TRACE METAL SPECIATION IN THE COCHIN ESTUARY

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UNDER THE FACULTY OF MARINE SCIENCES

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CERTIFICATE

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

Cochin - 682 016
April, 1992

Dr. Jacob Chacko
Supervising Teacher

DECLARATION

I hereby declare that the thesis entitled *TRACE METAL SPECIATION IN THE COCHIN ESTUARY* is an authentic record of research work carried out by me, initially under the supervision and guidance of the late Prof. (Dr.) P.N.K. Nambisan, former Director, School of Marine Sciences and presently under the supervision and guidance of Dr. Jacob Chacko, Reader, Chemical Oceanography Division, School of Marine Sciences, Cochin University of Science and Technology, and that no part of it has previously formed the basis of the award of any degree, diploma, associateship, fellowship or other similar title or recognition.

Cochin - 682016
April, 1992

SHIBU M. PAUL

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LIST OF PUBLICATIONS

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2. Shibu M.P.,Jacob Chacko and Balchand A.N. (1992). A behavioural profile of cadmium in a tropical estuarine environment - a speciation approach. *Second European Conference on Ecotoxicology*, Amsterdam.

3. Shibu M.P., Jacob Chacko and Balchand A.N. (1992).Copper transport and species transformations in a tropical estuary. (Under preparation).

4. Shibu M.P., Jacob Chacko and Balchand A.N. (1992). Anomalous behaviour of zinc in a tropical estuarine environment. (Under preparation).

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CHAPTER 1
INTRODUCTION

I. Concept of Speciation
II. Approaches in Trace Metal Speciation
III. Estuarine Behaviour of Trace Metals
IV. The Cochin Estuary
V. Scope of the Present Study

From prehistoric times, the banks of rivers and estuaries have been the nerve centres of civilization and industrialization. Increasing human influence with scant regard for preserving the health of waters has ultimately resulted in their being contaminated with and impacted by toxic substances of diverse origin and nature. The human eagerness to perform better and better, with respect to production of food, energy and convenience products, in order to improve the standard of living, has led to the introduction of many hazardous, non-degradable, chemicals into the aquatic ecosystems, the presence of which has attracted serious concern of the environmentalists. The alarming rate of pollutant input far exceed that of nature's cleansing processes and has consequently resulted in an ecological imbalance.

Once the pollutants enter the environment, they are subjected to a variety of physical, chemical, geological and biological processes, that bring about their disintegration or sometimes, their ultimate removal. Persistant chemicals, that do not breakdown, stand to pose serious environmental problems.

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

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

I. Concept of Speciation

The results of the investigations that followed the "Minmata disaster", proved that it was caused by the bioaccumulation of methylated mercury (formed by microbial transformation) and not by ionic mercury. This has triggered studies into the then unknown differential toxicity of different species of the same metal by initiating attempts to understand the environmental processes in terms of metal species transformations, its significance in bioaccumulation and eventually the degradation of these toxicants.

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*The term "trace metal/trace element" is used in current literature to designate those elements which occur in trace amounts in natural systems. For all practical purposes, the terms such as "trace metals", "trace inorganics", "heavy metals", "microelements" and "micronutrients" are treated as synonymous with the term "trace elements", (Wittmann, 1983).

The terms `species' and `speciation' have, in reality been borrowed from biology. In biology, the term `species' refers to "a class of individuals having common attributes and designated by a common name". In chemistry, `species' refers to the "molecular form (configuration) of atoms of an element or to a cluster of atoms of different elements". However, chemically, the term `speciation' has been used in many different contexts (Bernhard *et al.*, 1986); chemical speciation studies involve,

(a) the analysis of species leading to their identification and quantification in a defined area or in a volume - (species analysis)

(b) the description of the abundance (or numerical distribution) of species of an element in a volume (species distribution or abundance)

(c) the assessment of the reactivity of a given species-(species reactivity) and

(d) quantification of the transformation of one species into another (species transformation).

Every element is capable of forming at least a few molecular species. Depending on the conditions, an element may occur in the environment just as a single molecular species, or if more species of an element are present, with the concentration of one of them being higher than the concentration of the others. The total concentration of the element can be used to assess its environmental impact only when it is present entirely as a single species. Since the chemical reactivity (behaviour) of the element depends on the chemical species in which it is present, and since the most abundant species is not always the most reactive one, the total concentration of an element cannot be taken as a true indicator of the behaviour of the element. It is now known that the chemical speciation of a metal together with the reactions involved in the transformation of species is often the factor determining the extent to which the metal can affect the aquatic environment (Forstner and Wittmann, 1983). The relevance of chemical speciation in determining the availability of metals to organisms has been reported by

Nielsen and Anderson (1970); Black (1974), Pagenkopf *et al.*, (1974) and Florence (1977). Factors affecting the above are the nature of complexation, the degree of hydration, the oxidation state, the ionic strength of the solution and the nature of the sorptive processes. Geochemical processes occuring during transport of metals to the sea also influence speciation and result in inter-species transformations between labile and complexed ions. Stronger sorption of metal complexes than of free metal ions at interfaces and complexation or adsorption by colloids prevent precipitation in the estuarine environments (Stumm and Bilinski, 1972). Further evidence from the literature (Fukai, 1974 and Whitfield, 1975) demonstrates the importance of the organically bound metal fractions in determining the abundance of the dissolved state of the respective metals.

Many species have in their molecules, some groups that are strongly bound to the central atom and other groups that are only weakly bound. When the matrix changes, the weakly bound groups may be replaced while the stronger ones withstand the matrix generated transformations (Bernhard *et al.*, 1986). A natural field to witness such reactions is offered during the study of trace metals in the estuarine and nearshore regions by means of chemical speciation. The attempt to describe the metal species would then lead to an understanding of most of the biogeochemical processes in the fluvial aquatic environment.

II. Approaches in Trace Metal Speciation

Natural waters provide a favourable environment for speciation studies because of the prevailing variable chemical matrix and the variety of metal forms which may exist there. There have been three major approaches to the elucidation of the speciation of metals in natural waters (Harrison, 1987).
(a) Modelling studies based upon the knowledge of stability constants of ion pairs and metal complexes
(b) Laboratory studies on simplified systems and
(c) Analytical studies of real water samples

Though the first two approaches have been widely used, they cannot adequately describe the complexity of natural waters (e.g. the presence of humic substances of poorly defined composition or of colloidal metal-oxide species) and hence generate reliable results only in rather simple systems. Although the third approach, i.e, the actual analytical determination of species in a real water sample, is fraught with problems, some successful attempts have been made to overcome these and establish a preferential acceptance of this route in such studies.

To date, no scheme has been developed by which one can pinpoint a particular species or fraction as the best bioavailable form of a particular metal. There is therefore no established procedure for trace metal speciation and scientists approach the theme using different schemes depending on the nature of the problem that they are faced with. In this context, naming a particular metal species too proves difficult. Since no technique is available for an unequivocal characterization of a specific metal form at the concentrations normally encountered in natural waters (dissolved or particulate), it is necessary to revert back to the concept of operational definition of species, documented earlier in the context of sediments (Tessier *et al.*, 1979). Some of the frequently used schemes are discussed below.

Batley and Florence (1976a) proposed a scheme in which Chelex-100 resin separation, ASV technique and U.V. irradiation were applied simultaneously. Within this scheme, they were able to subdivide the total dissolved metal into seven different classes. The classifications offered by this scheme are possibly more complex than is required to define biological availability, although this has not been demonstrated by toxicity testing. Moreover the analysis time of eight hours required per sample would preclude its application to routine analyses. Another drawback of this scheme is that many of the fractions are well below the detection limits in natural waters.

Figura and Mc Duffie (1980) proposed another scheme utilizing the dissociation kinetics of metal complexes on Chelex-100 resin. They defined four classes of the metals viz. inert, slowly labile , moderately labile and very labile. This scheme is simple and it is likely that this type of operational approach could be useful in relating metal concentrations to bioavailability. It may also be noted that this scheme does not provide mutually exclusive separations.

Hart and Davies (1981) developed a relatively simple analytical speciation scheme involving membrane filtration, Chelex-100 resin extraction and dialysis to provide information on the forms of trace metals in natural waters. The fractions they defined using this scheme included particulate, ion exchangeable, dialysable and bound metal. This scheme is helpful in evaluating the estuarine processes with the aid of a computer model. The existance of a considerable extent of overlap among the species is a drawback of this speciation scheme.

In the present study, a simple speciation scheme (see chapter 2: Fig. 2.1) has been developed, defining four species viz. dissolved Chelex-100 labile metal (CLM), dissolved organically bound metal (OBM), particulate exchangeable metal (PEM) and total particulate metal (refered to as PTM). The operational definitions, the analytical procedures adopted, their merits etc. are described in the next chapter.

III. Estuarine Behaviour of Trace Metals

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

During estuarine mixing the trace metals in the dissolved and particulate forms can behave either conservatively or non-conservatively depending on various physico-chemical factors such as pH, Eh, suspended solids load, increasing ionic strength and the extent of solid-solution exchange. Another important factor which can influence the behaviour of trace metals in estuaries is the hydrogenous precipitation of Fe and Mn oxides in the low salinity region. The freshly formed colloidal particles are excellent scavengers of dissolved constituents in natural waters either by lattice substitution or surface adsorption processes. The estuarine behaviour of iron has received considerable attention due to the fact that hydrolysis of Fe (III) in river water is one of the most likely reactions that can occur when its pH is increased by mixing with seawater.

There are somewhat conflicting reports on the behaviour of trace metals during estuarine mixing and this has led to a controversy in the past. Much of the disparity between the results of different workers may be accounted for reasons such as decomposition of pre-existing solids (which release the incorporated metals), differences in rate of mixing, nature of solids supplied by the end members and dependancy of solids association of trace metals on the grain size distribution. Muller and Forstner (1975), Jouanneau *et al.*, (1983), Duinker (1983) and George (1989) have reported a decrease of particulate associated metals in various estuaries, while Windom *et al.*, (1988 & 1991) have reported the conservative behaviour of particulate associated as well as dissolved metals. Bourg (1983) suggested that the uptake or release of trace elements by pre-existing solids in estuaries is probably related to ion-exchange processes, at least for some elements.

Some of the reports on the trace metal distribution in the Indian estuaries include that of Paul and Pilli (1983a), in the Cochin estuary, Satyanarayana *et al.*, (1985) in the Visakhapatnam Harbour, and Zingde *et al.*, (1988) in the Mindhola river estuary.

