochin estuary was found to be the organic and sulphidic fraction, the relative contribution from which was estimated to be of 33.9 to 44.9% of the total copper concentrations. The very high values for Cu5 at station No.2 and 4 were attributed to the input of organic matter rich sewage sludge at these sites and the comparatively low values for Cu5 at the barmouth indicated the retention of the contaminants in and around the receiving sites itself. The strong positive correlation between the organic C content of the sediment and Cu5 as well as the correlation between the total copper and organic C content indicated that the organic C content of sediments is a main factor controlling the geochemistry of copper in the surface sediments of Cochin estuary.

Apparently equitable percentage of Cu5 was observed in the sediments of Chaliyar estuary with a marginal enhancement in the sediments of the barmouth region. This was attributed to the settling of suspended colloidal aggregates of stable organic complexes of copper in the overlying waters by the coagulation of colloidal particles under the influence of high ionic strength. The Cu5 values progressively increased from 1.08 to 10.9 towards down stream with a relative contribution of 18.2 to 26.15% to the total copper content of the sediments.

In the coastal sediments of Kerala a greater percentage of copper was present in the non-labile residual form except at Calicut where the Cu5 outweighs the Cu6 fraction. The percentage-wise distribution of Cu6 varied from 21.2 to 54.51%. The order of abundance of various fractions of Cu in the coastal sediments increases as Cul < Cu3 < Cu2 < Cu4 < Cu5 < Cu6

The distribution pattern of Cu6 was similar to that of total copper content of the sediments indicating that the labile fractions of copper entering the marine environment underwent mineralization and were converted into stable residual form.

The values of Cu6 fraction in the sediments of Cochin estuary varied from 2.23 to 18.4 µg/g with very high values at station Nos.2 and 4 indicating anthropogenic inputs and

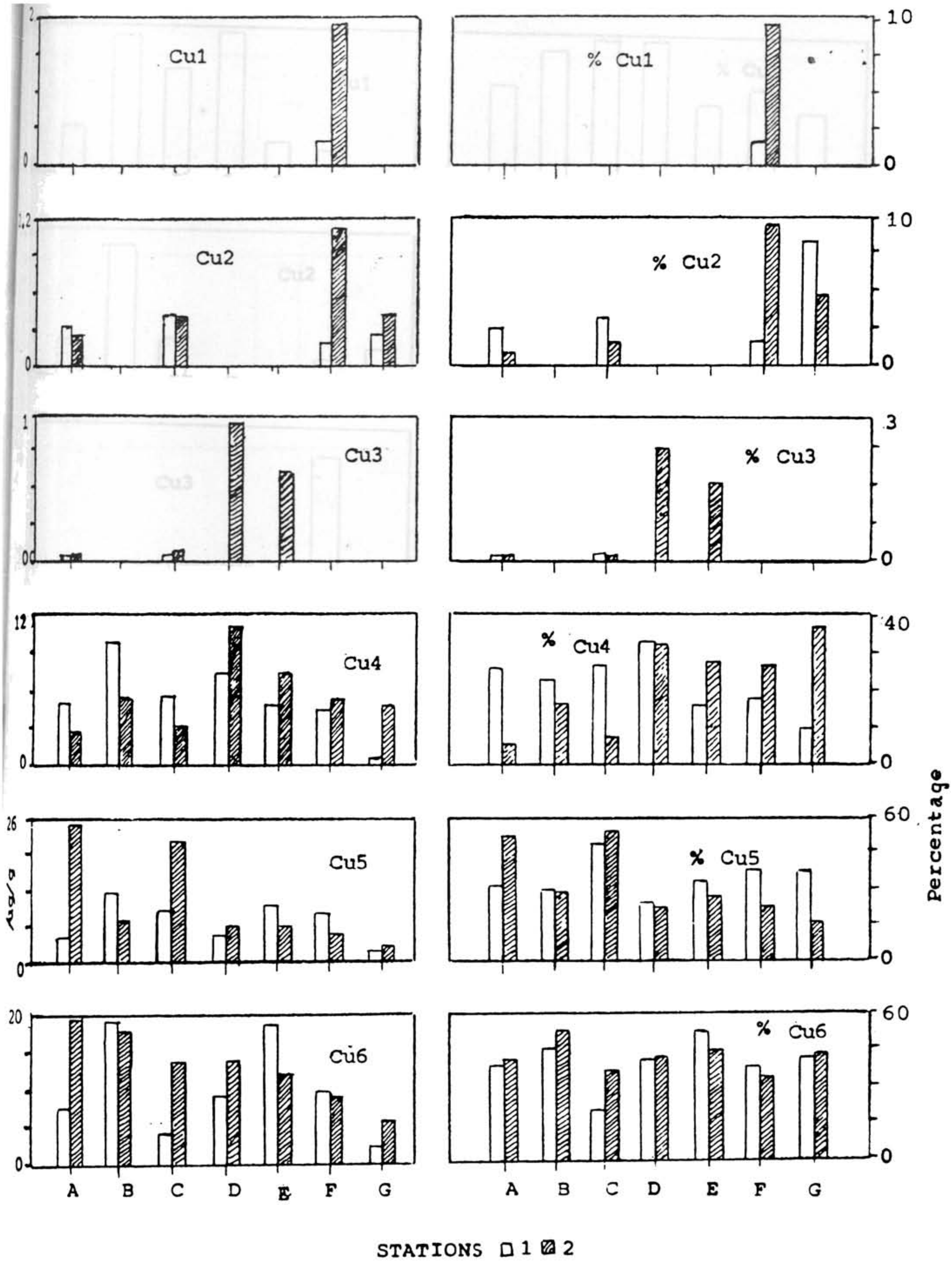


FIG.5.3.1. The distribution pattern of various fractions of Cu in the sediments of Kerala Coast.

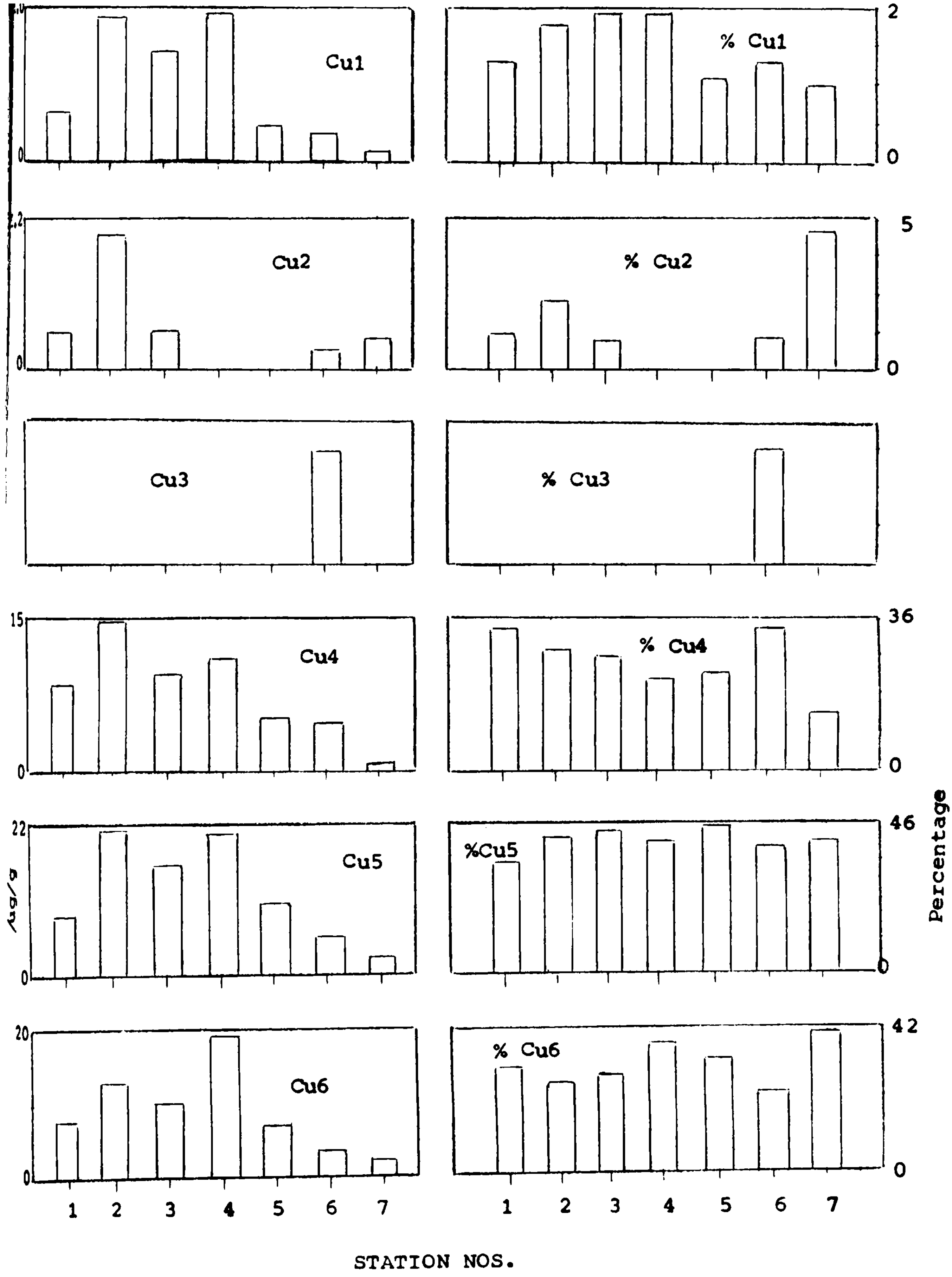


FIG.5.3.2. The distribution pattern of various fractions of Cu in the sediments of Cochin estuary.

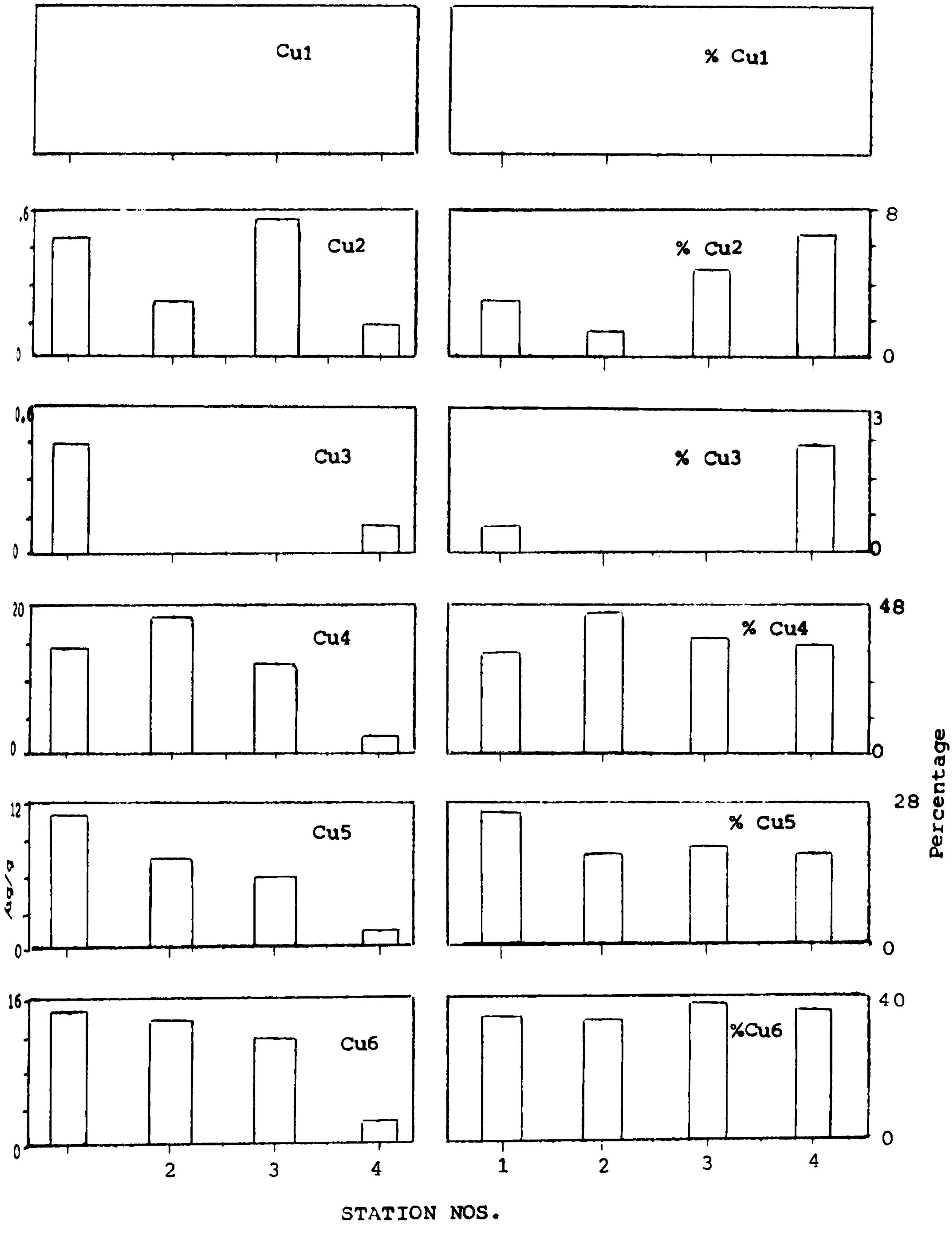


FIG.5.3.3. The distribution pattern of various fractions of Cu in the sediments of Chaliyar estuary.

Location	E.F.	C.F.	E.R.F.	M.R.F.	O&S.F.	R.F.	Total Cu ($\mu g/g$)	Reference
Los Angels harbour	bdl	5.7	3.5	5.7	2.2	76.4	416	Gupta and Chen,1975
Yukon-SPM	2.3	5.7	3.8		3.3	87.3		Gibbs,1973
Mobile bay,Site 1			0.24	6.11	32.63	61.02	38	Brannon et al,1977
Site 2			0.05	13.83	41.71	51.41	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	48.4	14.5	34.2	202	Forstner,1982
Weser estuary	1		<1	57	1	41	27	Calmano and Forstner,1983
Rotterdam harbour	9		47	37	4	3	1062	-do-
Neckar river	3		<1	72	9	16	242	-do-
Yellow river	1.3	4	6	37	27	24	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	1.17	3.08		14.65	49.69	47	Samanidou and Fytiamos,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		32	6.3	55	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	71.21	12	Kunhikrishnan Nair,1992.
Kerala Coast Range	bdl	<0.07	<2.9	5.4-35.7	16.5-55	21.2-54.5	5.1-48.1	Present study
Cochin Estuary range	1.08-1.90	<2.5	<1	13.5-34.1	34-45	22.8-40.6	5.5-51.3	-do-
Chalivar Estuary range	bdl	<3.5	<1	18.5-26.1	18.2-26.2	34-38.1	5.9-39.6	-do-

Table 5.3 Percentage of copper fractions reported in sediments from different geographical locations.

bdl - below detection limit.

the retention of Cu contaminants at the receiving sites itself. The relative contribution of Cu6 was found to be from 22.75 to 40.59%.

More or less equitable percentage of distribution of Cu6 in the sediments of Chaliyar estuary along with progressive increase in absolute values of both Cu6 and CuT has shown that the main source of copper in the estuary was of land origin, and the settling of suspended particles as a confluence of estuarine mixing causes the progressive increase in absolute value towards the barmouth.

Table 5.3 furnishes percentage-wise distribution data on various fractions of copper in the sediments from different regions of the world. The results of present study are also compared with the compiled previous data.

5.4 Zinc

Zinc is a required and benificial element in human metabolism. Deficiency of Zinc leads to growth retardation in children. Enventhough Zinc minerals are very abundant, due to the lack of solubility, it is present in natural waters only as a minor constituent.

Zinc is also toxic to aquatic organisms; the degree of toxicity varies among species and as the quality of water. Since fauna and flora are particularly sensitive to an over supply of zinc, the release of this metal has been regarded as the chief detrimental influent.

The main pollutant sources of zinc are industrial effluents, sewage sludge, mining effluents, agricultural sources such as animal wastes, fertilizers, pesticides and eroded soil. Klein *et al.* (1974) and Dean *et al.* (1972) have presented and compiled data on the concentration of zinc in the effluents from various industries and the major industrial uses of zinc.

The significance of pH and chloride ion concentration on the behaviour of heavy metal pollutants was studied by Hahne and Kroontje (1973) and the results indicated that both chloride and hydroxy complexes contributed to the mobilization of Zn^{2+}. The adsorption behaviour of Zn(II) on clay minerals in the presence of a complexing agent was studied by Huang *et al.* (1988). Kiekens (1990) summarised the environmental chemistry of Zinc. Holliday and Liss (1976), Danielsson *et al.* (1983) and Paulson *et al.* (1989) have reported the conservative behaviour of Zn in large unpolluted estuarine systems while Duinker and Nolting (1982) and Campbell *et al.* (1988) have reported the non-conservative behaviour of zinc in polluted estuary.

Total zinc content of the sediments varied from 7.42 to 148.75 µg/g along Kerala Coast, 29.29 to 290.49 µg/g in the sediments of Cochin estuary and from 25.37 to 70.56 µg/g in the sediments of Chaliyar estuary. Zinc was found to be the third abundant heavy metal in the sediments of Chaliyar estuary and Kerala Coast while comparable amounts of Zn and

Mn were present in the sediments of Cochin estuary. This is attributed to the anthropogenic input of zinc into the Cochin estuary (Sankaranarayanan *et al.*, 1978; Paul and Pillai, 1983; Ouseph, 1987; Nair *et al.*, 1990 and Shibu *et al.*, 1990) Figs. 5.4.1, 5.4.2 and 5.4.3 depict spatial distribution patterns of various fractions of zinc in the sediments of Kerala Coast, Cochin estuary and Chaliyar estuary.

The exchangeable fraction of zinc was found to be below detection limit for most of the coastal sediment samples. The ionic strength of the coastal waters causes the desorption of Zn^{2+} ions from the adsorbed sites due to the low affinity of Zn towards clay minerals (Mitchell, 1964). The difference in adsorption behaviour of copper and zinc is attributed to the polarization effects, since both copper and zinc have similar ionization potentials and the only difference between Cu^{2+} and Zn^{2+} is the presence of an unpaired electron in the 3d orbital of copper, whereas there is no such unpaired electrons in the 3d orbital of Zn^{2+}. The values of Zn1 in the sediments of Cochin estuary ranged from 0.03 to 5.35 ug/g with a relative contribution of 0.07 to 1.84% towards the total zinc. The very high percentage as well as the absolute value of Zn1 at station No.2 is attributed to anthropogenic input of Zn from the sewage sludge drained at and around this station. Previous investigators also noted the same trend (Nair *et al.*, 1991, Kunhikrishnan Nair, 1992) Zn1 values ranged from 0.095 to 0.29 µg/g in the sediments of Chaliyar estuary with a relative contribution of 0.12 to 0.59% of the total metal. A progressive downstream decrease in Zn1 values both in absolute and relative terms was observed with a 2 - fold enrichment in absolute values at the barmouth. The observed down stream decrease in Zn1 might be due to the desorption of metal under the increasing influence of calcium and magnesium with sea water mixing. The enhancement in the absolute values of Zn1 at the barmouth could be attributed to the enhanced availability of exchange sites because of the settling of finer suspended particles as a consequence of estuarine mixing.

The relative contribution from Zn2 is also less for the coastal sediments, ranging from 0.29 to 2.36%. On the contrary Zn2 fractions have significant contribution to the total metal in the estuarine sediments. According to Miller *et al.*, (1972), during estuarine mixing, due to the increase in pH, the solubility product of Calcium carbonate is drastically reduced and $CaCO_3$ is precipitated in the mixing zone carrying heavy metals from solution with it. Deurer *et al.*, (1978) has also reported the co-precipitation mechanism for Zn and Cd with calcium carbonate minerals in the lake sediments. The progressive down stream enhancement of Zn2 values in the sediments of Cochin estuary can be attributed to the co-precipitation with calcium carbonate during estuarine mixing. The very high value of 27.99 μg/g of Zn2 at station No.2 might be due to the enrichment in the phosphate rich sewage sludge since the high affinity of phosphate for zinc being a well established factor (Burrow, 1987; Kiekens, 1990). The sheltered sedimentary environment at station No.2 (Pillai, 1989) also assists the retentivity of the anthropogenic input of Zn in the sediments of station No.2 itself. The enrichment of Zn2 at station No.3 of Chaliyar estuary could be attributed to the influence of phosphatic fertilizers applied to the agricultural lands.

Contribution from Zn3 is also much less in the coastal sediments except for Cochin coast. However, the Zn3 has significant contribution towards total zinc in the sediments of Cochin and Chaliyar estuaries, ranging from 1.98 to 4.47% and 1.12 to 3.18% respectively. In both the estuaries the distribution pattern of Zn3 resembled that of Mn3 as was expected. The depletion of Zn3 in the coastal sediments might be due to the formation of insoluble sulphides, in suboxic sediments. Huerta-Diaz and Morse (1990) have reported that the metals associated with manganese oxides could be released first and made available for sulphide formation before those associated with iron oxides.

The Zn4 values ranged from 1.13 to 16.51 μg/g with a relative contribution of 2.78 to 19.35% in the sediments of Kerala coast. The distribution pattern of Zn4 resembled that of Cu4 and Fe4 except for Canannore. The percentage contribution from Zn4 was found to be much more in estuarine sediments ranging between 20.2 and 34.34% of total Zn in Cochin estuary and between 14.9 and 28.97% of ZnT in the sediments of Chaliyar estuary. The high Zn content observed in the moderately reducible fraction of estuarine sediments corroborated with the opinions about close association of Zn and colloid iron oxides (Brehler and Wedepohl, 1970). The distribution pattern of Zn4 more or less resembled that of Cu4 and Fe4 in estuarine sediments also.

The Zn5 was found to be the most abundant fraction of zinc in the sediments of Kerala Coast. The absolute values ranged from 1.55 to 56.5 µg/g with a relative contribution of 20 to 67.4% of the total zinc in the coastal sediments. In the estuarine sediments of Cochin also, Zn5 was found to be the most abundant fraction. Comparatively high Zn level in the organic and sulphidic fraction is probably associated with the sulphidic part of this fraction, as zinc may even in estuarine conditions, form sulphide minerals. However, according to Luther et al.(1980), elevated zinc concentrations favour the co-precipation of Zn and Fe sulphide minerals, particularly pyrite, which also has been identified in the sediments of the Krka River Estuary (Prohic, 1984) and in the sedimets of Baffin Bay and Mississippi Delta (Huerta-Diaz and Morse, 1990). The relative contribution from Zn5 was found to vary from 14.9 to 28.7% of the total Zn in the sediments of Chaliyar estuary. The absolute values ranged between 3.8 and 19.49 µg/g. Comparatively low percentage of Zn5 in the sediments of Chaliyar estuary might be due to the lack of contribution from sulphides because the formation of sulphides require a very high concentration of zinc in the sediments, which was not the case with the sediments of Chaliyar estuary. The distribution pattern of Zn5 was found to be more or less similar to that of Fe5.

The residual fraction of Zn was found to be the second most abundant fraction of Zn in the coastal sediments of Kerala. The Zn6 values ranged from 4.65 to 44.28 µg/g with a relative contribution of 26.4 to 62.7% of the total zinc. The very high percentage of Zn6 in the sediments of Quilon was attributed to the coarse sandy texture and the low organic carbon content of the sediments. The order of abundance of various fractions of zinc in the coastal sediments was observed to be Zn5 > Zn6 > Zn4 > Zn2 > Zn3 > Zn1. A notable feature in the distribution of Zn6 was the minimum variability observed among the coastal sediments from various stations excluding stations off Quilon.

The Zn6 values varied between 14.45 and 46.21 µg/g contributing 12.9 to 52.3% towards the total Zn in the sediments of Cochin estuary. In absolute values sediments of station Nos. 4 and 2 had the highest content of Zn6. The enrichment of Zn6 at station No.4 is attributed to the detrital origin of this fraction (Salomons and Forstner, 1980) whereas the low percentage of Zn6 at station No. 2 indicated that the anthropogenic inputs of Zn were usually present in labile 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.*,

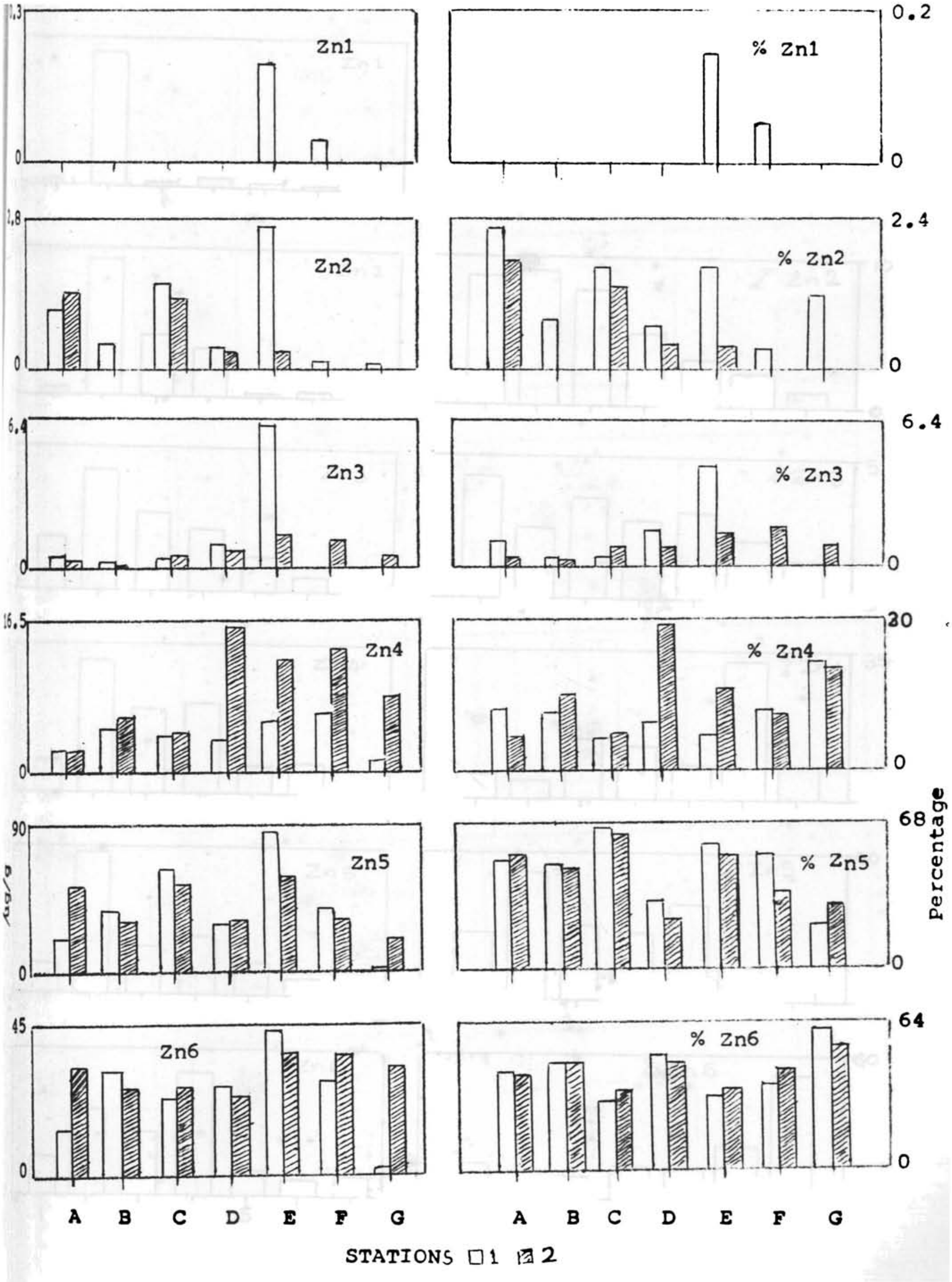


FIG.5.4.1. The distribution pattern of various fractions of Zn in the sediments of Kerala Coast.