Speciation studies in the estuarine environment are limited due to the complexity of the estuarine processes and the difficulty in explaining the observed results. Duinker and Kramer (1977) studied the dissolved electroactive concentrations of Zn, Cd, Pb, & Cu in River Rhine and North Sea waters at natural pH. The study was extended to observe metal behaviour at lower pH against the complexing capacity of natural water samples by spiking them with the ionic species of the metal concerned. A major breakthrough was achieved when Hart and Davies (1981) described the speciation of Cu, Cd, Pb, Zn and Fe in the Yarra river system using a simple speciation scheme and a computer model to interpret the results. In another attempt, weakly and strongly bound Cu, Pb & Cd were determined in the dissolved and particulate fractions of water samples from Oslofjord (Nilsen and Lund, 1982). A differentiation was made possible by use of different sequences in filtration, acidification and digestion.

In the tropical estuarine systems, only very few speciation studies have been reported hitherto. Speciation studies have been carried out in the Mandovi and Zuari estuaries (George, 1989) and the species analysed in the above study included total particulate metal, dissolved ASV labile metal and dissolved bound metal. In the Cochin estuary, Paul and Pillai (1983b) and Shibu *et al.*, (1990) have reported on trace metal speciation studies and these will be extensively referred to in this study.

IV. The Cochin Estuary

The Cochin estuary, the longest on the west coast of Kerala State extends between 09°40′- 10°10′N and 76°15′- 76°30′E. It has a length of about 70 km and a width varying between a few hundred meters to about 6 km. It covers an area of ≈ 300 km^2 and falls under the category of a tropical positive estuary (Pritchard, 1952; Fairbridge, 1980). Since the year 1976, the hydrographic conditions of this estuary have undergone extensive changes (Anirudhan, 1988) by way of i) interbasin transfer of water from Periyar river to Muvattupuzha river to facilitate the hydroelectric project (the water stored in a dam across Periyar river has been diverted to Muvattupuzha river after the production of electricity). ii) construction of a saltwater barrier (Thanneermukkam bund on the southern part of the estuary) iii) extensive dredging and harbour operations. The seasonal salinity distribution in this estuary largely depends upon seawater intrusion and changes in influx of river water. Depending upon the degree of mixing between the freshwater and saltwater, the estuary may vary from a well mixed type to a stratified type (Sankaranarayanan *et al.*, 1986).

In the past, Cochin estuary was extensively investigated upon for its hydrographical features (Rama Raju *et al.*, 1979; Lakshmanan *et al.*, 1982; Balchand, 1984; Pillai, 1989); biological productivity (Gopinathan *et al.*, 1984; Joseph, 1989) and its nutrient chemistry (Lakshmanan *et al.*, 1987; Anirudhan, 1988; Nair *et al.*, 1990 and Saraladevi *et al.*, 1991). Only a limited number of studies have been carried out on the distribution and behaviour of trace metals in this estuary. Sankaranarayanan and Rosamma Stephen (1978) have reported on Fe, Mn, Cu and Zn levels (in surface and subsurface particulate associated metals) for the first time in this estuary. Paul and Pillai (1983 a & b) have reported the distribution and speciation of various trace metals in this estuarine waters. In their study, they divided the estuary into three zones,the background zone, the industrial zone and the backwater zone with an aim to assess the metal pollution in the industrial zone. The metal species studied by them include cationic, anionic, non-ionic and non-dialysable fractions of Cu, Cd, Zn and Mn. The sediment associated metals have been extensively investigated in recent years by Ouseph (1987 & 1990) (Pb, Zn, Cr, Cd and Hg), Nair *et al.*, (1990) (Cd, Cu, Co, Cr, Fe, Mn, Ni, Pb, and Zn) and Nair *et al.,* (1991) (fractionation of sediment associated Cd, Cu, Pb & Zn). These fractions include, exchangeable, carbonate bound, Fe & Mn bound, organically bound and residual metals. Shibu *et al.,* (1990) have reported metal speciation in the dissolved and particulate phases in this estuary. The fractions included Chelex-100 labile ASV, U.V.-Chelex-100 labile ASV, dissolved metals (AAS), exchangeable and total particulate metal fractions.

The information hitherto available on trace metals in the Cochin estuary has only served to generate a periferal understanding of the behaviour of metals during estuarine mixing and to a limited extent, of their seasonal variability and to kindle an interest in metal speciation studies. This investigation is the first rigerous, systematic attempt at elucidating the complex phenomenon of metal speciation.

V. Scope of the present Study

The trace metal distribution in the Cochin estuary is considerably influenced by the tropical features of the location and by human activities. The lower Periyar river and the Cochin estuary have been particularly selected for this investigation in view of the impact of trace metals on the estuarine ecosystem as well as in attempt quantify the phenomenon of metal speciation in the waters of a tropical coastal plain waterbody. If the concentration in the water media is very low, then, many of the fractions that could be estimated by speciation schemes for metals will fall below the detection limits, a factor which is undesirable. Previous reportsmpt quantify the

phenomenon of metal speciation in the waters of a tropical coastal plain waterbody. If the concentration in the water media is very low, then, many of the fractions that could be estimated by speciation schemes for metals will fall below the detection limits, a factor which is undesirable. Previous

reportse in:

1) describing the spatial and seasonal variations of metal species in this estuary

2) in assessing the influence of various environmental processes on the metals (estuarine metal reactivity) and in quantifying the species abundance
3) in understanding the processes of transport and species transformations during metal transfer through an estuarine salinity gradient
4) in estimating the budget (mass balance) for trace metals in this estuary and
5) in comparing the behaviour of the four metals viz. copper, cadmium, lead and zinc in this estuary.

The study would also delineate the features of metal speciation which modify the chemical regime of ionic elements that traverse natural boundaries in aquatic environments, especally in those tropical areas prone to multivariate geographical settings.

CHAPTER 2

MATERIALS AND METHODS

A) EXPERIMENTAL DESIGN

I. Speciation Scheme
II. Description of Location
III. Analytical Techniques
IV. Collection and Treatment of Tamples
V. Experimental Procedure

B) TROPICAL SETTING

I. Standard Suite
II. Hydrographical Features

A-I. Speciation Scheme

The scheme on metal speciation is outlined in Fig. 2.1. The operationally defined species are defined below:

Chelex-100 Labile Metal - (CLM fraction):

This is the fraction of dissolved metal retained by the Chelex-100 resin column on extraction from filtered water sample. This includes free ions as well as kinetically more labile complexes than Chelex-100-metal complexes (de Mora *et al.*, 1987).

Organically Bound Metal - (OBM fraction):

The filtered aqueous phase was U.V. irradiated in presence of H_2O_2 and then eluted through a Chelex-100 column as described above. The difference in metal concentrations

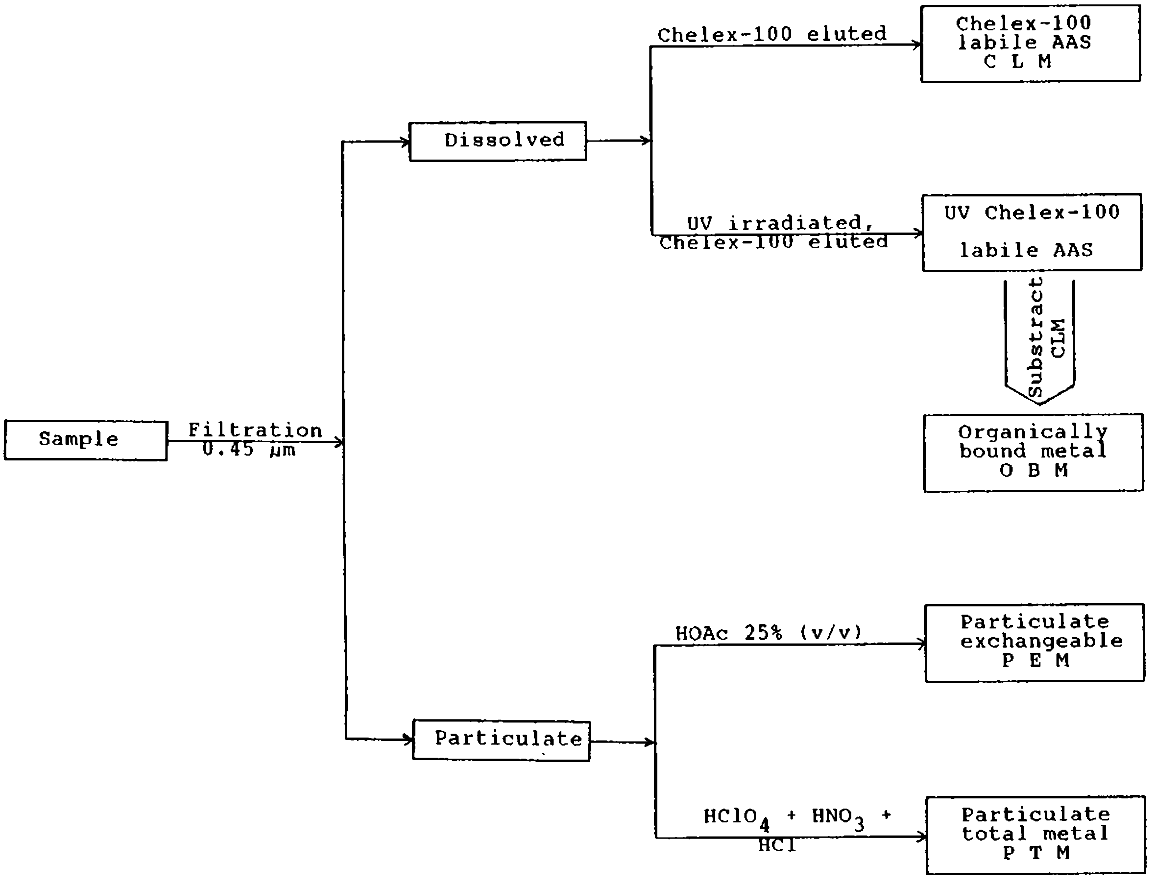


Fig. 2.1 Speciation scheme

between this value and the CLM fraction is taken as the organically bound metal (OBM fraction). This includes organically associated metals present in the dissolved phase. Brugmann *et al.*, (1983) have shown that this procedure measures almost all the dissolved metal.