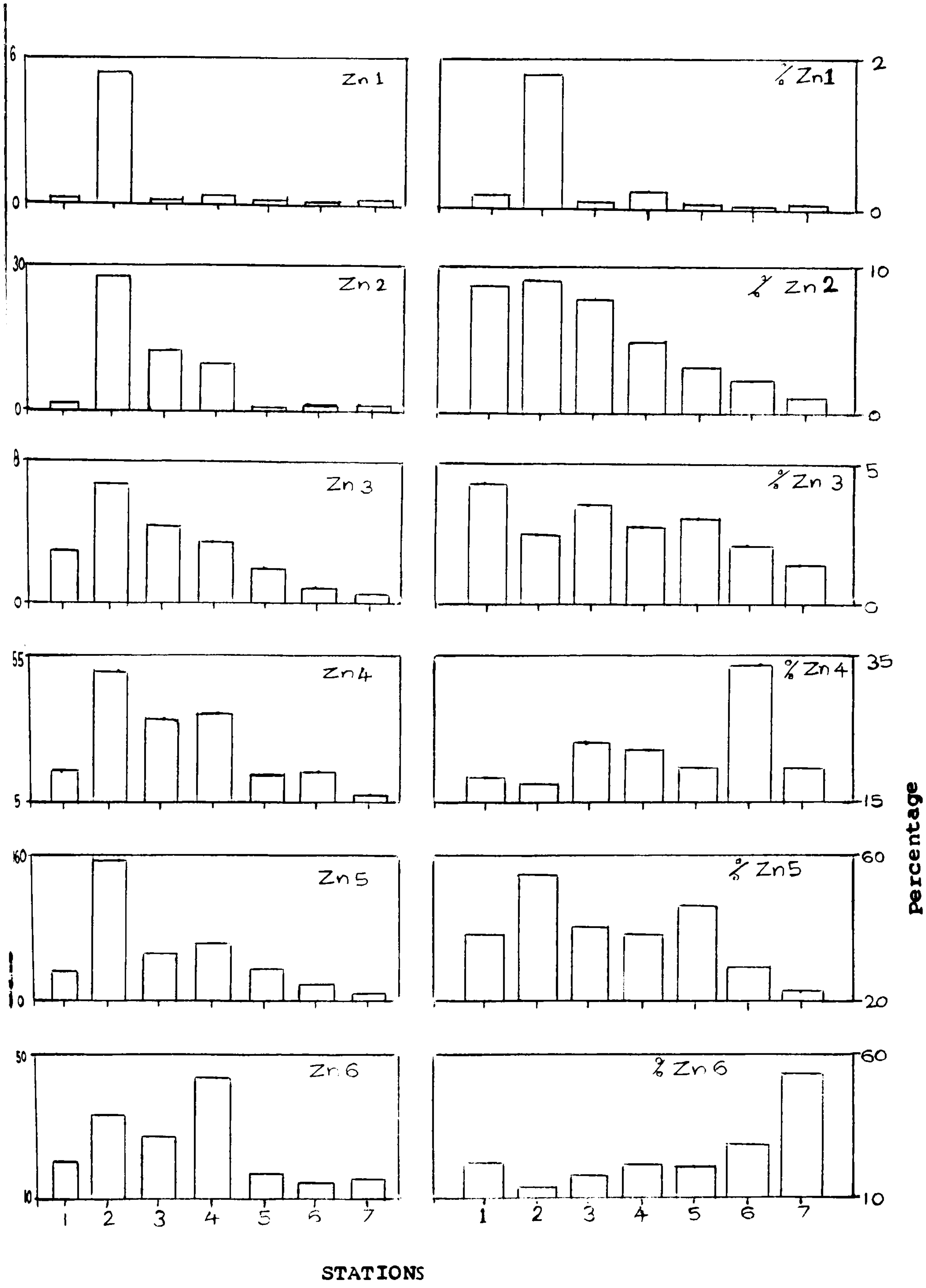


FIG.5.4.2. The distribution pattern of various fractions of Zn in the sediments of Cochin estuary.

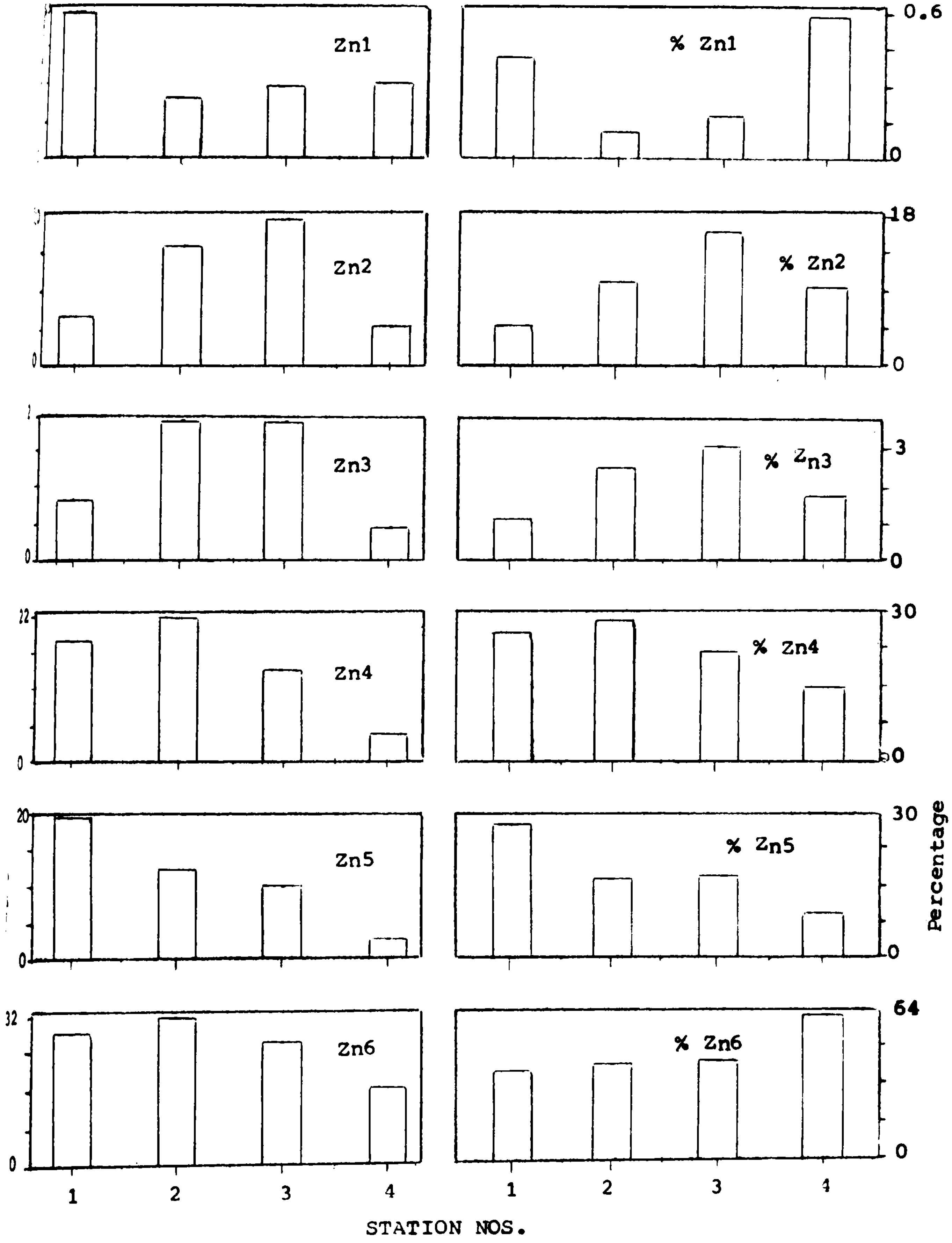


FIG.5.4.3. The distribution pattern of various fractions of Zn in the sediments of Chaliyar estuary.

Location	E.F.	C.F.	E.R.F.	M.R.F.	O & S.F.	R.F.	Total Zn /µg/g	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	33.7	8.3	12.7	921	Forstner,1982
Weser estuary	4		45	38	2	12	350	Calmano and Forstner,1983
Rotterdam harbour	1		59	37	1	3	1130	-do-
Neckar river	3		48	34	2	13	610	-do-
Subae river-unpollluted			9.6		17.3	73.1	31	Patchineelam and Forstner,1983
- Polluted			34	42.4	6.2	17	1117	-do
Yellow river	0.3	1	3	19	24	52	40	Hong and Forstner,1983
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 estuary	1.76	4.21	13.65		50.36	30.02	81	-do-
Pennsylvania (sludge)	0.5	17		34	6	42	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	Kunhikrishnan Nair,1992
Kerala coast Range	bdl	0.29-2.36	bdl	2.78-19.45	20-67	26.4-63	7.42-148.75	Present study
Cochin Estuary	.07-1.8	1.4-9.6	1.98-4.47	20.2-34.3	23-54	13-52	29.3-290.5	-do-
Chaliyar Estuary	0.12-0.59	4.8-16.1	1.12-3.2	15-29	15-29	39-64	25.37-70.6	"

Table 5.4 Percentage of zinc fractions reported in sediments from different geographical locations.
bdl - below detection limit.

1990). The order of abundance of various fractions of Zn in the surface sediments of Cochin estuary decreased in the order Zn5 > Zn6 > Zn4 > Zn2 > Zn3 > Zn1

In the surficial sediments of Chaliyar estuary Zn6 was found to be the most abundant fraction and the order of abundance of various fractions as observed was Zn6 > Zn4 > Zn5 > Zn2 > Zn3 > Zn1. The higher percentage of Zn6 along with the lower values for ZnT indicated that at present there is no serious threat of Zn pollution in the Chaliyar estuary.

The results of present study are compared with available data on partitioning of Zn in sediments, recorded for various aquatic systems from different parts of the world, (Table 5.4). The major difference observed was in the percentage - wise distribution of Zn6 in the Cochin estuary as reported by Kunhikrishnan Nair (1992), which is attributed to the non-differentiation of moderately reducible fraction in his methods.

5.5. Lead

Lead is a cumulative poison to human beings. The large affinity of Pb^{2+} for thiol and phosphate containing ligands inhibits the biosynthesis of haeme and thereby affects membrane permeability of kidney, liver and brain cells. This results is either reduced functioning or complete breakdown of these tissues. Metabolism of Pb and Ca are similar both in their deposition and in mobilization from bone. Since Pb can remain immobilized for years, metabolic disturbances can remain undetected. Under normal conditions more than 90% of the lead retained in the body is in the skeleton. Although lead is a non-essential element it is present in all tissues and organs of mammals. The main sources of input of lead are atmospheric fall out (Piotrowicz *et al.*, 1973; Duce *et al.*, 1972; Shiomi, 1973; Patterson *et al.*, 1976, Huntzicker *et al.*, 1975; Goldberg, 1975 a), smelting operations and highway runoff along with sewage sludge. Though many investigators studied the toxicity effects of lead, the data on the behaviour of lead in aquatic environment is meagre, mainly because of the associated analytical problems (Elbaz - Poulichet *et al.*, 1984, Windom and Smith, 1985).

The total lead content of the coastal sediments varied from 17.9 to 80.9 µg/ g, from 33.2 to 117.06 µg/g in the sediments of Cochin estuary and from 20.1 to 88.1 µg/ g in the sediments of Chaliyar estuary. A unique feature noted in the distribution of Pb was its depletion in labile form towards offshore region. It might be due to the precipitation as $PbCl_2$ by exceeding the very low solubility product of $PbCl_2$ ($Ksp = 1.7 \times 10^{-5}$) under the influence of high chloride ion concentrations in the marine waters.

In the coastal sediments Pb1 fraction was found to be below detection limit for all the station due to the precipitation of $PbCl_2$ due to the high activity of chloride ions in the coastal water, since the concentration of metal ion in the initial stages of precipitation is primarily dependent upon the activity of the anionic species, in the solution (Forstner, 1979). In the sediments of Cochin estuary Pb1 content varied from 1.5 to 7.8 µg/g with a relative contribution upto 7.08% to the total Pb content of the sediment samples. The high content of Pb1 at station Nos.2 and 4 are attributed to the anthropogenic input of lead to these stations through sewage sludge. Comparatively higher value of Pb1 at station No.2 is due to the dredging operations carried out in this region. Though the distribution pattern of Pb1 in the Cochin estuary resembled that of Cu1 and Zn1 much higher concentration of Pb was observed in the exchangeable fraction compared to Cu and Zn both in absolute and relative terms. This could be explained on the basis of the selective affinity of the clay minerals for lead. Mitchell (1964) established the following - empirical sequence for the affinity of heary metals towards clay minerals : Pb > Ni > Cu > Zn. Soong (1974) accounted for these effects with the explanation that lead has a special affinity for the clay mineral structures due to its ionic radius, which is very similar to that of potassium. At the same time, lead is also capable of replacing potassium in the montmorillonite lattice (Marshall, 1949).

In the surficial sediments of Chaliyar estuary Pb1 content varied from 0.91 to 3.4 µg/g contributing 3.83 to 8.09% to the total Pb. In Chaliyar estuary also the percentage contribution of Pb1 was found to be much higher compared to Zn1 or Cu1. The very high values for Pb1 observed at station No.3 might be due to same anthropogenic input corroborated with the Mn1 value, at station No.3. The percentage wise decrease at the barmouth is due to precipitation of $PbCl_2$, because of the high activity coefficients of chloride ions in the overlying bottom warers of the barmouth.

Comparatively higher percentage of Pb2 was found to be present in the coastal sediments of Kerala. Except for Kasargode stations, the Pb2 content of off shore sediments was found to be below detection limits which might be due to the preferential precipitation of $PbCl_2$, since the solubility product of $PbCl_2$ is very low compared to other heavy metal and alkali metal chlorides. The concentration of chloride ions are very high in the sea water having ionic concentration approximately 5.46×10^{-1} for 35×10^{-3} salinity which is very high compared to the solubility product of $PbCl_2$ ($Ksp = 1.7 \times 10^{-5}$). Though the solubility product of $PbCO_3$ is still lower, the relative abundance of chloride ions in the seawater causes the preferential precipitation of $PbCl_2$ even in presence of verylow concentration of labile form of Pb^{2+}. The high percentage of Pb2 at Kasargode stations was attributed to the mineralogical peculiarities of the sediments of Kasargode (Murthy et al., 1973).

The Pb2 values ranged from 0.91 to 7.5608 µg/g with a percentage wise contribution of 1.84 to 13.4% to PbT, in the surficial sediments of Cochin estuary. The Pb2 values of surficial sediments of Chaliyar estuary varied between 0.45 and 5.15 µg/g contributing 2.25 to 12.14% towards PbT. The distribution pattern of Pb2 in Chaliyar estuary resembled that of Mn2. Coprecipitation with $CaCO_3$ (Popova, 1961) might be the reason for the enrichment of Pb2 fraction towards the barmouth.

Pb in the easily reducible fraction was found to be very low, below detection limits for most of the sediment samples of the coastal and estuarine regions. On the other hand considerable amount of Pb was found to be present in the moderately reducible fraction. The reduction and mobilization of manganese in the sediments at a higher oxygen potential (Tessenow and Baynes, 1975) than that for ferric complexes might be the reason for the depletion of Pb in easily reducible fraction; more than 85% of which was reported to be associated with hydrous oxides of Mn (Brannon et al., 1977). The Pb4 values ranged from below detection limit to 11.4 µg/g with a relative contribution upto 22.85% towards the total Pb content of the coastal sediments. As was seen in the case of Pb2, Pb4 values also showed a decline towards the off shore region. Though relative contribution from Pb4 was considerable in the surficial sediments of Cochin estuary, the distribution pattern did not show any peculiar trend. Very high values of Pb4 at station No.4

could be attributed to the anthropogenic input. However both the absolute and relative values of Pb4 showed a sharp decline towards upstream, in the surficial sediments of Chaliyar estuary. The distribution pattern resembled that of Fe4, with very high values at the barmouth (both absolute and percentage values).