Particulate Exchangeable Metal - (PEM fraction):

This fraction constitutes acetic acid leachable metal associated with the particulate phase. The acetic acid extraction is significant because it is one of the weakest chemical attacks that can be effectively used to remove metals from sites and forms that are potentially available to the biota (Rantala and Loring, 1985).

Particulate Total Metal - (PTM fraction):

The particulate total metal fraction is the metal obtained by strong acid digestion ($HClO_4$+ HNO_3+ HCl) of the particulate matter.

A major advantage of the proposed scheme is that the fractions are independently estimated (i.e, no overlap between the fractions). Since separate aliquots were used for CLM and OBM the possibility of a shift in the natural equilibrium is eliminated. In this connection, it may be noted that any shift in equilibrium can bring about interspecies transformations. Since the dissolved labile (CLM) and particulate exchangeable (PEM) fractions are highly susceptible to environmental changes, the inclusion of these within the scheme will be helpful in the understanding of estuarine processes and also of the species transformations that take place in the highly reactive mixing zone. Another advantage of this scheme is the practice of conducting physical separation of the dissolved and particulate phases which can definitely retain the prevailing equilibrium of inter-phasial speciation.

A-II. Description of Location

Water samples were collected from six locations in the Cochin estuary and the lower reaches of the Periyar river (Fig. 2.2) starting from Station 1 at Cochin barmouth (saline region) to Station 6 in the fresh water zone of the Periyar river. River banks adjacent to Station 3, is a coconut husk retting ground. Station 5 is situated 200m downstream of the effluent discharge area from the outfalls of a fertilizer industry and a Zinc smelter. Station 6 is situated upstream of the industrial belt and it is relatively unpolluted. Salinity intrusion into Periyar river from Cochin barmouth is generally observed upto Station 4 during periods of low to moderate discharge. For the convenience of discussion Stations 1, 2 & 3 are considered as estuarine Stations and Stations 4, 5 & 6 as fresh water Stations. All surveys were timed to coincide with the phase of high tide in the estuary.

The sampling survey was conducted on a monthly basis using a fibre glass dinghy ("Flying Fish" of the School of Marine Sciences) eliminating any possible metal contamination from the collecting vessel. The survey extended for 12 months from December 1988 to November 1989. The whole year is divided into three seasons - premonsoon (February-May); monsoon (June-September) and postmonsoon (October-January).

A-III. Analytical Techniques

All the metal analyses were carried out on a Perkin-Elmer PE 2380 atomic absorption spectrophotometer. Extreme care was taken in preparing the reagents, precleaning of glass wares and containers and blank corrections were applied wherever necessary. All the chemicals used were of Merck Suprapur grade and deionized double distilled water was used for the preparation of the reagents and rinsing of glasswares and containers. For AAS determinations, the coefficients of variations for six determinations were: Cu 2%, Cd 4%, Pb 8%; and Zn 6%.

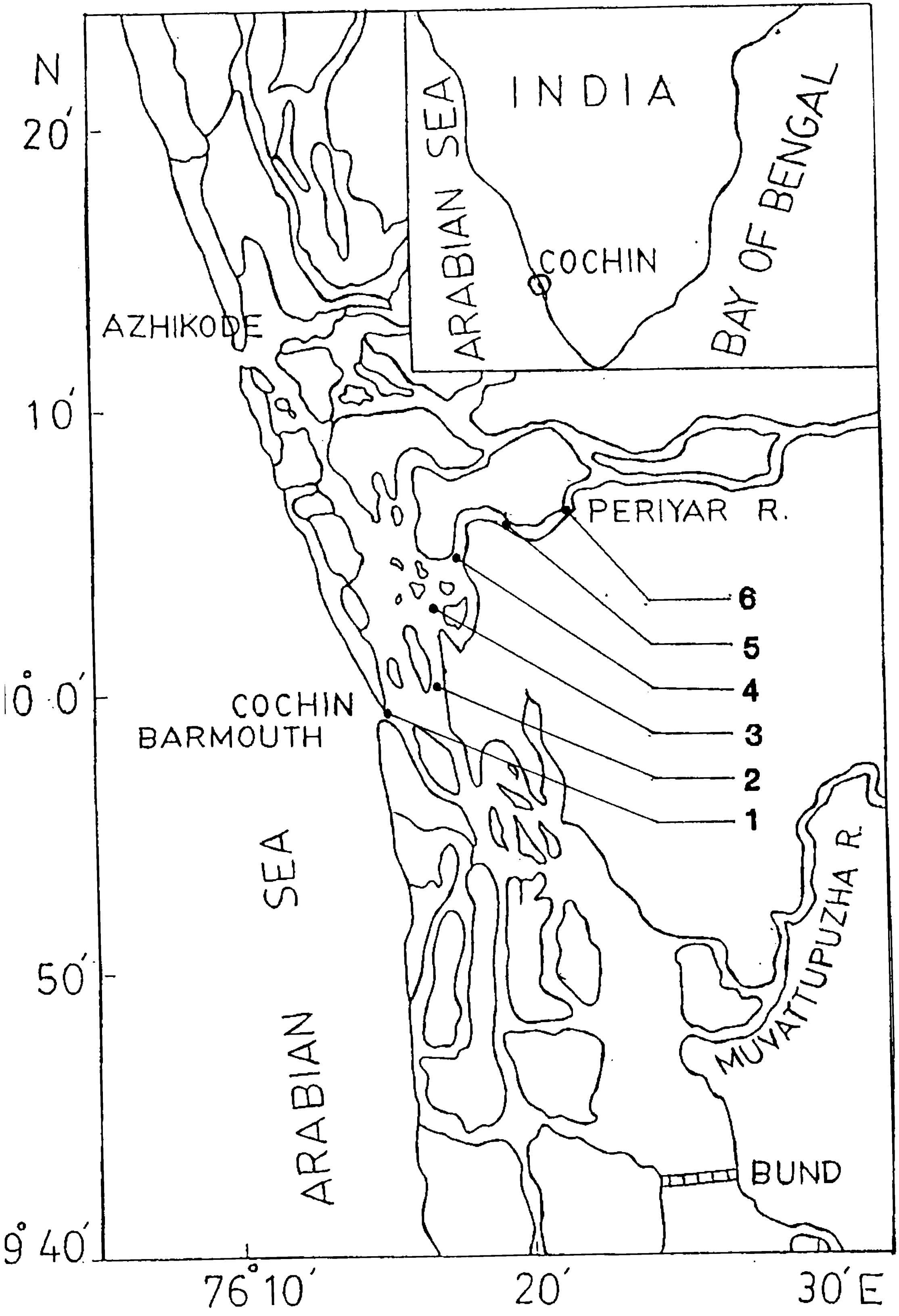


Fig. 2.2 Map of the Cochin estuary showing locations of sampling sites

A-IV. Collection and Treatment of Samples

Water samples (5l) were collected (0.5m below the surface) using a precleaned, acid washed, teflon water sampler (Hytech). The samples were filtered immediately after collection, through acid washed, preweighed, 0.45 µm Whatmann membrane filters. The first 500 ml sample was discarded and the remainder (≈ 4l) was stored at natural pH in a refrigerator at 4°C as suggested by Florence, (1977). The particulates retained on membrane filters were dried at 40°C and cooled in a vaccum dessicator to constant weight.

A-V. Experimental Procedure

i) Preparation of Chelating Column:

The chelating resin (Chelex - 100: 100 - 200 mesh) supplied by Bio-Rad Laboratories was precleaned by suspending in 2M HNO_3 and washing with deionized double distilled water several times to remove fines. It was then loaded into a 1.5cm diameter glass tube fitted with a teflon stopcock. The resin was washed with 30ml 2M HNO_3 and then with deionized double distilled water until the pH of the effluent was > 4. It was then converted into the ammonia form by passing 2M NH_4OH through the column and washing with deionized double distilled water until the pH of the effluent was ≈ 7. More details on the preparation and maintanance of Chelex columns were adopted from Florence, (1977).

ii) Chelex-100 Labile Metal (CLM)

Two litres of the filtered water sample was passed through a pre-prepared Chelex-100 column at a rate of 1-1.5 ml min^{-1}. The metals retained on the column were recovered in 15 ml 2M HNO_3 and analysed on AAS.

iii) Organically Bound Metal (OBM)

250 µl (30%) H_2O_2 was added to 500 ml of the filtered sample and this was then U.V. irradiated (450 W lamp) for 5 - 6 hours with continuous stirring. The total organic carbon measurements on this sample showed that all the organic matter was destroyed by this procedure. This sample was then eluted through Chelex column and analysed as above. From this value, CLM content was substracted to obtain the OBM value.

iv) Particulate Exchangeable Metal (PEM)

The particulate matter retained on the membrane filter was treated with 5 ml 25% (v/v) acetic acid and kept overnight with occasional shaking. The solution was then filtered (0.45 µm membrane filter) and the residue washed three times with HOAc (1 ml each) and made upto 10ml for analysis at AAS to obtain the particulate exchangeable metal concentration.

v) Total Particulate Metal (PTM)

The particulate matter was leached at 90°C with 10ml of a HNO_3+ $HClO_4$ + HCl mixture (1:1:3) for 6 hours (APHA, 1985). The acidic solution was centrifuged at 6000 rpm and the final solution made up to 10 ml with 0.1N HCl and analysed at AAS. This procedure gives the total particulate metal.

B-I. Standard Suite

The physico-chemical parameters (standard suite) likely to influence the concentration and distribution of different metal species in the Cochin estuary along with predominant factors that control them are summarised in Table 2.1.

Table 2.1

Parameter	Analytical Method	Controlling Factor
1.Temperature	Hg in glass thermometer (1/10°C)	Climate
2.Suspended Solids	Filtration	Weathering, discharge, tide & productivity
3.Salinity	Strickland & Parsons (1977)	River discharge & tidal action
4.Dissolved Oxygen	---do---	Productivity & reaeration
5.pH	Philips pH Meter	Ionic strength
6.Dissolved Organic Carbon	APHA. (1985)	River inputs & anthropogenic activity
7.Particulate Organic Carbon	El Wakeel & Riley (1957)	Fluvial transport, urban run off & productivity

B-II. Hydrographic Features

The study on the hydrographical parameters of the Cochin aquatic environment is of great importance while attempting to characterize the general features, distribution pattern, relative abundance and estuarine modifications during transport of trace metals. The distribution features of various environmental parameters studied are shown in Fig. 2.3.

The temperature in this estuary showed only moderate variations. The values, as expected, were high during premonsoon (February - May) and low during monsoon (June - September). The minimum value recorded was 26°C in June 1989 and maximum value was 33°C in April 1989. The monthly

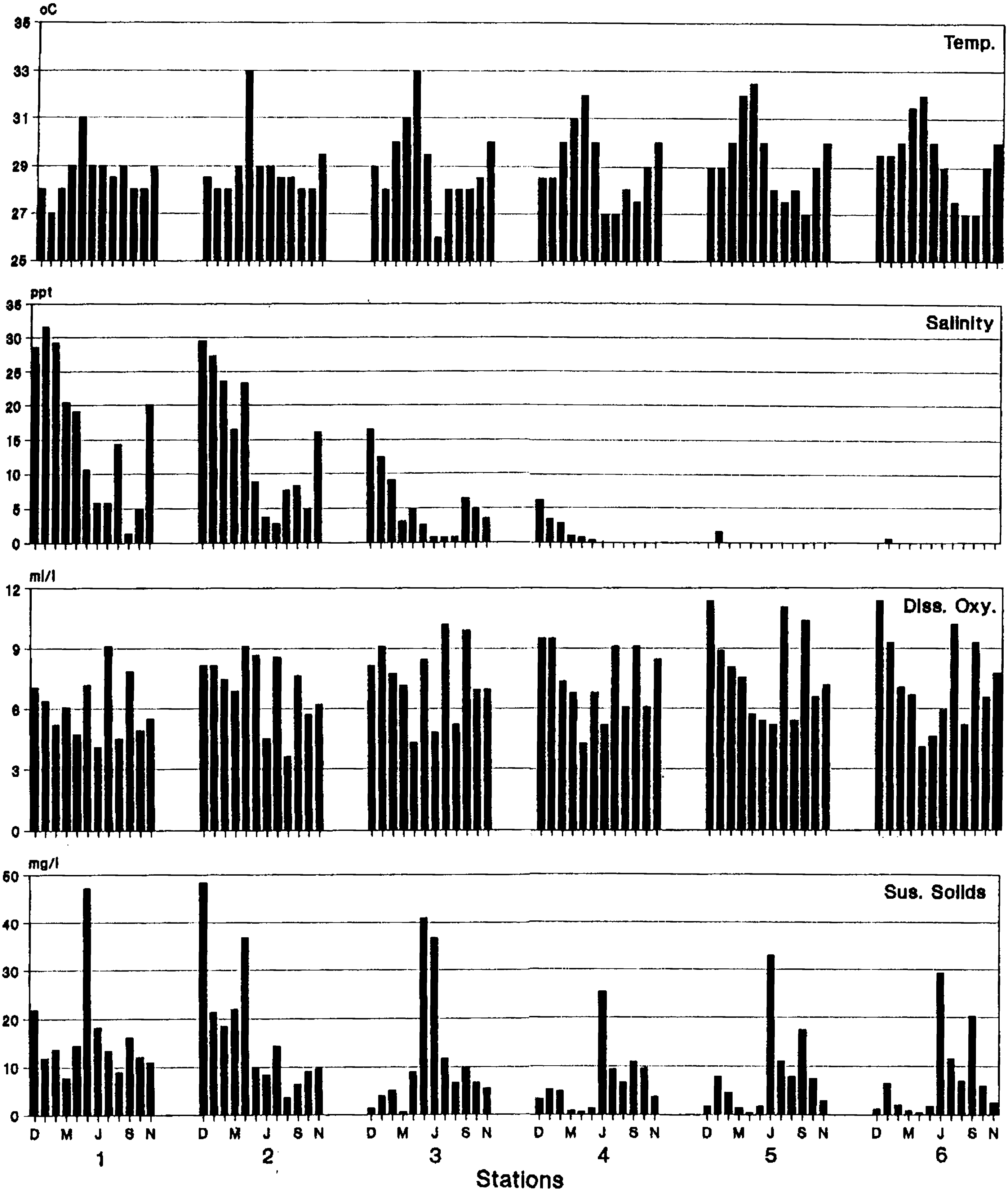


Fig. 2.3 Monthly distribution of hydrographic parameters at Stations 1 to 6 (D-December 1988 to N-November 1989)

(contd...)

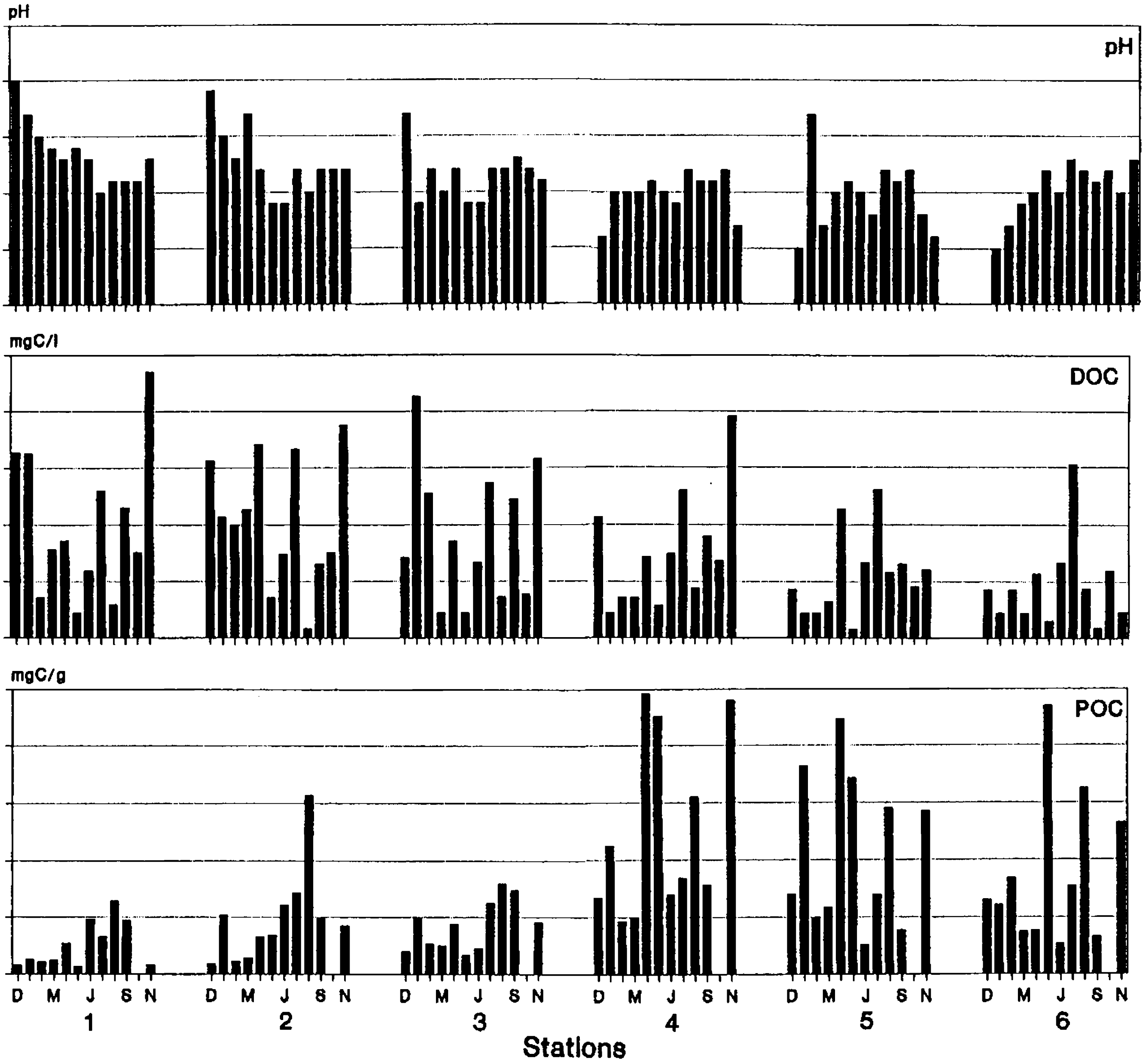

pH
8.5
8
7.5
7
6.5
6
pH
mgC/l
500
400
300
200
100
0
DOC
mgC/g
500
400
300
200
100
0
POC
D M J S N
1
2
3
4
5
6
Stations

Fig. 2.3

temperature variations were minimal at the two estuarine Stations (Stations 1 & 2) except in April 1989 and were appreciable at the other four Stations (Stations 3, 4, 5 & 6).

The distribution of suspended solids generally showed an increase towards the lower estuary. The maximum recorded value was 49 mg l^{-1} in May 1989 at Station 1. The consistantly high values in the saline region (Stations 1 and 2) can be explained as due to tidal influence causing modification of the estuarine circulation thereby resulting in resuspension of the bottom sediments.

The salinity distribution in this estuary is strongly dependent on sea water intrusion through the Cochin barmouth and changes in discharge of river water. The estuarine features alter between a well mixed type during premonsoon and a stratified type during monsoon (Qazim and Gopinathan, 1969 Wellershaus, 1971; Lakshmanan *et al.*, 1987). In the present study, upto Station 3, the water was saline throughout the year. At Station 4 the salinity intrusion was noticeable only during periods of very low discharge (December to May). At Stations 5 & 6 freshwater conditions prevailed throughout the year except during January 1989 when saline water intruded upstream.

The dissolved oxygen (DO) is an important water quality parameter in assessing the extent of water pollution. In the Cochin estuary during the period of this study, however, no highly deoxygenated conditions occurred. To summarise, the DO values were low in the saline region (Station 1) compared to the upper Stations 5 & 6. A noticeable feature of the DO distribution was that the values decreased through premonsoon to a minimum value in June during monsoon and then increased to high values in December. The range of oxygen values varied from 4.1 ml l^{-1} to 11.4 ml l^{-1} during the period of observation.

Many of the life processes are dependent on and are sensitive to the hydrogen ion concentration (pH) of the surrounding medium. The pH also influences to a large extent the speciation (abundance of the fraction) of metals in aquatic environments as well as decide their inter-phasial partitioning (between dissolved and particulate). The factors influencing the pH in this estuary are mild like photosynthesis and the extent of salinity changes during salt water intrusion. During the period this study, the pH variation was negligibly small compared to the observations made by Anirudhan (1988). The values noted occur in a small range of 6.5 to 8.0.