In the coastal sediments of Kerala, a very high percentage of Pb was seemed to be bound with the organic and sulphidic fraction indicating the contribution from precipitated sulphides and chlorides of Pb in the coastal environment, as the extractant used (ammonium acetate) after H_2O_2 digestion was capable of dissolving $PbCl_2$. The relative stability of organic complexes of Pb (Irving - Williams, 1948; Gold berg, 1965 and Bowen, 1966) is also a main factor in the enrichment of Pb in the organic and sulphidic fraction.

In the surface sediments of Cochin estuary Pb5 values ranged from 5.3 to 22.9 μg/g in terms of absolute value and in relative terms from 16.2 to 32.6% with a percentage wise increase towards the down stream. The very high percentage of Pb5 at station No.5 is attributed to the enrichemnt followed by 'eutrophication' due to the high phytoplankton productivity of this area as was reported by Joseph and Pillai (1975). The distribution pattern of Pb5 in the surface sediments of Chaliyar estuary closely resembled that of organic carbon content of the sediments. The Pb5 values ranged from below detection limit (recorded for the upper most station) to 18.97 µg/g with a relative contribution upto 21.5% of total lead in the sediments of Chaliyar estuary. A similar distribution pattern for Cu5 and Zn5 and more or less the comparable percentage of these three metals were observed in the sediments of Chaliyar estuary. This implied that the organic matter content of the sediments is the main controlling factor, which determined the relative partitioning of these three metals in the organic and sulphidic fraction of the surface sediments of Chaliyar estuary.

Pb6 was found to be the most abundant of the lead fractions determined in the sediments of both coastal and estuarine regions. In the coastal sediments of Kerala the values varied between 6.3 and 50.64 µg/g with a percentage wise contribution upto 100%. The increased percentage of Pb6 along with the reduced values for PbT in the offshore sediments suggested that the other forms of lead recorded in the sediments were quite unstable and were susceptible to transformation at high saline conditions. A unique feature noted was the depletion of labile fractions of Pb in the sediments of offshore stations and this forms a corroborative evidence to the above suggestion. In short lead in marine environment was highly 'immobilized' by transformation into stable residual form.

In the sediments of Cochin estuary Pb6 values ranged from 14.46 to 58.93 µg/g, contributing 32.6 to 75.84% to the

PbT. The very high percentage Pb6 even in the sediments receiving anthropogenic input of lead indicated that the labile fraction of lead in the estuarine environment has only a very small residence time, which got converted rapidly to the stable residual form, at the site of input itself.

The percentage of Pb6 in the surficial sediments of Chaliyar estuary was also very high contributing upto 87.0% of the total Pb content. The percentage wise distribution pattern of Pb6 resembled that of Mn6, while in terms of absolute values the distribution pattern was more or less similar to that of Cu6. Murthy and Veerayya, (1981) and Satayanarayana et al., (1985) have reported that in nearshore environments metals like copper and lead were associated with the smallest size sediment particles. These particles flocculated only when subjected to rapid environmental changes as estuarine mixing. The enrichment of both total and various fractions of lead observed at the barmouth of Chaliyar estuary could be attributed to the settling of flocculated suspended particles.

Figs. 5.5.1, 5.5.2 and 5.5.3 depict the spatial distribution pattern of various fractions of pb in the sediments of Kerala Coast, Cochin estuary and Chaliyar estuary. The results of the present study are compared with the data reported by several investigators from different geographic locations of the globe, details of which are furnished in Table 5.5.

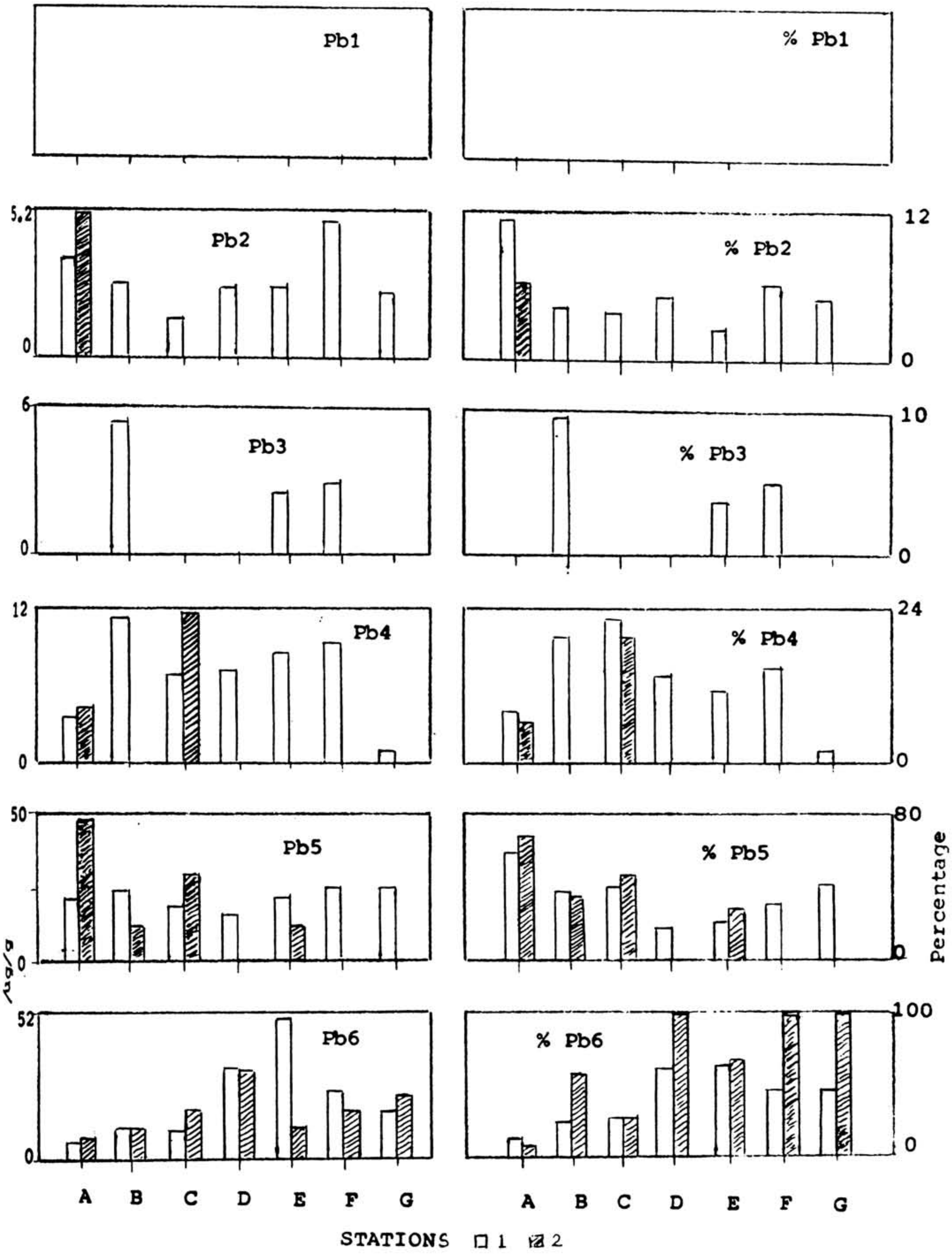


FIG.5.5.1. The distribution pattern of various fractions of Pb in the sediments of Kerala Coast.

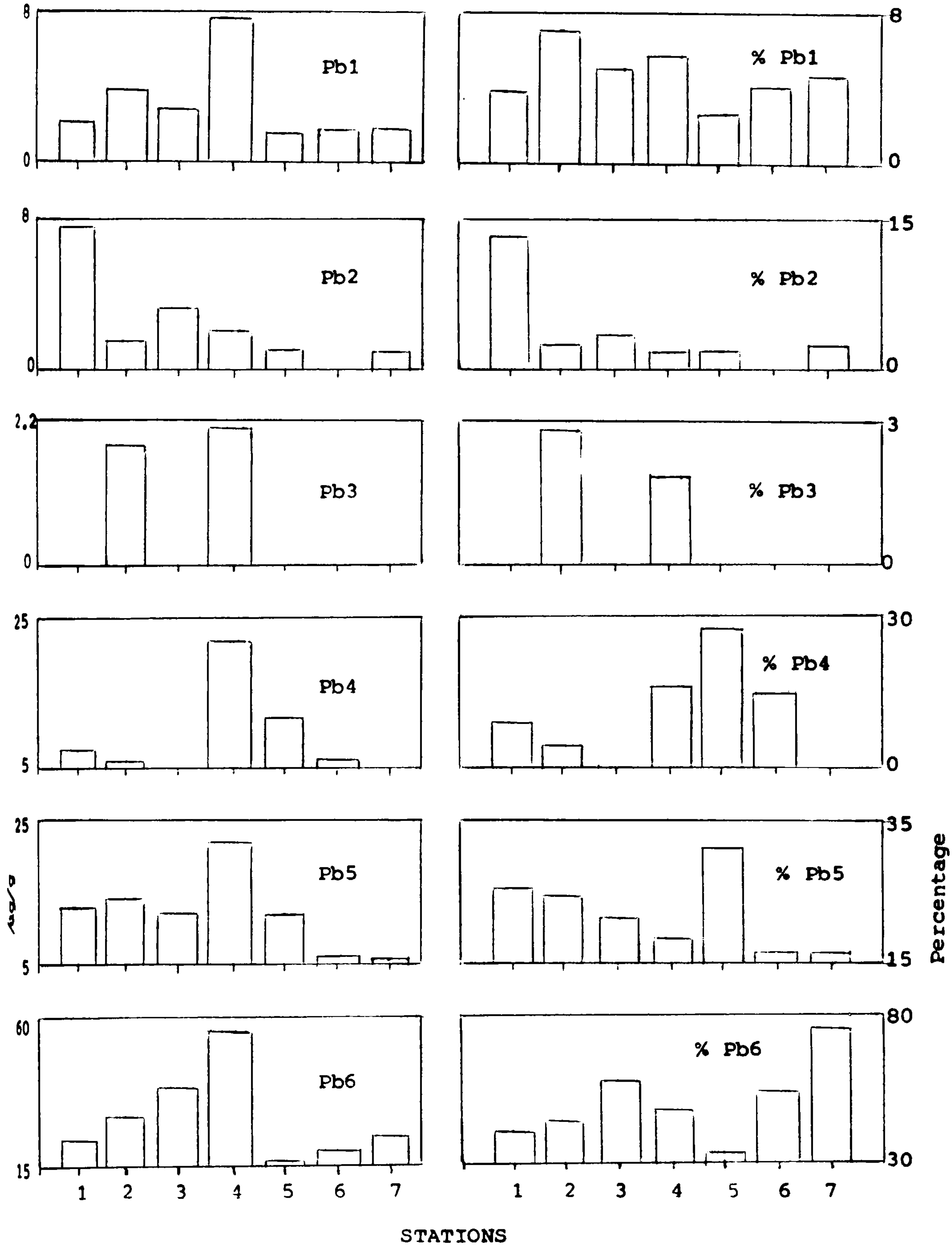


FIG.5.5.2. The distribution pattern of various fractions of Pb in the sediments of Cochin estuary.

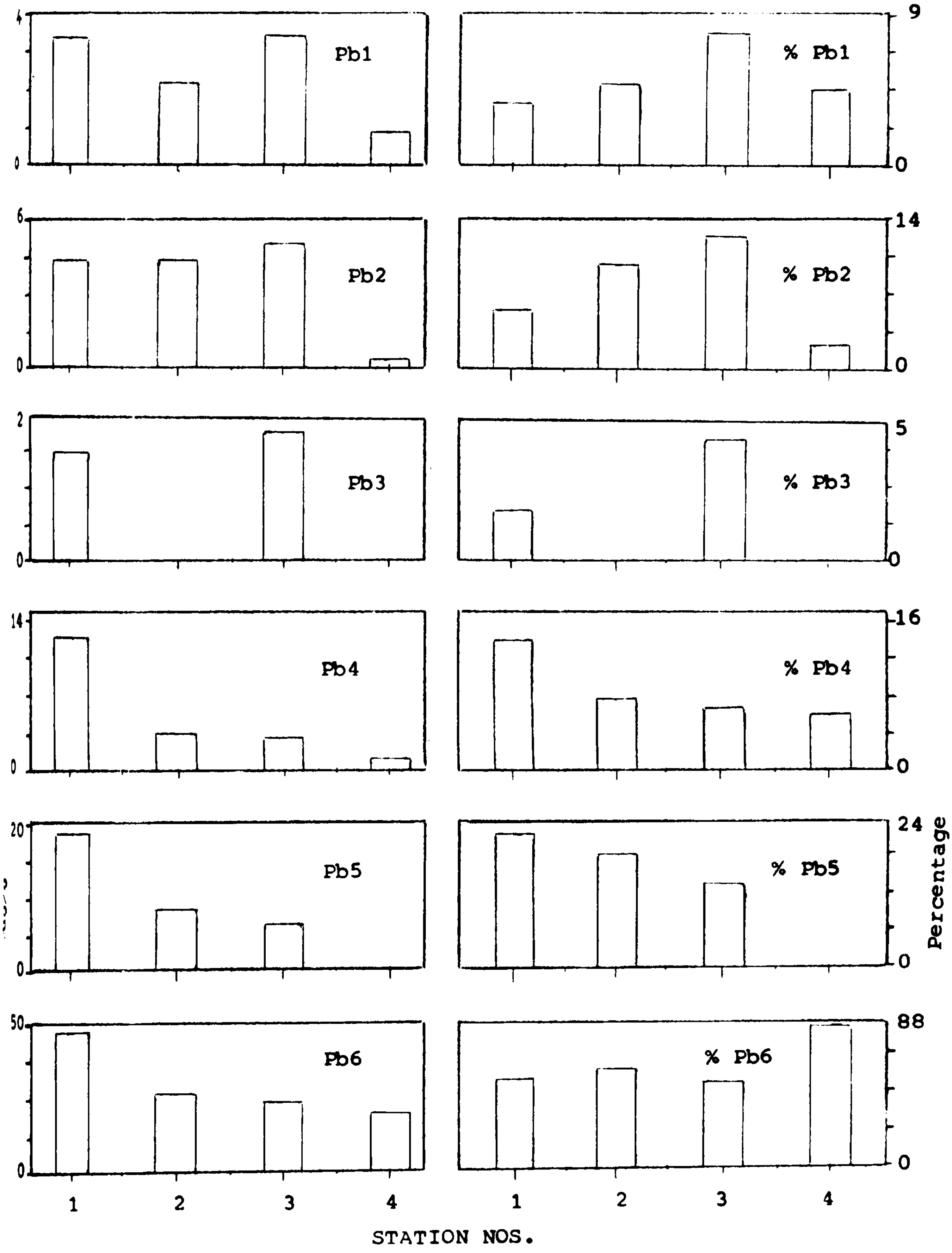


FIG.5.5.3. The distribution pattern of various fractions of Pb in the sediments of Chaliyar estuary.