The dissolved organic carbon (DOC) content was scattered in distribution throughout the year. The DOC values were generally low at Stations 5 & 6 and high in the estuarine Stations 1, 2 & 3. In this estuary the DOC values varied between 14 mg C l^{-1} (at Station 5 during May 1989) and 470 mg C l^{-1} (at Station 1 during November 1989). At the estuarine Stations, the DOC values were relatively high during November to February whereas it was low during monsoon months. The above behaviour of DOC has been attributed to varying biological productivity as reported earlier by Gopinathan *et al.*, (1984) and Joseph, (1989).

The particulate organic carbon (POC) in this estuary also showed considerable variation. However the values showed a consistant decrease towards the saline region. The POC values were high in the three uppermost Stations 3, 4 & 5 and low in the estuarine Stations. The POC values ranged between ≈ 500 mg C g^{-1}at Station 4 during April 1989 and ≈ 10 mg C g^{-1}at Station 1 during May 1989.

CHAPTER 3

COPPER

I. Introduction

Copper is relatively abundant in the earth's crust (24 to 55 µg g^{-1}: Alloway, 1990) and moderately soluble in water. The world median concentration of Cu in the aquatic environment is reported to be 3 µg l^{-1} in the range 0.2 to 30 µg l^{-1}in uncontaminated freshwater systems; 0.03 to 0.23 µg l^{-1} in surface seawater and 0.2 to 0.69 µg l^{-1} in deep seawater (Bowen, 1985). The background level of Cu in uncontaminated freshwater sediments range from 0.8 to 50 µg g^{-1} (Forstner and Wittmann, 1983). The acceptable Cu levels in drinking water range widely from country to country: 10 mg l^{-1}(Australia and Japan), 1 mg l^{-1}(US) (Flemming and Trevors, 1989) and in our country it is 0.05 mg l^{-1} (IS 10500., 1983).

The annual world production of Cu has been increasing rapidly from 5.8×10^9 Kg in 1968 to 8.3×10^9 kg in 1985 (Forstner and Wittmann, 1983; Bowen, 1985). The anthropogenic activities by which Cu enters the soil, the sediment and water are the processes of smelting and mining, industrial effluent discharges, urban runoff and application of fertilizers, algicides, fungicides and molluscicides. The form taken by this metal in natural waters (ionic, complexed, or precipitated) and hence its bioavailability, depends on environmental factors such as pH, Eh, soil and sediment type, water hardness, organic content etc. and in estuaries, especially on salinity, freshwater discharge, mean residence time and the suspended solids load. These factors influence the environmental setup giving rise to conditions of copper deficiency or toxicity. Natural transformation takes place during chemical complexation, precipitation and adsorption by which copper is removed from water into the sediments (Salomons and Baccini, 1986) and thus sediments act as a sink for pollutants, particularly metals. Most cupric salts readily dissolve in water to give the free copper (II) ion in the hydrated form $[Cu(H_2O)_6^{2+}]$. Copper (II) ion is a strong complexing agent and the free cationic form has a great tendency towards hydrolysis. The stability of complexes depends on the chemical nature of the metal ion and the binding energy of the functional groups of the ligands. The copper (II) ions form strong complexes with the electron donor groups in organic compounds (O, N & S). In general, the stability of chelates, such as Cu-humic complexes is inherently greater than those of closely related nonchelate complexes.

Available reports on copper partitioning are contradictory. Gibbs (1977) has reported that copper is transported mainly through the particulate phase in Amazon and Yukon rivers (97 & 82%) and 65% in the Elliot Bay (Paulson *et al.*, 1989). On the other hand it is reported to be only about 40% in the Susquehanna river (Mc Duffie *et al.*, 1976) and about 25% in the Yarra river system (Hart and Davies, 1981). In the Cochin estuary too, higher percentage of dissolved copper has been reported (Paul and Pillai, 1983a). Duinker (1983) has reported on the initial removal of copper at low salinity region, while Windom *et al.*, (1988) and Paulson *et al.*, (1989) have reported conservative behaviour of copper during estuarine mixing. In the Cochin estuary, the present study showed a mixed behaviour for copper i.e. particulate associated fractions decreased towards the saline region while the dissolved fractions recorded an increase. During an earlier survey (Shibu *et al.*, 1990) an extensive organic association of copper was observed as has been reported from elsewhere (Florence, 1977; Hasle and Abdullah, 1981; Negishi and Matsunaga, 1983).

II. Results

Chelex-100 Labile Metal (CLM)

This fraction is determined as that retained in the Chelex-100 resin column which includes both ionic and weakly bound metal (those complexes having low dissociation constants than Chelex-100 metal complex). The monthly distribution of CLM fraction at the Stations 1 to 6 is shown in Fig. 3.1. The general features point out an enhancement in the metal level towards the lower estuarine region. The metal concentration varied between near detection limit in January 1989 at Station 6 and 1.41 µg l^{-1} at Station 1 in March 1989. Station 6 indicated lower concentrations with intermediatory peaks. A higher content of CLM was observed at the downstream Station 5 in October 1989 and at Stations 4 & 5 in November 1989. The values at the Stations in the estuarine waters represent a mixed behaviour of low and high content indicating a higher variability, characteristic of estuarine influences.

Fig. 3.2a depicts the seasonal changes of CLM fraction at all the selected locations. A general increase of this fraction was observed towards the lower reaches of the estuary. At all the Stations, the monsoonal values were lower than the premonsoonal and postmonsoonal values, and the premonsoonal content was the highest in the lower estuary (Stations 1 & 2). At Stations with intermediate salinities the CLM fraction varied between 0.3 to 0.6 µg $l^{-1}$for most of the periods of the year.

Organically Bound Metal (OBM)

This fraction was also found to increase in content from the upper to the lower estuary (Station 6 to 1). In the freshwater region the organically bound fraction of copper was negligibly small during many of the monthly collections, but however during the lean flow periods of the river, appreciable levels have been detected. Moderate to high values were

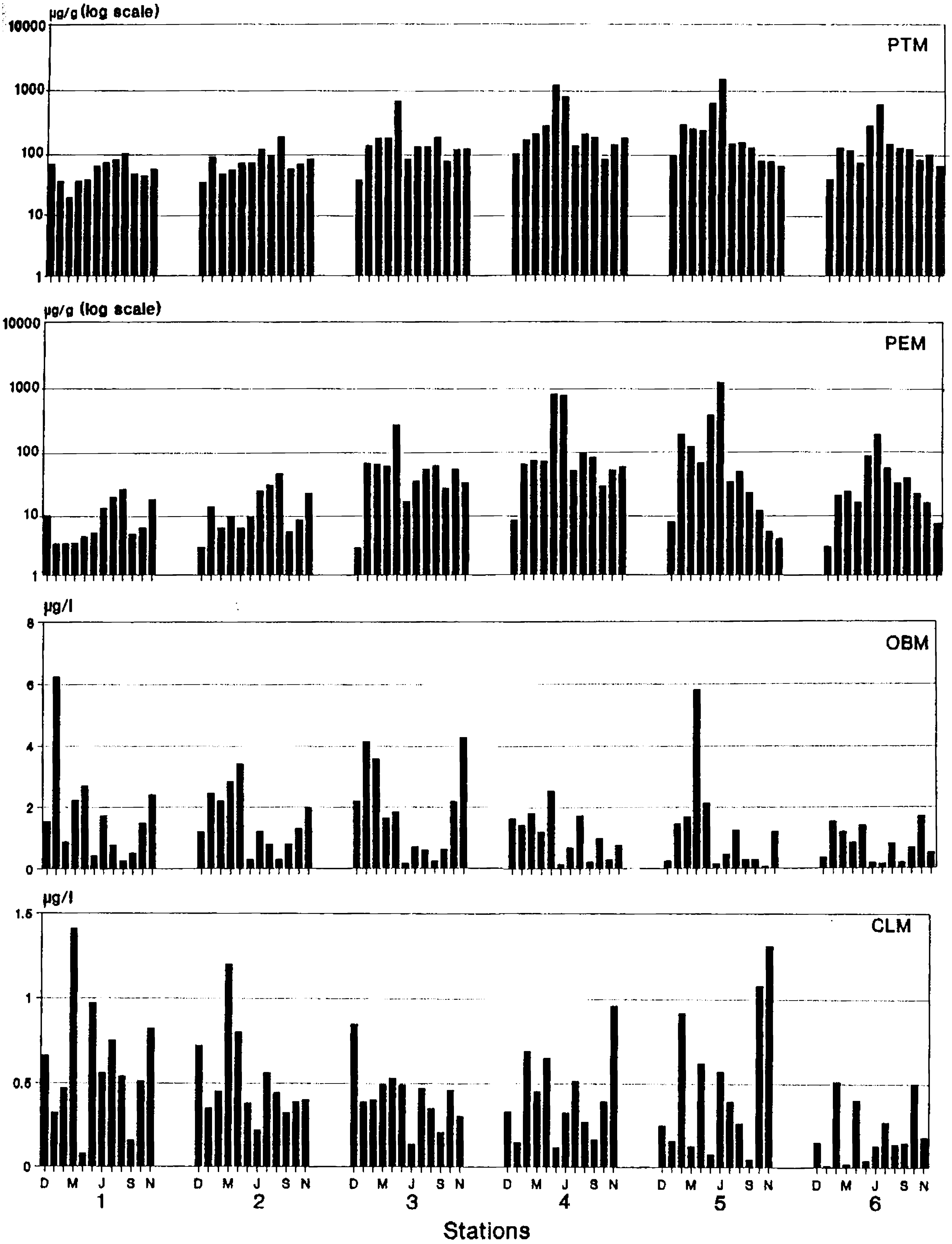


Fig. 3.1 Monthly distribution of copper fractions at Stations 1 to 6 (D-December 1988 to N-November 1989)