Location	E.F.	C.F.	E.R.F.	M.R.F.	O&S.F.	R.F.	Total µg/g	References
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	38.6	5.2	54.1	118	Forstner,1982
Weser estuary	2		2	41	2	53	69	Calamano and Forstner,1983
Rotterdam harbour	<1		66	18	1	15	256	-do-
Neckar river	<1		2	22	28	48	150	-do-
Subae river-unpolluted						100	25	Patchineelam and Forstner,1983
-polluted			17.8	44	30.1	8.1	1775	-do-
Yellow river	0.3	16	4	51	<1	30	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 estuary	0.23	24.65	19.72		29.55	25.85	156	-do-
Aliakmon river	0.21	24.68	16.09		35.40	23.62	95	-do-
Pennsylvania (sludge)	4.20	2.60		8.4	13.0	72.0	204	Elliot et al.,1990
Nile river-range	bdl-2.1	bdl-9.6	bdl-0.6	12.8-33.3	26.7-70	7.6-36.7	15-184	Elsokkary and Muller,1990
Cochin Estuary	2.86	4.32	5.68		10.37	76.78	15	Kunhikrishnan Nair,1992
Kerala Coast Range	bdl	bdl-11.7	bdl-9.1	2.3-23	bdl-60	14-100	17.9-80.9	Present Study
Cochin Estuary Range	<7.08	1.81-13.4	bdl	bdl-29.1	16.2-32.6	32.6-75.4	33.2-117.1	-do-
Chaliyar Estuary Range	3.8-8.1	2.3-12.1	bdl	1.4-4.2	bdl-21.5	53.5-87.04	20.1-88.1	-do-

Table 5.5 Percentage of lead fractions reported in sediments from different geographical locations.
bdl-below detectable limit

Can we [illegible] Pb [illegible]
[illegible]

Though lead is very toxic to biota, studies showed that the 'bioavailability' of lead in the estuarine and marine environments is much reduced through the geochemical 'immobilization' of this metal in these environments.

5.6 Cadmium

The chemistry of cadmium is similar to that of lead and zinc. Cadmium is found in nature largely in the form of the sulphide and as an impurity in zinc and lead ores. The abundance of Cd is much less than that of zinc.

Cadmium may enter surface waters as a consequence of mining and smelting operations. Cd may be present in waters from electro plating plants, pigment works, textile and chemical industries (Alloway, 1990) Ground water Cd concentrations as great as 3.2 mg/l have resulted from the seepage of Cd from electroplating plants (WHO, 1982). Metal and plastic pipes constitute an additional possible source of Cd in waters.

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Cd is toxic to man. The reproductive organs may be affected after the administraton of very small doses. Cd is concentrated in the kidneys. There is some evidence that Cd may be carcinogenic to experimental animals and it has been implicated in human prostate carcinoma. A specific disease known as "itai - itai" has been observed in Japan (Friberg et al., 1974).

In the aquatic environment fish and certain invertebrates have been found to be sensitive to very low levels of Cd in water. As a result of bioaccumulation, certain edible organisms may become hazardous to the ultimate consumer. In the view of the accumulation of cadmium in the human body, the factors influencing its biomagnification 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 emission etc. are recommended (WHO, 1982).

Studies on the behaviour of cadmium in aquatic envioronments received attention along with the studies on copper, zinc and lead. The chemistry, bio-chemistry and biology of cadmium has been described by Peterson and Alloway (1979). A compilation "cadmium in polluted sediments" has been performed by Forstner (1980) for J.O.Nriagu's work on 'Biogeochemistry of Cadmium'. 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. The release of cadmium into the dissolved phase from the contaminated particulates of Gironde estuary has been reported by Jouanneau *et al.* (1990). Previous investigators have reported the anthropogenic input and the accumulation of Cd in the surface sediments of Cochin estuary (Nair, *et al.*, 1990; Nair *et al.*, 1991; Shibu *et al.*, 1990, Paul and Pillai, 1983; Kunhikrishnan Nair, 1992). However, published data on the distribution of Cd in the Chaliyar estuary is not yet avilable.

Estuarine behaviour of Cd is well documented and shows a general tendency to desorption in macrotidal estuaries (Boyle et al., 1982, Edmond et al., 1985; Duinker et al, 1982; Boutier et al, 1989).

Cadmium was found to be the least abundant metal in the sediments during the present study. In the coastal sediments CdT values ranged from 1.14 to 5.17 µg/g where as the sediments of Cochin estuary have CdT content upto 9.36 µg/g. The notable feature observed in the Chaliyar estuary was not only the very low CdT content of sediments but the 100% lithogenous origin also for barmouth, irradicates the existence of any possibility of anthropogenic input of Cd into the estuary. Below detection limit values other than for residual fraction restrains any further discussion pertaining to the partitioning of Cd in the sediments of Chaliyar estuary. The distribution pattern for various fractions of Cd in the sediments of Cochin estuary and Kerala coast are depicted in Fig 5.6.1 & 5.6.2.

The values of Cd ranged from 0.25 to 1.12 µg/g in the coastal sediments and from 0.012 to 0.22 µg/g in the sediments of Cochin estuary. The percentage wise distribution of Cd in the coastal sediments (up to 25.9% of CdT) was found to be very high compared to the other 5 metals studied. This implied that Cd was highly mobilised in coastal environment. Higher concentration of dissolved Cd in the coastal waters and depletion in suspended particulate matter provided corroborative evidences. Thus the high content of Cd in the coastal sediments could be attributed to the leach out of Cd from the suspended particulates, a fraction of which was solubilised and the rest occupying the exchangeable sites on the surface sediments. Recently Boutier et al.(1993) have reported the enrichment of dissolved Cd in the high saline waters of Loire estuary due to the desorption from suspended particulates. The Cd content in the sediments of Canannore was found to be minimum whereas the particulate Cd was as high as 23.34 µg/g in the bottom waters at this station.

The percentage wise contribution of Cd1 ranged from 0.81 to 2.99% of the total Cd in the sediments of Cochin estuary. Station No.4 has high values for Cd1 indicating some anthropogenic input. Higher percentage of Cd1 in the upstream sediments can be attributed to the removal of Cd from the dissolved fraction of Cd in the overlying waters at low salinity region as reported by Sholkovitz (1978) and Boutier et al. (1993). The depletion of dissolved Cd observed in the low saline estuarine waters, also supports this arguement.

In the coastal sediments the values of Cd2 varied from below detection limit to 0.78 µg/g with a relative contribution upto 25.14%. This could be attributed to the coprecipitation of $CdCO_3$ along with $CaCO_3$ as was described by Seibold (1964).

The Cd2 values in the sediments of Cochin estuary varied from 0.22 to 1.1 µg/g contributing 5.2 to 16.7% of CdT. The distribution of Cd2 showed a progresssive increase towards downstream indicating the coprecipitation of insoluble $CdCO_3$ with $CaCO_3$ during estuarine mixing as a result of pH increase. During estuarine mixing, the pH of river water will increase, consequently the solubility product of $CaCO_3$ is drastically reduced. $CaCO_3$ is precipitated in the mixing zone, carrying heavy metals from solution with it. Patchineelam (1975) has reported 10 fold enrichment of Cd in the $CaCO_3$ precipitate of Elbe River estuary as a result of the mixing of normal river water with alkaline effluents from an industrial plant. The observed low percentage of Cd2 at station No.5 was due to the relative low phophate content in this fraction of the sediment of this station, since the phosphate bound metal was also having significant contribution towards the so called `carbonate fraction'.

The very low content of Cd in the easily reducible fraction even below detection limits for most of the sediment samples from the coastal and estuarine region demands no further discussion.

Cd4 has significant contribution in the coastal sediments ranging upto 24.1% of CdT. The absolute values vary from 0.17 µg/g to 0.57 µg/g. According to Boutier et al. (1993), a fraction of dissolved cadmium in fresh water is present in a colloidal state, associated with hydrous iron oxides and humic acids. This fraction is removed from solution with the colloids at low salinity when flocculation occurs due to the augmentation of the divalent cations activity. Jenne (1976) stressed the role of clayminerals as mechanical substrate for the precipitation and flocculation of organics and hydrous iron oxides. In the coastal environment under the influence of high ionic activity, these clay particles settle down, thus causing an increase in the concentration of tracemetals in moderately reducible fraction in (Coprecipitated with hydrous iron oxide) coastal sediments. The minimum values for Cd4 observed in the sediments of Alleppey coast could be attributed to the relative desorption of Cd^{2+} (Van der Weijden *et al.*, 1977) due to the destabilisation of the iron-oxide in the organic-rich sediments (Jonasson, 1977) of Alleppey.

In the sediments of Cochin estuary the Cd4 values ranged from below detection limits to 0.1271 µg/g contributing upto 4.15% to CdT. The high percentage of Cd4 at station 5 was attributed to the flocculation of colloidal Cd present in the fresh water associated with hydrous iron oxide and humic acid, at low salinity region (Boutier et al. 1993).

However the absolute values of Cd4 increased towards down stream with more or less uniform distribution at and around the barmouth. Settling of fine suspended particulates having hydrous iron oxide coating as a consequence of estuarine mixing accounts for the above trend.

The percentage wise distribution of Cd5 in the coastal sediments varied from 20.18 to 52.07% with below detection limit values for the sediments of the Kasargode and Calicut coasts. The depletion of Cd5 in these coasts could be attributed to the release of Cd at the sediment seawater interface due to the low stability of organic complexes of Cd. Rohatgi and Chen (1975) have reported that upto 96% of Cd was released from suspended particulates from their studies on the effects of seawater on the concentration of trace metals in waste water particulates.

The Cd5 values in the sediments of Cochin estuary varied from 0.2356 to 4.2 µg/g with a relative percentage contribution from 8.63 to 44.93% The high percentage of Cd5 in estuarine region indicated the precipitation of Cd as sulphide during estuarine mixing.

The residual fraction of Cadmium Cd6 varied from 1.35 to 2.48 µg/g contributing upto 68.09% of CdT, except for the sediments of Cochin and Quilon coast, which are solely devoid of residual cadmium. Hence it could be inferred that the Cd determined in the sediments of these coasts are not of lithogenous origin ie: with respect to Cd, Cochin and Quilon coasts are highly polluted.

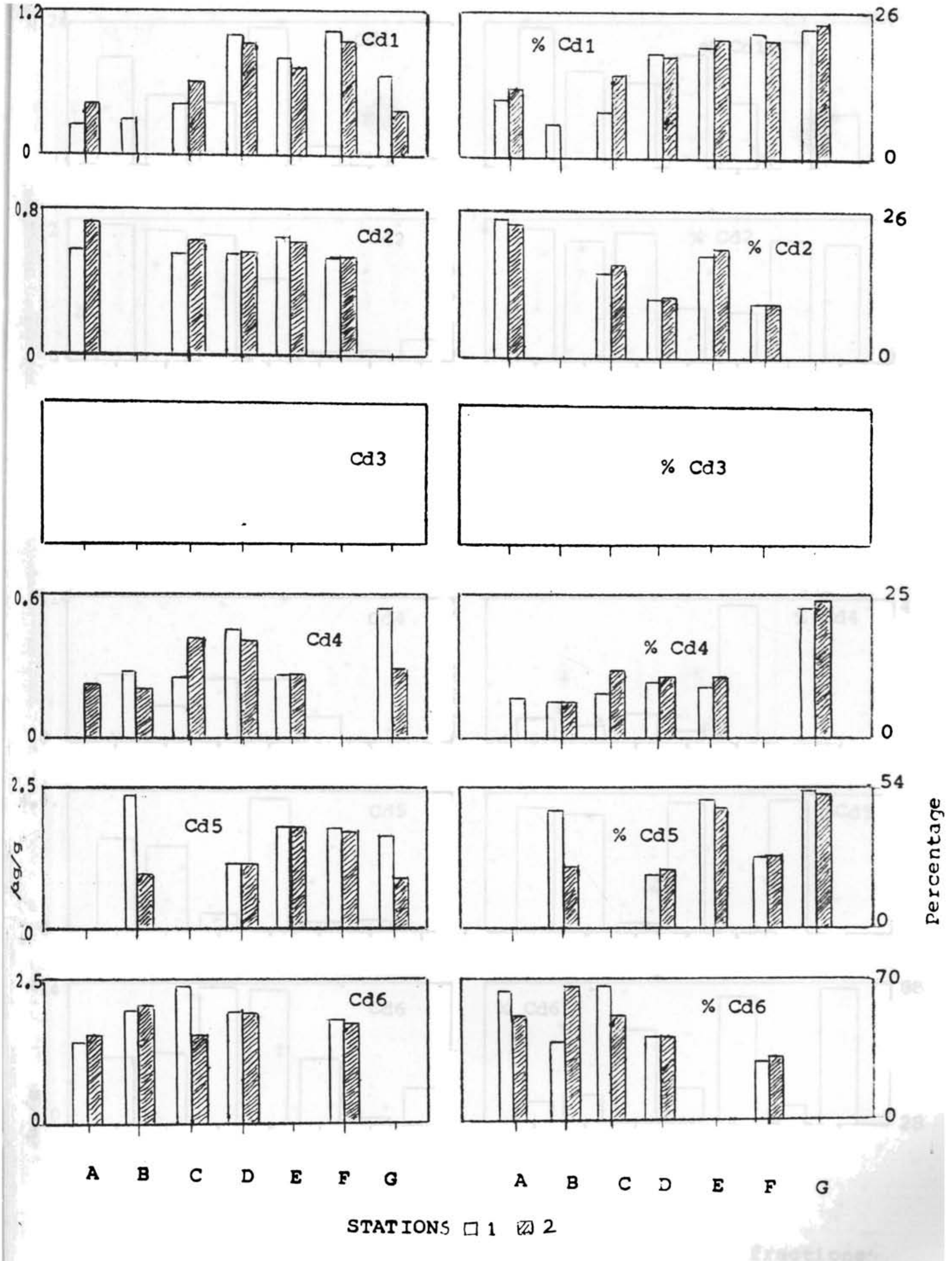

FIG.5.6.1. The distribution pattern of various fractions of Cd in the sediments of Kerala Coast.

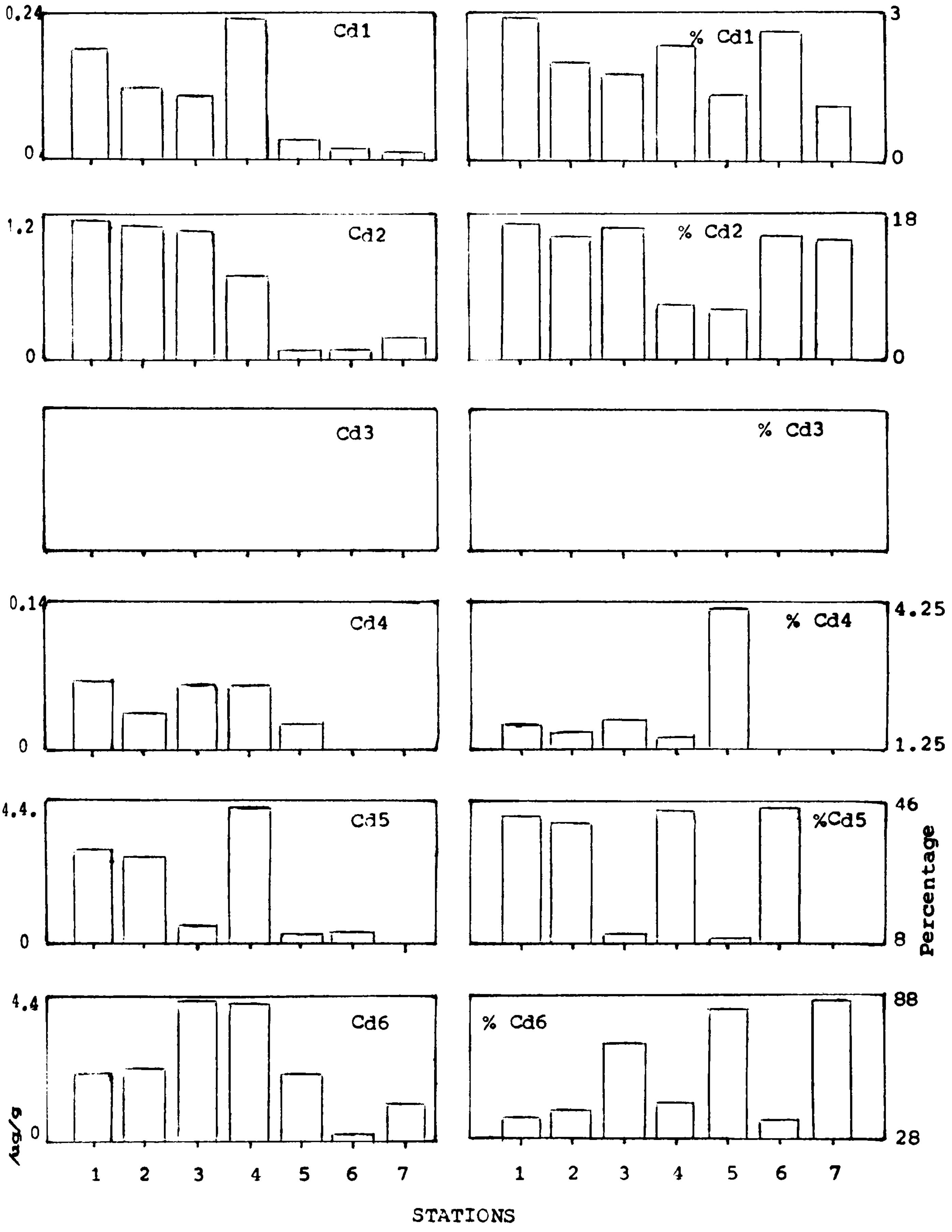

FIG.5.6.2. **The distribution pattern of various fractions of Cd in the sediments of Cochin estuary.**

Location	E.F.	C.F.	E.R.F.	M.R.F.	O & S.F.	R.F.	Total Cd /ug/g	Reference
Los Angels harbour	1	5	9	34	38	14	2.2	Gupta and Chen, 1975
Yamaska river-SPM	26	49	12		<1	12	59.8	Tessier etal. 1980
St. Francois river-SPM	28	31	13		<1	27	4	-do-
Rhine river	26.7		42.3	1.9	16.8	12.3	9	Forstner, 1982
Weser estuary	18		47	24	9	2	2.6	Calmano and Forstner, 1983
Rotterdam harbour	16		60	16	6	2	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	2.4	18.2	1.4	27.6	-do-
Yellow river	12.9	22	3	43	2	18	0.1	Hong and Forstner, 1983
Axios river	10.79	24.89	29.60	1	19.05	15.67	17.6	Samanidou and Fytianos, 1987
Axios estuary	9.59	35.53	22.16		10.77	22.13	13.5	-do-
Aliakmon estuary	1.03	15.25	41.43		24.80	17.49	1.7	-do-
Aliakmon river	1.22	13.54	42.82		24.10	18.32	2.0	-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	4.8-36.4	6.2-22.7	1.4-9.1	0.1-1.1	Elsokkary and Muller, 1990
Cochin Estuary-MEAN	5.76	7.48	8.13		34.90	43.73	1.7	Kunhikrishnan Nair, 1992
Kerala Coast Range	9.4-25.9	bdl-25.1	bdl	bdl-24.1	20.1-52.07	bdl 68.09	1.14-5.17	Present study
Cochin Estuary Range	0.8-2.9	5.2-16.7	bdl	bdl-4.2	8.63 44.93	35-80.8	0.97-9.4	-do-
Chaliyar Estuary range	bdl	bdl	bdl	bdl	bdl	100	bdl 0.75	-do-

Table 5.6 Percentage of cadmium fractions reported in sediments from different geographical locations.

bdl below detection limit

Cd – Kerala Coast – [illegible] [illegible]

The Cd6 values in the sediments of Cochin estuary varied from 0.35 to 4.39 µg/g contributing 35.67 to 84.82% of CdT. The low percentage of Cd6 and the high concentration of total Cd in the sediments of station No.4 clearly indicated the anthropogenic input of Cd through sewage sludge drained in and around station No.4. The relative percentage as well as absolute value of Cd6 at station No,3 was found to be higher indicating some anthropogenic input in the mineral form. The rock phosphate cargo handling at the near by harbour might be the enrichment factor for Cd6 at station No.3.

5.7 The significance of geochemical partitioning in the coastal ecosystem.

During the last two decades, considerable interest has been shown in the pathways of tracemetals in estuarine and coastal environments. The accumulation of these metals in various geochemical fractions of sediments as a result of domestic and industrial discharges is considered to be an important parameter for assessing environmental contamination. The spatial distribution pattern of the various geochemical fractions of tracemetals has been discussed in the previous sections of this chapter. In this section an attempt has been made to evaluate the significance of partitioning of tracemetals in the estuarine and coastal sediments of Kerala. Though the spatial distribution patterns were informative of the origin and pathways of tracemetal contaminants, a further discussion on the fate of these tracemetal contaminants in the aquatic environment is required.

For evaluating the behaviour of various metal fractions in the estuarine and coastal sediments, metal values recorded at the upper estuary, lower estuary and near shore regions were compared. Values of station No.7 of Cochin estuary and station No.4 of Chaliyar estuary represented the upper estuarine values. Station 1 values of both the estuary were taken as the representative of the lower estuarine region while the values for near shore sediments of Cochin and Calicut coasts were considered as that for the coastal region. The pie diagrams in figs 5.7.1 and 5.7.2 depict the quantification of various fractions of tracemetals in the sediments of upper estuarine (riverine), lower estuarine and near shore regions of Cochin and Calicut coast.

It is obvious from the figures that the exchangeable fraction of all the six metals except lead showed a lower-estuarine enrichment while the enrichment of exchangeable fraction in the sediments of coastal environment was observed in the case of only three metals : iron, manganese and cadmium. The maximum enrichment was noted in the case of cadmium in the coastal sediments followed by iron and manganese. The order of abundance of the percentage of exchangable metals decreases as Pb > Mn > Zn > Fe > Cu > Cd in Chaliyar estuary. While in the Cochin estuary the relative abundance decreases in the order: Pb > Mn > Cd > Cu > Zn > Fe, and in the near shore sediments the relative

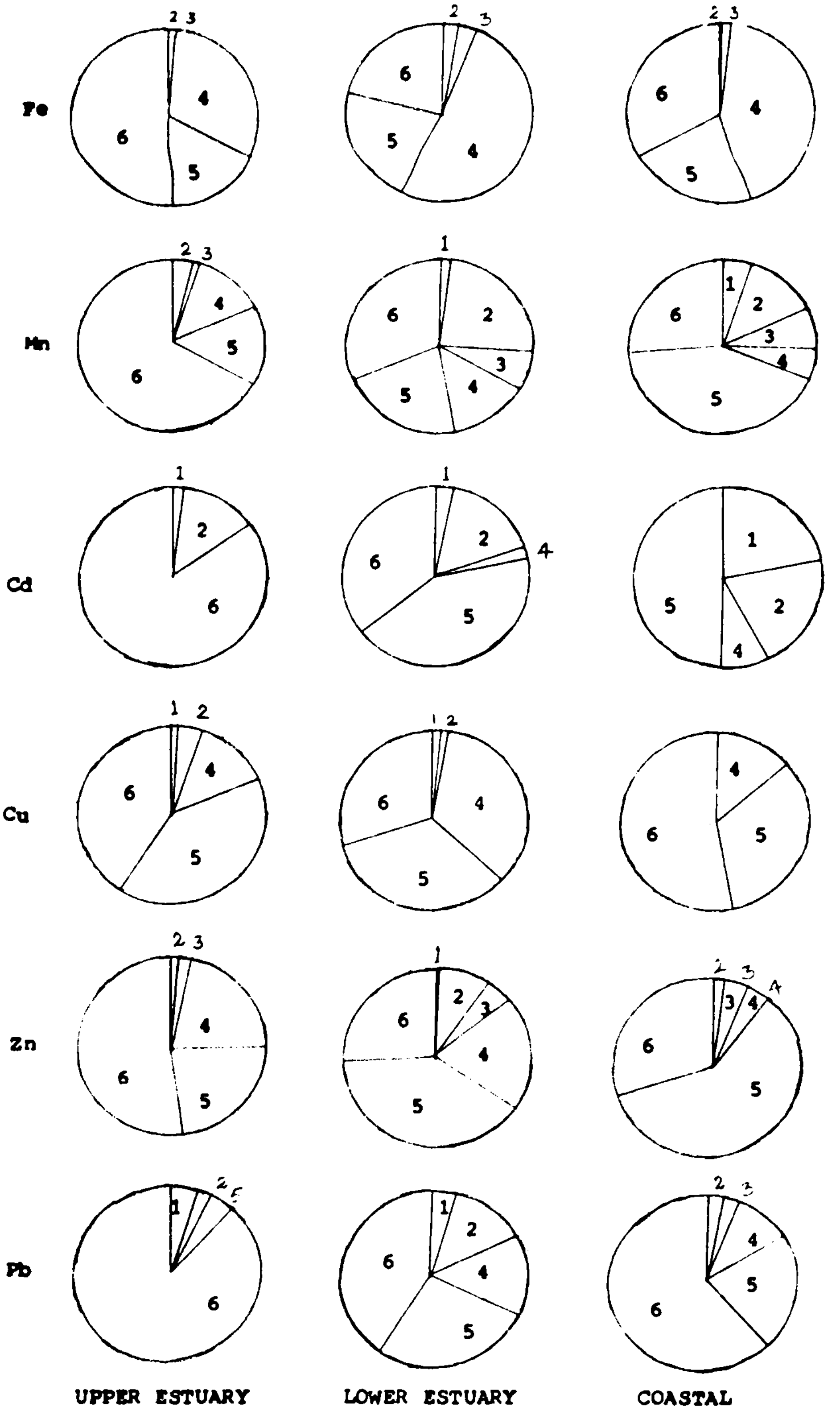

Fig. 5.7.1. Various fractions of trace metals in the sediments of upper Estuarine, Lower Estuarine and Near shore regions of Cochin Coast.

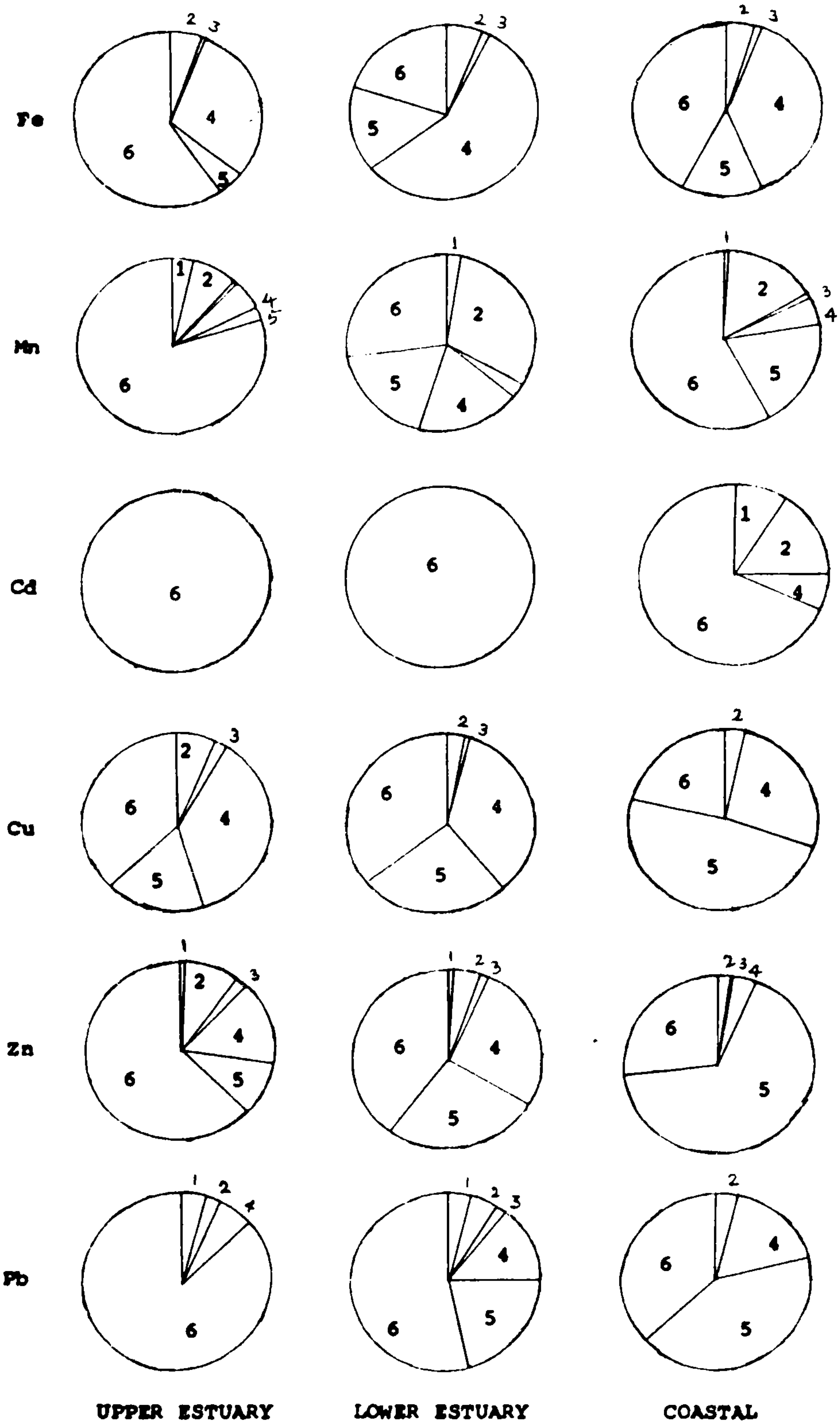

Fig. 5.7.2. Various fractions of trace metals in the sediments of Upper Estuarine, Lower Estuarine and Near shore regions of Calicut Coast.

abundance of percentage of exchaangeable fraction is in the order: Cd > Mn > Zn > Fe > Cu > Pb Van der Weijden et al. (1977) established the order of decreasing desorption of metals into 1:1 sea water and normal sea water is : cd > Zn > Mn > Ni > Co > Cu > Cr, and for Fe amd Pb no desorption was found. The order observed for the near shore sediments of Kerala Coast agreed with the same except for Mn and Cu. In the light of very low percentage of Cu in this fraction, the variability shown by Cu can be neglected whereas the variabilitry of Mn could be attibuted to its peculiar reactivity in estuarine and coastal environments. In estuarine sediments Pb and Cd also showed significant variability. But the very low concentration of Cd in the sediments makes it insignificant. The high percentage of Pbl in estuarine sediments, could be explained on the basis of the high affinity of Pb towards clay minerals. Mitchell (1964) had established the following empirical affinity sequence of heavy metals towards clay minerals, Pb > Ni > Cu > Zn. Soong (1974) accounted for these effects with the explanation that lead has a special affinity for the clay mineral structures due to its ionic radius, which is very similar to that of potassium. At the same time, lead is also capable of replacing potassium, in the montmorillonite lattice (Marshall, 1949).