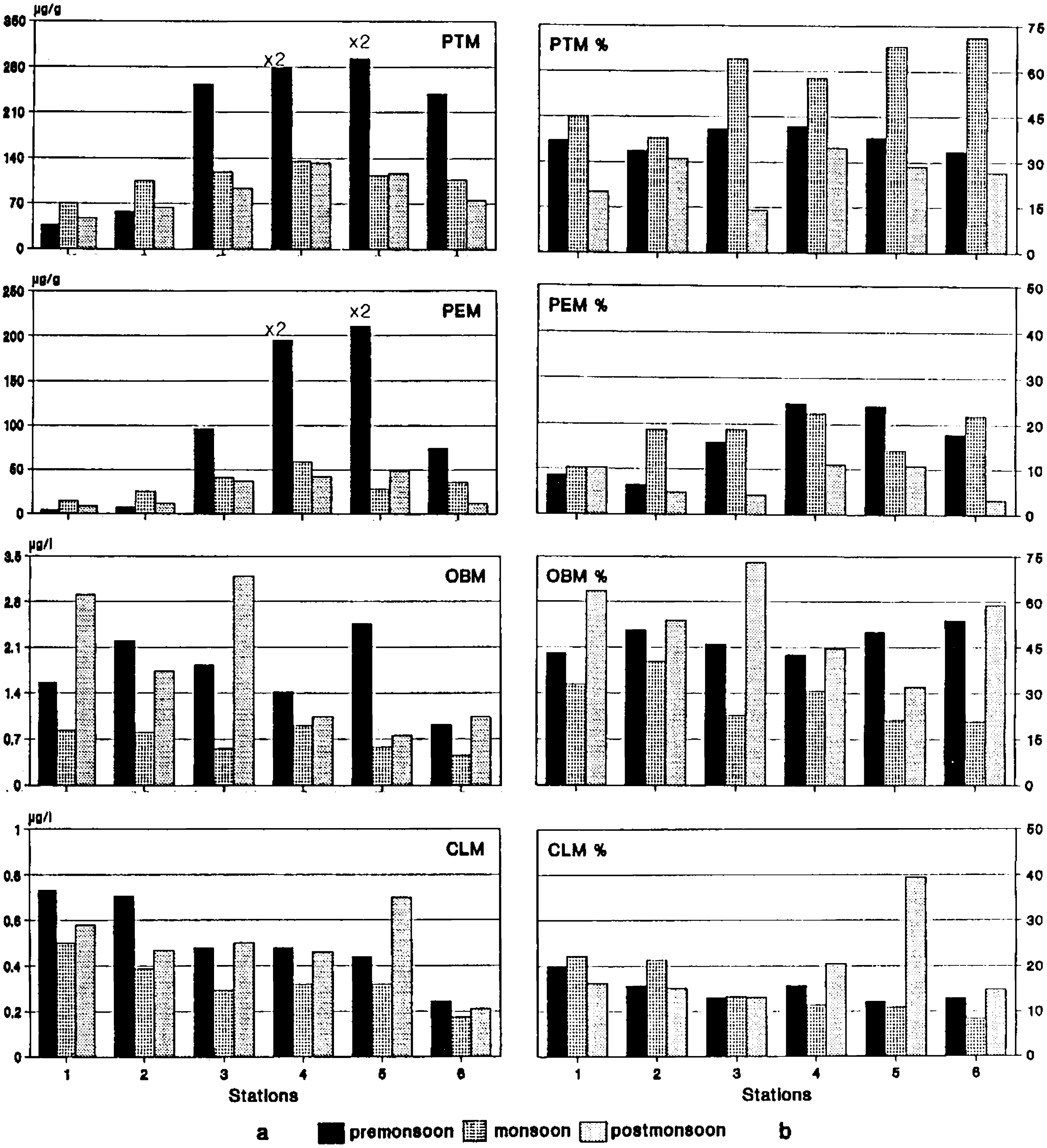


Fig. 3.2 Seasonal variation of Copper fractions
a) absolute values b) percentages

observed at all Stations during the first phase of the study. Two exceptionally high values were recorded at Stations 1 & 5 in January 1989 and March 1989, respectively. A better understanding of the distribution of this fraction can be arrived at considering the seasonal variations (Fig. 3.2a). During the premonsoon season, Station 5 recorded the highest content while Station 6 recorded a low content irrespective of the seasons. During the monsoon season, OBM values did not reflect any appreciable spatial variation. The postmonsoon is a time for gradual enhancement of this fraction longitudinally, down estuary.

Particulate Exchangeable Metal (PEM)

A near normalized, Gaussian type distribution of Cu-PEM at Station 6 in the freshwater zone modifies to a monotonic type variation at Station 1 at the seaward end. At Station 6, the content of copper within this fraction gradually increased from December 1988 to May 1989 and thereafter dropped smoothly till November 1989. The intermediate Stations, however, showed a mixed response with larger variations being observed at Stations 2 & 5 and identical concentrations at Stations 3 & 4. Exceptions were noticed in April and May at Stations 4 and 5. In the present study the PEM values varied between 2.7 $\mu g\ g^{-1}$ at Station 3 during December 1988 and 1158 $\mu g\ g^{-1}$ at Station 5 during May 1989. The seasonal trends of this fraction gave rise to sharp features (Fig. 3.2a). Significant differences were observed in the distribution of premonsoon averages from that of monsoon and postmonsoon - both spatially and seasonally, the values showed a greater abundance at Stations 3, 4 and 5. This aspect has been dealt with in detail in subsequent discussions.

Total Particulate Metal (PTM)

The behaviour of this fraction is more or less similar to that of PEM and has a predominant seasonal significance. On the whole, the Cu-PTM showed a decrease towards the lower estuary. The minimum recorded value was 18.08 $\mu g\ g^{-1}$ at

Station 1 in February 1989 and the maximum value was 1354 μg g^{-1} at Station 5 in May 1989. The monthly distribution profile focuses attention on a gradually decreasing trend at Stations 5 & 6 from the commencement of monsoon to the end of the survey whereas another feature of an increasing trend from the start of the premonsoon (February) to August 1989 at Stations 1 & 2 was also evident. The content of Cu-PTM was generally < 100 μg g^{-1} at Stations 1 & 2 whereas it was > 100 μg g^{-1} at the remaining Stations. The seasonal fluctuations (Fig.3.2a) were very much akin to the PEM distribution pattern. The premonsoonal values (averaged seasonally) far exceeded those of the monsoon and the postmonsoon (except at Stations 1 & 2).

Percentage Abundance of Different Fractions

Fig.3.2b pictorially represents the relative percentages of the three fractions, CLM, OBM and PTM (PTM includes PEM), considered seasonally for Stations 1 to 6. For this calculation the value of PTM and PEM are expressed in μg l^{-1} and CLM + OBM + PTM is considered as the total metal.

The predominant features are:

1) The CLM fraction occupied roughly 10 to 20% of the total (CLM + OBM + PTM) whereas OBM was seen to vary from 20 to 60% and the PTM from 15 to 70%.

2) The PEM fraction (< 25%) was randomly seasoned.

3) Station 6 in the freshwater zone exhibited similar seasonal behaviour in the case of CLM and OBM fractions and a low monsoonal content is sandwiched between higher premonsoon and postmonsoon abundance. The reverse was true for the PTM fraction. The PEM variability indicated low fractional abundance during postmonsoon.

4) Station 5 held a very high fractional amount of CLM during postmonsoon whereas PTM was more abundant during monsoon and PEM during premonsoon.

5) Near equal amounts of OBM and PTM fractions were observed in relation to lower content of CLM, percentage wise, during premonsoon at Station 4. During monsoon the amount of Cu-PTM far exceeded the other two fractions, again at Station 4 which showed wide seasonal disparities.

6) The CLM percentage abundance at Station 3 was seasonally homogenous where as OBM predominated during postmonsoon and PTM during monsoon.

7) Stations 1 & 2 exhibited a cyclic behaviour for the fractions CLM and PTM (however this is related to relative OBM amounts)- values increased from premonsoon to monsoon and then decreased to lower than the premonsoonal percentage values during postmonsoon, and to probably follow suit. The OBM fractions recorded a reverse trend at these Stations with the premonsoon abundance being lowered during the monsoon season and shooting up during the postmonsoon season.

8) The PEM variability dependent on other fractions showed no consanjuine relationship with the seasonal percentage distribution. This fraction mostly remained around 15% of the net total but at times accounted for up to 24% , remaining well within the PTM percentage values at Stations 3, 4 & 5, particularly. Within the relative variations between Stations the percentage PEM was the lowest during postmonsoon.

Regression Analysis

The results of the regression analysis did not show any significant correlation between the different fractions of copper except for an excellent positive correlation between PEM and PTM ($r = 0.96$). Against environmental parameters, CLM showed no significant correlations. The OBM showed significant positive correlations with salinity ($r = 0.44$) and DOC ($r = 0.42$) The PEM and PTM showed highly significant negative correlations with salinity ($r = -0.51$ and $r = -0.53$) and suspended solids ($r = -0.32$ each). These fractions also showed excellent positive correlations with POC ($r = 0.55$ and $r = 0.64$) ($p < 0.001$ and $n = 72$).

III Discussion

The behaviour of metals associated with particles during estuarine mixing had been closely investigated in the past (Evans and Cutshall, 1973; Duinker and Nolting, 1978; Keeney-Kennicutt and Presley, 1986; Windom *et al.*, 1983 & 1988;

Elbaz-Poulichet *et al.*, 1987; Kuwabara *et al.*, 1989; George, 1989; Schmidt, 1990; Shibu *et al.*, 1990). Some of the authors have also attempted to fractionation phenomena. The behaviour of dissolved copper or its species in various estuaries are conflicting. Duinker (1983) reported an initial removal of copper in the low salinity region of the Rhine estuary, whereas an addition of dissolved copper was reported in the Cochin estuary (Paul and Pillai, 1983a), in the Savannah and Ogeechee esturies (Windom *et al.*, 1983) as well as in the Mandovi and Zuari estuaries (George, 1989). On the other hand, a conservative behavior of copper during mixing was reported in the Bang Pakong estuary (Windom *et al.*, 1988).

i. Spatial and seasonal variation

All the fractions of copper studied are low at Station 6 in the freshwater zone which is a relatively uncontaminated location. Both the dissolved species showed an irregular distribution pattern with a marginal increase towards the lower estuary. The increase of CLM at Stations 1 & 2 may be due to the initial flocculation and subsequent remobilization from the sewage effluent discharged at a point between Stations 2 & 3. The mixing /remobilization experiments of Paulson *et al.*, (1991) using unfiltered sewage effluent showed that there was an initial flocculation followed by remobilization from both the flocculated and original particles which can release ≈ 25% of the total copper from the sewage effluent. They also found that the slow settling particles released copper into the upper water column. Another possible mechanism contributing to the increase of Cu-CLM at Stations 1 & 2 would be the remobilization from the sedimentary phase due to microbial degradation of oranic matter. Flemming and Trevors (1989) have noticed this process helping to add significant amounts of copper to the dissolved phase. Windom *et al.*, (1983) also observed a remobilization of copper from the sedimentary phase in the Savannah and Ogeechee estuaries at salinities > 20%. In the Cochin estuary also a similar remobilization at the high salinity region was previously reported (Paul and Pillai, 1983a). The laboratory mixing experiments of Salomons and Bril

(1990) using Fly river sediments showed that 15 to 20 % of the total copper is amenable to release in the estuarine environment which they attributed to replacement of copper held at the ion exchange positions especially by Mg^{2+} ions. The bound metal fraction in the Cochin estuary continuously enhanced towards the lower estuary and showed a drop only at Station 1. The relatively high values for this fraction in the estuarine Stations are not unexpected because of the high organic matter content at these Stations. The copper values at Stations 1 and 2 are influenced by the sewage out fall at the upstream of Station 2. The exceptionally high values in CLM fraction observed at Station 5 during postmonsoon are the result of inputs from the industrial area. It may be surmised from the comparison of CLM and OBM content at Station 5, during postmonsoon, that the anthropogenic inputs are generally in the labile form and that it gradually gets equilibrated with the natural pool. Windom *et al.*, (1983) have reported that during low runoff conditions, the residence time of water in the estuarine nearshore zone is longer than that during high runoff. Release from sediments, therefore would be expected to have a greater influence on the dissolved copper concentrations during low runoff. The low value of bound copper during monsoon is the result of low organic productivity and its associated organic complexation which is adversely affected by the low temperature and low intensity of light along with high river flow.