Recently Regnier and Wollast (1993) have also reported the enrichment of Pb in fine-grained sediment fraction of muddy sediments from Scheldt estuary. Elliot *et al.*, (1990) reported the high affinity of Pb for adsorbing sites in soils. Bilinski *et al.*, (1991) has also reported high affinity of Pb to estuarine particles. From all these studies it could be inferred that Pb has a high affinity for clay minerals and organic substances. As was mentioned earlier the high affinity of Pb to clay minerals could be attributed to its ionic raddi (Soong, 1974) while the stability of lead-organic complexes accounts for its affinity to organic substances (Irving and Williams, 1948) Thus the prime position of exchangeable lead in the abundance series pertaining to the estuarine sediments of Cochin and Chaliyar estuary could be well interpretted in terms of the established adsorption behaviour of this element. Since the exchangeability of ions depend on their ionic radii, ionic potential, electro negativity etc, the percentage values of exchangeable fraction of metals in the estuarine and coastal sediments are compared with these parameters. It is found that the tracemetal abundance series established in the present study for the coastal and estuarine sediments corresponded closely with the ionic radius, ionic potential and the solubility product of the respective metal hydroxide (Krauskpof, 1967, Figs.5.7.1', 5.7.2', 5.7.3).

The factors influencing the enrichment of metal fractions in the estuarine and coastal sediments have been discussed in detail along with the spatial distributions. It is obvious from the above discussions that the exchangeable fraction of tracemetals extracted with ammonium acetate is having

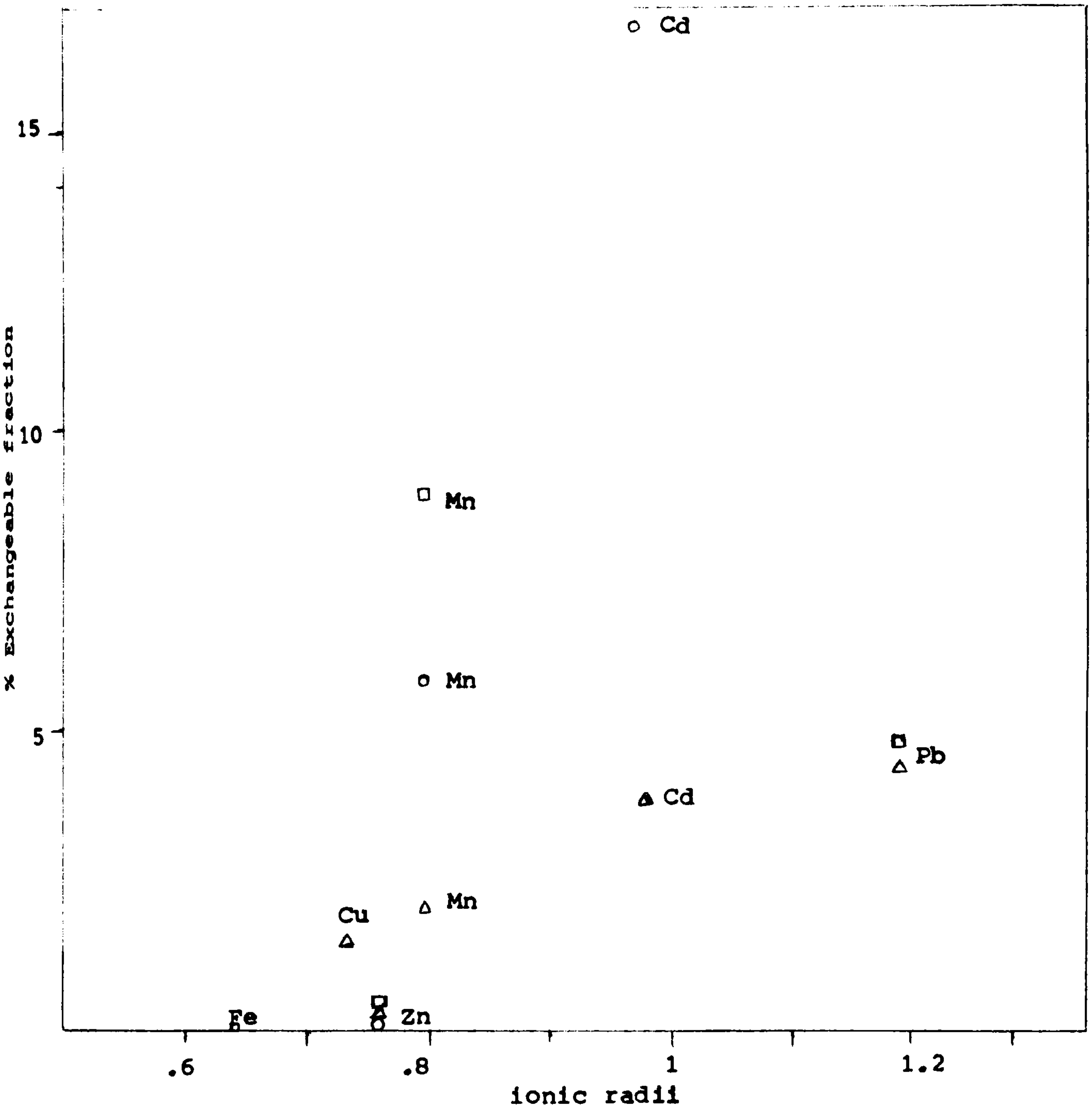

FIG.5.7.1'. Relation between percentage of exchangeable fraction and ionic radii : (○) coastal values, (△) Cochin estuary, (□) Chaliyar estuary.

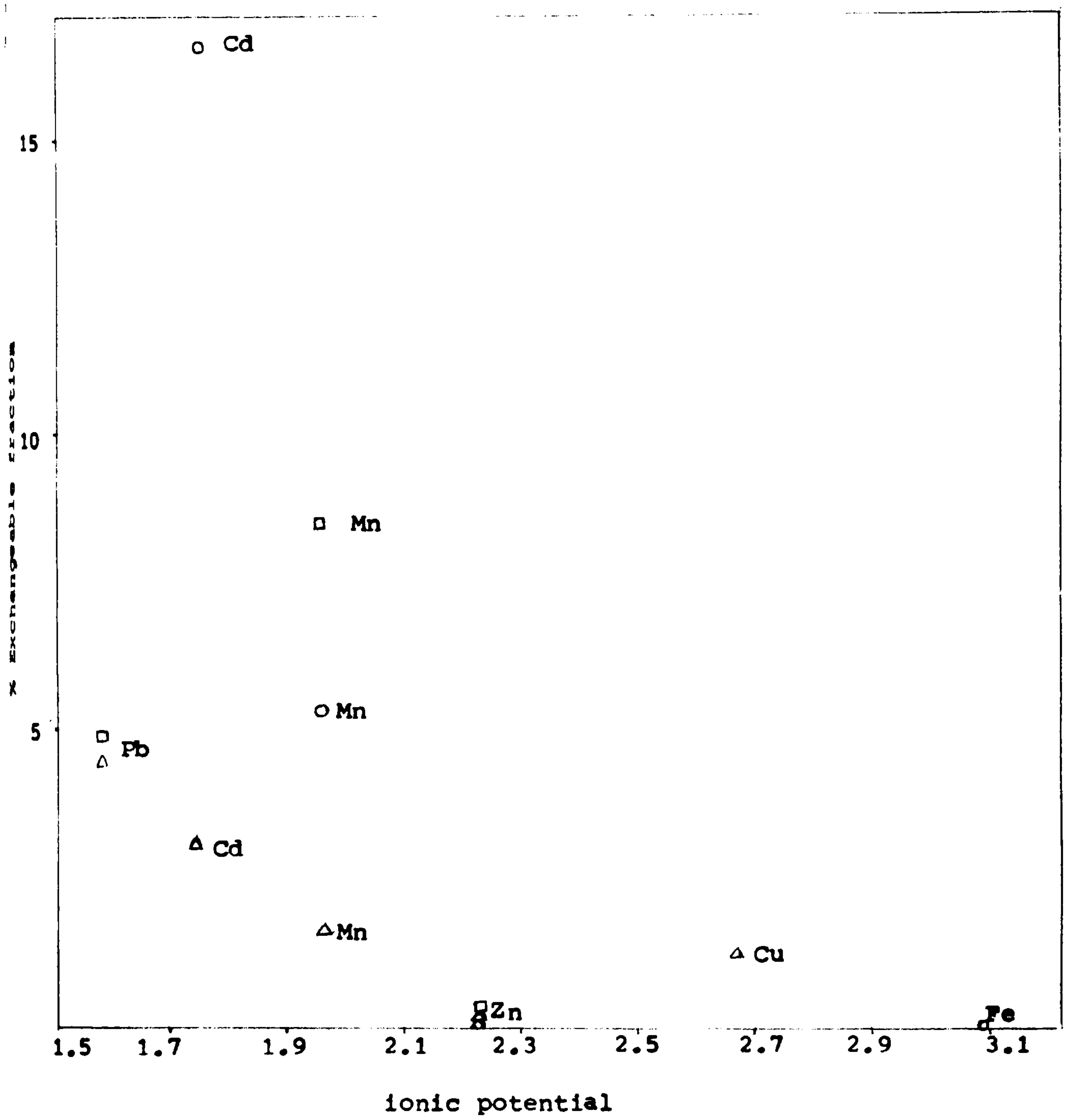

FIG.5.7.2′. Relation between percentage of exchangeable fraction and ionic potential : (○) coastal values, (△) Cochin estuary, (□) Chaliyar estuary.

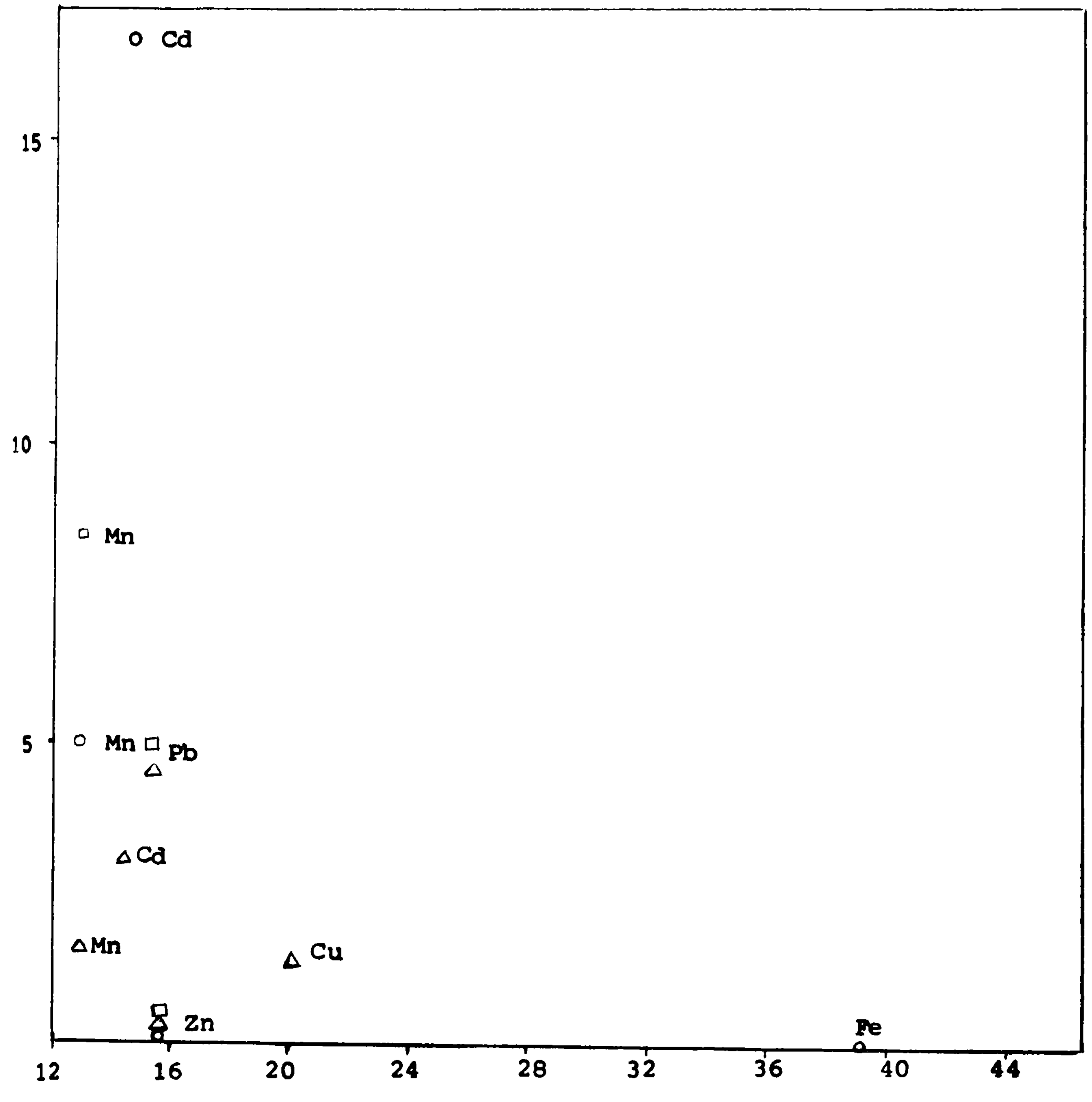

FIG. 5.7.3. Relation between percentage of exchangeable fraction and solubility product of metal hydroxide (-log Ksp) (○) coastal values, (△) Cochin estuary, (□) Chaliyar estuary.

separate identity and considerable significance in the results of the present studies, since the data obtained for this fraction could be explained with chemical aspects of the concerned metals and could provide much information about the fate of the most labile form of tracemetals in sediments ie: the enrichemnt of this metal fraction in the estuarine and coastal sediments revealed that eventhough the exchangeable fraction of most of the tracemetals under investigation are enriched in the estuarine environment, lead is one of the very toxic heavy metal which showed depletion towards the marine region ie: lead in the coastal environment is highly 'immobilised' whereas Cd is 'labilised' in coastal environment. Though Cd is labilised in the coastal environment, as the present concentration of Cd in the sediments is very small, the labilisation will not seriously affect the coastal ecosystem.

The mechanism of coprecipitation with carbontes, where by the heavy metal cations sorbed onto the surface becomes part of the crystal lattice, appear to be a very important means of limiting metal concentrations in the marine environment. Seibold (1964) points out that if it were not for these processes, the heavymetal content in sea water would have increased throughout the earth's history to several hundred milligrams per liter as a result of influxes from rivers and diagenitic remobilization from the sea floor.

The distribution pattern showed that the abundance of carbonate bound fraction of tracemetals is in the order Mn > Cd > Pb > Zn > Cu > Fe in Cochin estuary; Mn > Zn > Pb > Fe > Cu > Cd in Chaliyar estuary and Cd > Mn > Pb > Zn > Fe > Cu in the coastal sediments. Except for Cd, all other metals showed depletion of this fraction towards the coastal region, where as the carbonate fraction of all metals showed an estuarine enrichment, which could be attributed to the coprecipitation of tracemetal carbonates along with $CaCO_3$ during estuarine mixing. Patchineelam (1975) has observed a 10 fold enrichment of Cd in carbonate fraction due to coprecipitation with $CaCO_3$ and the precipitation of $CaCO_3$ favours an increase in pH. During estuarine mixing the pH of the river water increases, as a result the solubility product of $CaCO_3$ is drastically reduced and $CaCO_3$ is precipitated in the mixing zone. -LogKsp of metal carbonates, are plotted against the percentage of carbonate fraction of metals (Fig.5.7.4).

The greater percentage of carbonate fraction of Mn has already been discussed.

Very high concentration of phosphate in the sodium acetate (pH=5) extract indicated that the extractant leached out the phosphate bound metals also. Moreover strong positive correlation was observed between tracemetals and phosphate P in the sodium acetate extract.

The significance of two most labile fractions has

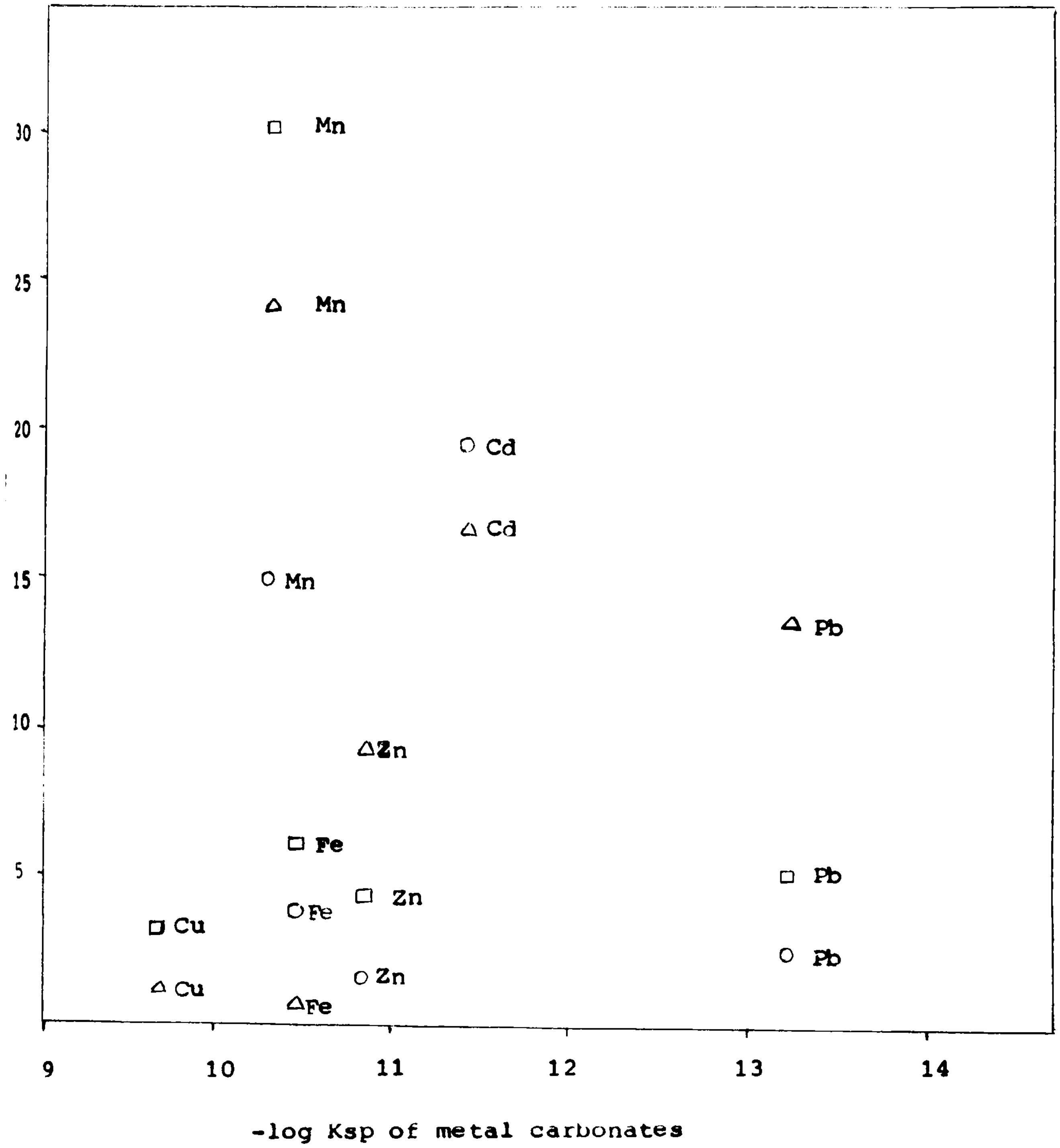

FIG.5.7.4. Relation between percentage of carbonate fraction and -log Ksp of metal carbonates : (○) Coastal values, (△) Cochin estuary, (□) Chaliyar estuary.

already been discussed in detail. Only a very low percentage of total metal was found to be present in the easily reducible fraction ie; in association with the hydrous oxide of Mn. Even the percentage of Mn was only 7.35% in the estuarine and coastal sediments. Previous investigastors have reported higher percentage of metals in the easily reducible fractions, compared to the present study results. Kersten and Forstner (1987) have reported an enhancement in the percentage of easily reducible fraction of heavy metals except for Fe when the sediment samples were subjected to sequential extraction procedure under oxidising conditions, due to the oxidation of easily oxidizable portions in the organic/sulphidic metal fractions. However, in view of the very low percentage concentration of easily reducible fraction of the metals under consideration, any further discussion could not be carried out on the significance of the easily reducible fraction in the coastal ecosystem of Kerala.

More than 40% of total Fe was found to be present in the moderately reducible fraction and the maximum enrichment was found with the estuarine sediments. The order of abundance of other metals in the moderately reducible fraction decreases as Cu > Zn > Pb > Mn > Cd in the estuarine sediments.

As was seen in the case of Fe, the percentage of modarately reducible fraction of other metals also decreased towards the coastal region. A very high positive correlation towards the coastal region. A very high positive correlation (r = 0.91) obtained between the Cu and Fe in the moderately reducible fraction indicated the association of Cu with the hydrous oxide of Fe.

The order of abundance of trace metals in the organic/ sulphidic phase of coastal sediments as Zn > Pb > Cu > Cd >Mn > Fe roughly followed the sequence of organic complex stability established by Irving Williams (1948). The very high percentage of organic/sulphidic Zn could be attributed to its detrital origin, as was evidenced by the very high enrichment of Zn in the tissues of estuarine and marine fish samples. All the metals except lead showed an enrichment in the organic and sulphidic fraction towards the coastal region.

As was expected the residual fraction of all metals in the present study showed a riverive enrichment. This fraction being the least mobile in the aquatic environment demands no further discussion.

5.8 Tracemetal levels in biomaterial.

In order to assess the accumulation of tracemetals in biota under natural conditions of the study area, four common species of fish samples and one prawn sample from the Cochin estuary and seven species of fish and three species of prawn samples from off Cochin were collected during sampling. The study of fish muscle tissue is one of the means of investigating the amount of heavy metals entering the human body through sea food. The concentration of six heavy metals under investigation were determined in the flesh (edible) and in the alimentary canal with liver of the samples. The results are shown in table 5.8.1. The data showed that the two toxic metals Cd and Pb were present only in the alimentary canal of *Scatophagus* sp., *Sphyraena* sp. and in Carangid fish whereas Cu, Zn and Fe was found to be present in all the species. Cu levels in the flesh part of the fish samples varied from 1.938 ppm to 5.874 ppm, whereas much higher level of Cu was present in prawn samples (15.5-34.8 ppm). Species of Carangidae fish from both estuarine and marine regions have the same values for Cu in the flesh part. Highest value for Cu in flesh was obtained for *Sphyraena* sp. Cu present in the alimentary canal varied from 7.75 to 42.63 ppm. Fe was found to be the most abundant heavy metal is biota also. Fe levels ranged from 31.78 to 1426.6 ppm in the edible part, and showed a depletion in the alimentary canal system. Fe concentration in prawn samples was also found to be less compared to fish. All the fish samples analysed indicated accumulation of Zn in the body and the concentration ranged from 16.43 to 42.25 ppm in the flesh of fish samples and from 44.21 to 57.12 ppm in prawns. The alimentary canal of two species analysed showed greater accumulation.

Mn and Cd was found to be present in alimentary canal of only one species, (*Sphyraena* sp.), while Pb was found to be present in the alimentary canal of most of the species analysed.

Eventhough the edible part of fish samples were not found to be concentrated with respect to Cd and Pb at presnet, the very high levels of Zn observed poses a threat. Perhaps this might be the reason of the enrichment of Zn in the organic and sulphidic fraction of the sediments. Since the metal enrichment varies from species to species, tissues to tissues and metal to metal, makes it difficult to arrive at a general conclusion.

METALS FROM BIOMATERIALS COLLECTED FROM COCHIN(μg/g) dry wt.

	Species	Part	Cu	Cd	Zn	Pb	Fe	Mn
	COCHIN ESTUARY							
1.	Percoidei	F	1.938	ND	42.25	ND	91.88	ND
2.	Sciaenidae	F	1.938	ND	24.65	ND	310.73	ND
3.	Carangidae	F	5.814	ND	23.47	ND	98.87	ND
4.	*Scatophagus* sp.	F	3.876	ND	21.13	ND	141.24	ND
	Scatophagus sp.	A.C	7.752	ND	19.17	12.08	476.69	ND
5.	*Penaeus indicus*	F	34.884	ND	47.73	ND	31.78	ND
	OFF COCHIN							
6.	*Cynoglossus* sp	F	1.938	ND	16.43	ND	102.40	ND
7.	*Sphyraena* sp.	F	3.876	ND	21.52	12.08	752.12	ND
	Sphyraena sp.	A.C	42.636	21.04	145.15	12.08	490.82	5.44
8.	Scombridae	F	5.874	ND	23.47	ND	77.68	ND
9.	*Rastrelliger kanagurta*	F	3.876	ND	21.52	ND	444.92	ND
10.	Carangidae	F	5.814	ND	30.91	ND	1426.60	ND
	Carangidae	A.C	15.504	ND	104.46	6.04	42.37	ND
11.	Chaetodontidae	F	1.938	ND	38.73	ND	77.68	ND
12.	*Latus* sp.	F	1.938	ND	16.04	ND	95.34	ND
13.	*Penaeus monodon*	F	27.132	ND	44.21	ND	275.42	ND
14.	*Penaeus* sp.	F	15.504	ND	50.47	ND	190.68	ND
15.	*Parapenaeopsis* sp.	F	34.804	ND	57.12	ND	98.85	ND

F - Flesh A.C - Alimentary canal

Table 5.8

ND - Not detected

CHAPTER - 6

SUMMARY

Analysis of the data obtained in the present study revealed that iron was the most abundant metal in the coastal environment of Kerala. Compared to Cochin estuary the concentration of zinc and cadmium were low in Chaliyar river estuary indicating lesser anthropogenic influence in this estuary. A notable feature is that in Chaliyar the Cd in the surface sediments is solely of lithogenous origin.

Partition studies provided valuable information about the origin, path way and the fate of trace metal contaminants in the coastal ecosystems of Kerala. In the nearshore region of Kerala, suspended particulates are the major sink for the trace-metals, other than iron. In the Chaliyar estuary, the sediment is the main repository for the metals like Cu, Zn, Mn and Fe. Very high amounts of metal inputs in Cochin estuary both in the dissolved and particulate forms make the partitioning complex among various phases in the aquatic environment. However, very high levels of Cu, Zn, Pb and Cd in the suspended particles of Cochin estuary indicate that in the estuarine environment, the suspended particles play a vital role by acting simultaneously as a source and sink for heavy metals.

The geochemical fractions of trace metals in the sediments revealed that in the coastal region of Kerala, more than 50% of the total metals in sediments was found to be associated with the non-lithogenous fraction, especially in the organic/sulphidic fraction. The percentage distribution of non-residual fraction for most of metals except for Pb was found to increase towards the marine region. Thus the `bio-availability' of those metals are increased many fold in the near shore region. Lead was found to be highly `immobilised' in marine region while Cadmium was labilised. Even though a large quantity of anthropogenic input of metals like Zn, Cd, Pb etc. have been detected in the Cochin estuarine system, the partition patterns showed the retentivity of the inputs in and around the sites of discharge itself, through the geochemical transformation of the metal species. High percentage of trace metals in the organic/sulphidic fraction of sediments and the observed correlation between metals and organic C content of sediments implied that the organic matter was the most important contributor to the metal enrichment in the sediments of the coastal ecosystem of Kerala.

Trace metal levels evaluated in the biomaterial indicated that though there exists no serious threat of toxic metal enrichment in the fish at present, high levels of Zn observed in the flesh part of fish cannot be ignored.

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