The mean residence time of water and particles in the aquatic environment plays a key role in determining the effect and extent of various processes taking place in the highly reactive estuarine zone. A higher residence time would result in a greater probability of the interactive processes attaining an equilibrium. Thus the residence time in turn depends on the river discharge and hence result in seasonal variations. The abnormally high values of PEM and PTM at Stations 4 and 5 are due to the anthropogenic inputs from the industrial area. The decrease observed in the particulate metal fraction towards the lower estuary can be attributed to various reasons: the desorption of copper from the particulate phase due to competitive replacement by Ca^{2+} and Mg^{2+} ions present in the medium as reported by Duinker (1983) and the dilution of metal-rich riverine particulates with less contaminated marine particles. Similar process has been reported eslewhere (Windom *et al.*, 1983; George, 1989).

The low values of particulate fractions (PEM and PTM) during monsoon is the result of two processes. During monsoon, due to high water discharge, the estuarine conditions change to freshwater and a corresponding decrease in the residence time of the particles occurs. Since desorption is kinetically a slow process compared to adsorption the removal process from the particulate phase is not very effective and in monsoon, the major influencing factor is physical dilution. The second factor arises from the composition of particles themselves. The high energy input during monsoon causes metal-depleted bottom particles to be resuspended and these constitute a major portion of the total particulate matter in the estuary. This consequently leads to a lowering in the content of particulate fractions. Duinker (1983) and Delfino and Otto (1986) also have observed similar phenomena in the Rhine estuary and Susquehanna rivers, respectively. During premonsoon, the variations were pronounced (Fig.3.2a) in the Cochin estuary. This is a period of high residence time for particles due to low river discharge conditions to undergo desorption processes effecting changes as observed in the PEM and PTM fractions. During postmonsoon the values of PEM and PTM are generally low. This reduction in metal level is coupled to periods of high organic productivity, when large quantities of organic ligands are released into the aquatic system (Kuwabara *et al.*, 1989; Slauenwhite and Wangersky, 1991). These ligands complex with the particulate associated metals and in the context of Cochin estuary high organic productivity reported by Gopinathan *et al.*, (1984) and Joseph (1989) in postmonsoon brings about the said feature.

ii) Estuarine metal reactivity

The flocculation processes in estuaries modify to a large extent the metal concentration and are closely related to the estuarine reactivity between dissolved and particulate matter and brings about changes in transport of different phases from estuaries to oceans (Bernhard *et al.*, 1986). In this connection there are three main processes which control the levels of copper in solution, its transformation into different forms, mobility in the aquatic environment and finally the availability to biota.They are 1) complexation 2) precipitation and 3) sorption. These processes and the resultant partitioning and bioavailability of copper are dictated by the chemistry of copper and of the environment (Flemming and Trevors, 1989). Of the above three processes, the most important one, which controls the copper speciation (or partitioning) in natural waters especially during estuarine mixing, is the sorption process. This process is responsible for the removal of copper from the dissolved phase to living and non-living particulate matter and finally to the sediment phase and often vice-versa (the desorption processes) back to the water column.

Reports on the behavioural pattern of copper during estuarine mixing are again conflicting. The removal of copper was observed in the Rhine estuary (Duinker and Nolting, 1978) and in the San Fransisco Bay during low discharges (Eaton, 1979). The CLM fraction of copper in the present study did not show any marked seasonal trends with salinity. Hart and Davies (1981) also could not notice any appreciable changes in the ion-exchangeable fraction of copper in the Yarra river system. Correlation studies showed no significant correlation for this fraction with any of the environmental parameters studied or with other fractions of Copper.

On an average, the organically bound fraction of copper accounts for about 43% of the total copper and its contribution varied from ≈ 28% (in monsoon) to ≈ 54% (in postmonsoon) which will be discussed in detail later. Trace metals released in the labile forms into the aquatic system, turn bound, on being associated with humics or complexed by organic materials or even precipitated from solution (Davies and Leckie, 1978; Hart and Davies, 1981). In fresh and seawater systems, organic ligands play a significant role than the inorganic ligands leading to complexation of dissolved copper (Sunda and Hanson, 1979). A high degree of organic complexation of total dissolved copper in freshwater rivers (75-99%) has already been reported (Linnik, 1984). In the present study too, about 73% of the total dissolved copper was found to be organically associated.

In waters of high biological productivity, there is a multiplicity of organic ligands in solution derived from autochthonous and allochthonous sources (Newell and Sanders, 1986). The dissolved organic carbon in natural waters may also competitively increase dissolved copper levels by altering partitioning (Sunda and Hanson, 1979). The DOC peptization and POC coagulation reactions can thus regulate the concentration of organically complexed elements such as Cu, Pd & Hg. Such reactions are particularly important in coastal waters with high organic loadings and in estuarine systems with high ionic strength gradients (Turner *et al.*, 1981). In the Cochin estuary, a high organic content has already been established (Vijayan *et al.*, 1976). The present study shows an increase of OBM fraction with increase of DOC content. The DOC-OBM plots are given in Figs.3.3 a, b & c for premonsoon, monsoon & postmonsoon. During monsoon the trend is nondistinct compared to that during premonsoon and postmonsoon. The regression analysis showed a highly significant positive correlation ($r = + 0.42$; $P < 0.001$) between these two parameters. No such relation had been observed for organically bound copper with DOC (Negishi and Matsunaga, 1983; Slauenwhite and Wangersky, 1991). The latter also reported that the quantity of the released DOC as well as the quality is of critical importance in determining the complexation of dissolved copper. The transport of degraded plant material and the influx of marine humic acids associated with algal blooms have been implicated as important sources of such organic complexing agents in most estuaries (Delfino and Otto, 1986: Jones *et al.*,1986).

In order to have a better understanding of the influence of

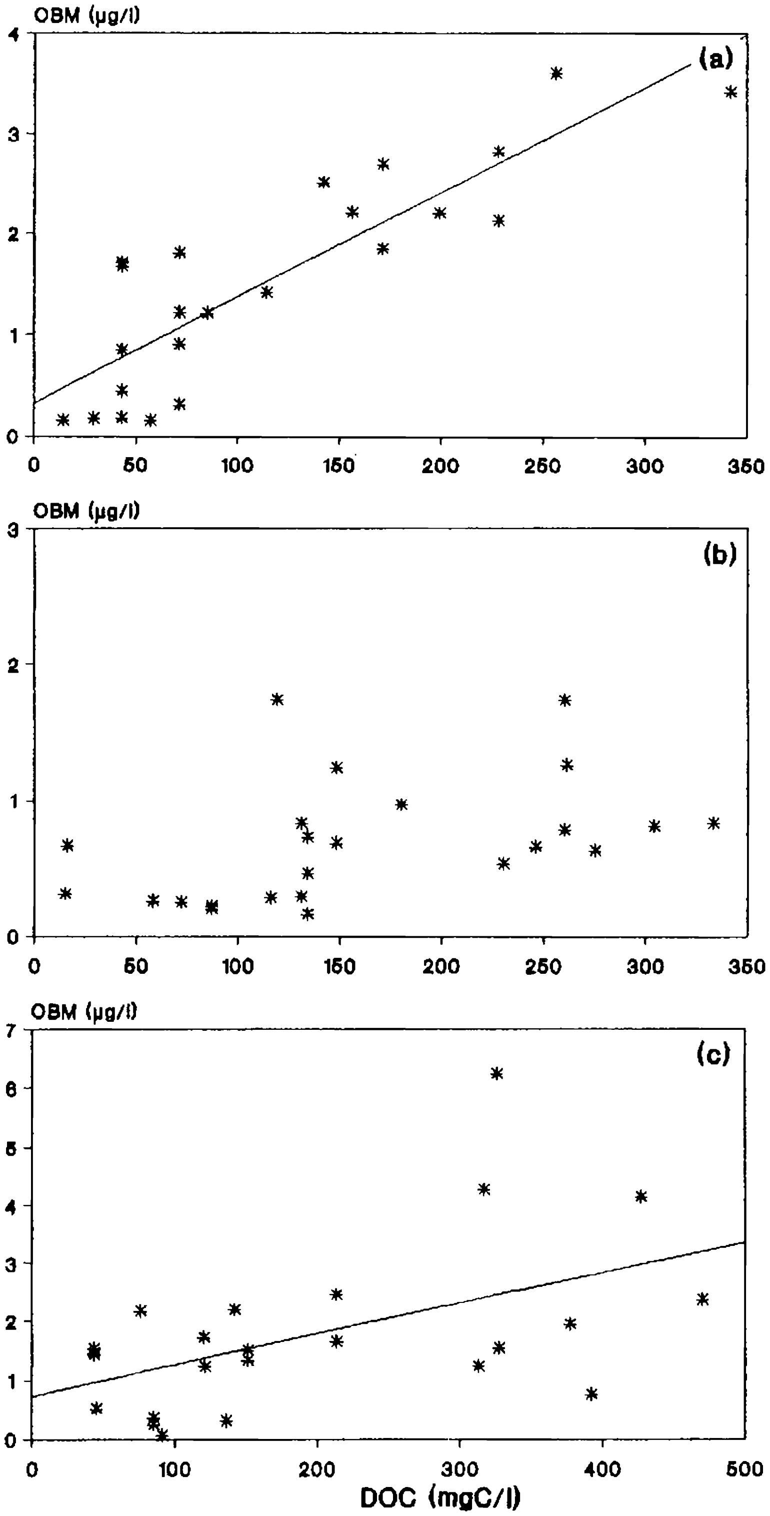


Fig. 3.3 DOC - OBM trend plots
a) premonsoon b) monsoon c) postmonsoon

salinity on particulate fractions the PEM and PTM values are plotted against salinity for the three seasons (Fig. 3.4 a, b & c for PEM and Fig 3.5. a b & c for PTM) In all these cases a sharp removal was observed at salinity <10%. This is mainly caused by the Ca^{2+} ions which replace the Cu^{2+} attached to the exchangeable positions as opined by Salomons and Bril (1990). This replacement is valid because of the high charge density of Mg^{2+} and Ca^{2+} compared to Cu^{2+}. The initial decrease is rapid during premonsoon and postmonsoon (periods of relatively low discharge) and gradual during monsoon (period of high discharge). The residence time of particles is sufficiently high during periods of low discharge, by which the particles will get adequate contact with saline water, enabling the Cu^{2+} ions on the particles to be exchanged with Ca^{2+} (Paulson *et al.*, 1989). However during monsoon, the decrease is gradual and the more dominating process may be field dilution. Additionally, during monsoon, the considerable increase in suspended solids may be yet another reason for this decrease as most of these particles are derived from the slightly acidic laterite soils and contains numerous free cation exchange sites. During initial stages of mixing the major ions instead of replacing copper ions, first occupy the vacant sites.

The seasonal Plots of PEM and PTM vs suspended solids (SS) are provided in Fig. 3.6 a, b & c and 3.7 a, b & c. Three remarkable features have been observed during each of the seasons:

(a) the premonsoon season exhibited a decrease in content of both particulate fractions in the low turbid waters. Presence of enhanced SS does not however lead to increase in both the fractions but the content remains mostly constant.

(b) The monsoon features both decrease as well as increase of the PEM and PTM - with increasing SS. Upto 18 mg l^{-1} there is a gradual decrease of PEM ($\approx$ 80 $\mu g\ g^{-1}$ to 10 $\mu g\ g^{-1}$) and PTM ($\approx$ 170 $\mu g\ g^{-1}$ to 65 $\mu g\ g^{-1}$). Further consequent to increase in the SS loads up to 30 mg l^{-1} the concentration levels of both the fractions show marginal increases to 50 $\mu g\ g^{-1}$ and 130 $\mu g\ g^{-1}$ respectively.

(c) An inverse relation to that of monsoon has been noted for

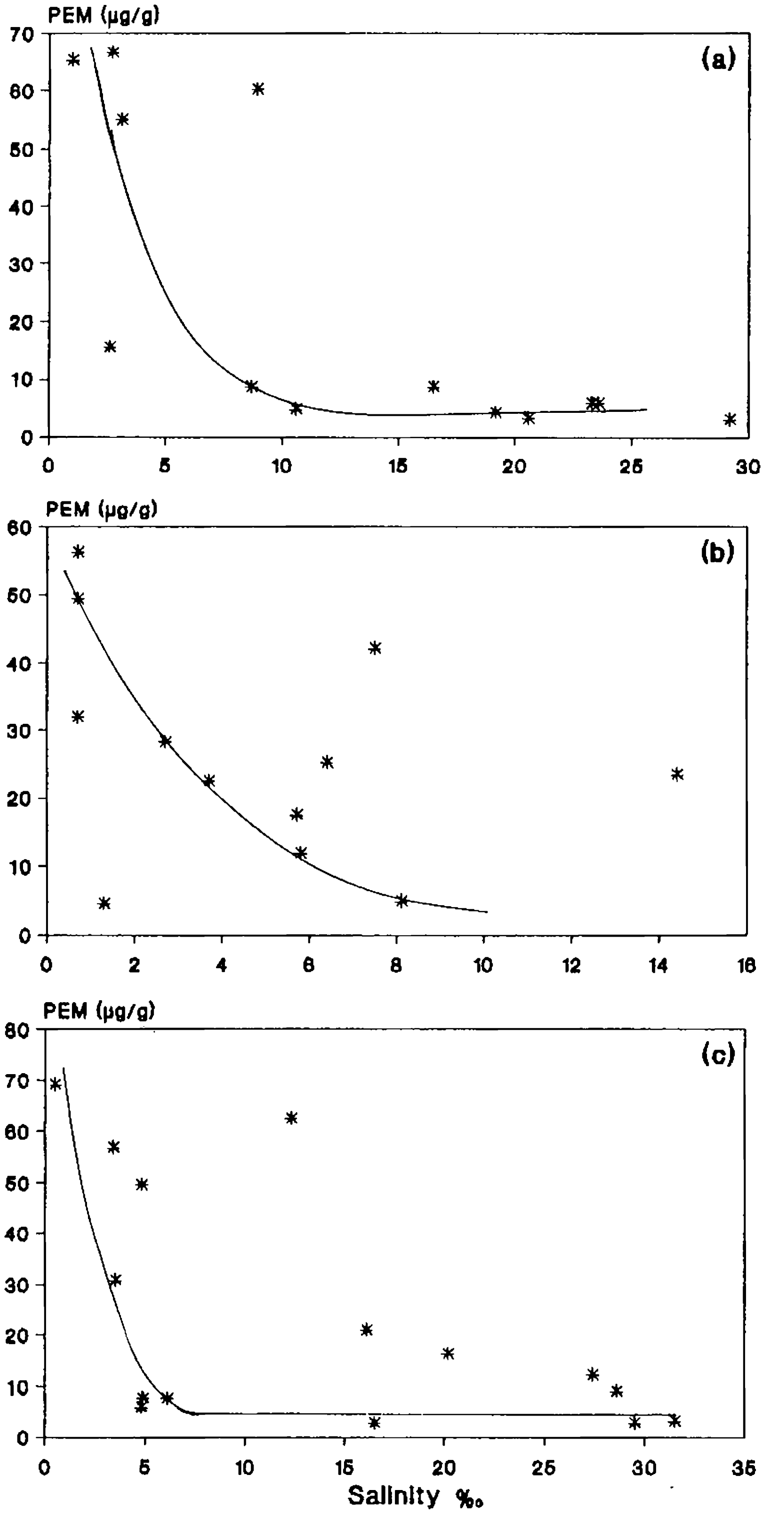


Fig. 3.4 Salinity - PEM plots
a) premonsoon b) monsoon c) postmonsoon

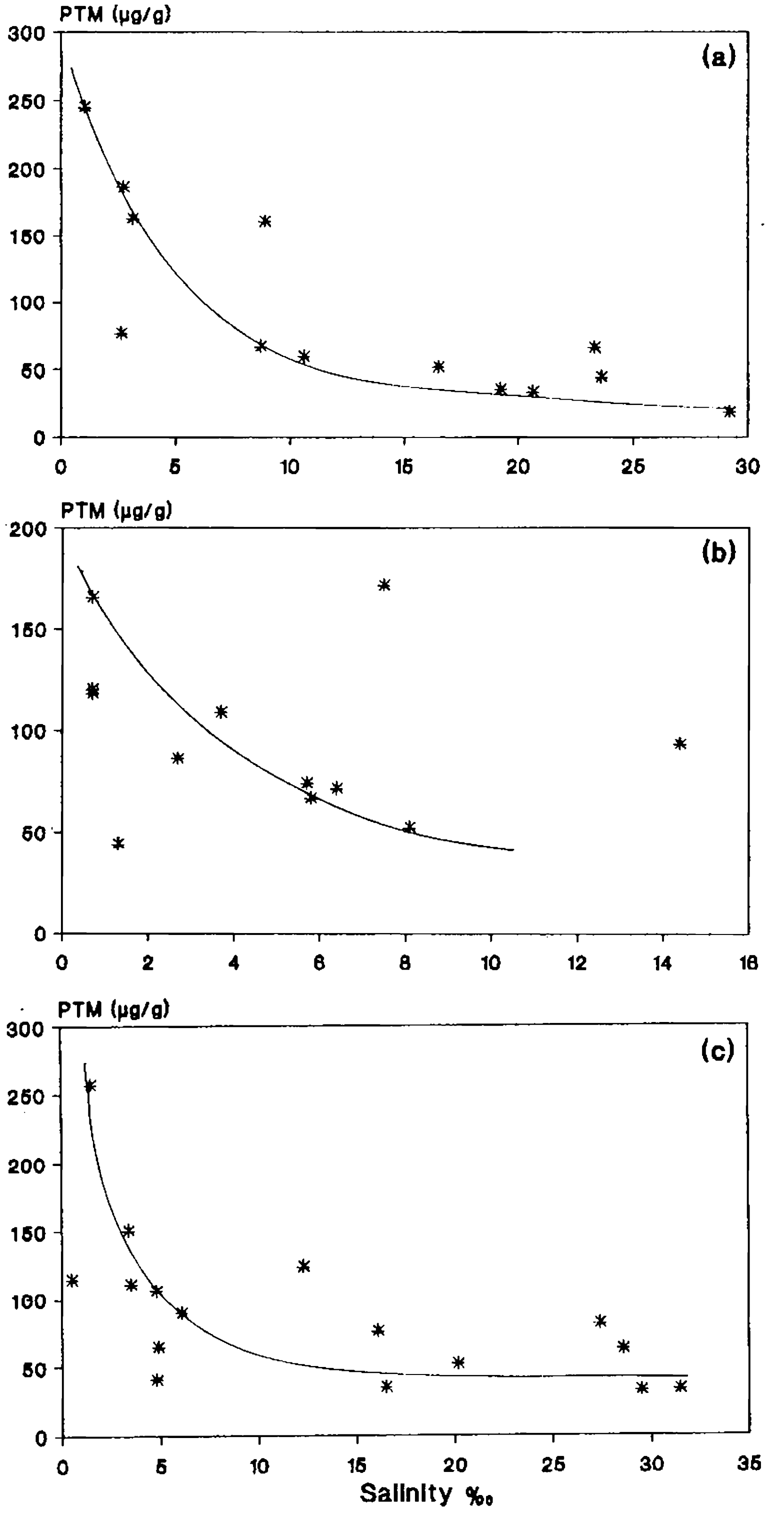


Fig. 3.5 Salinity - PTM plots
a) premonsoon b) monsoon c) postmonsoon

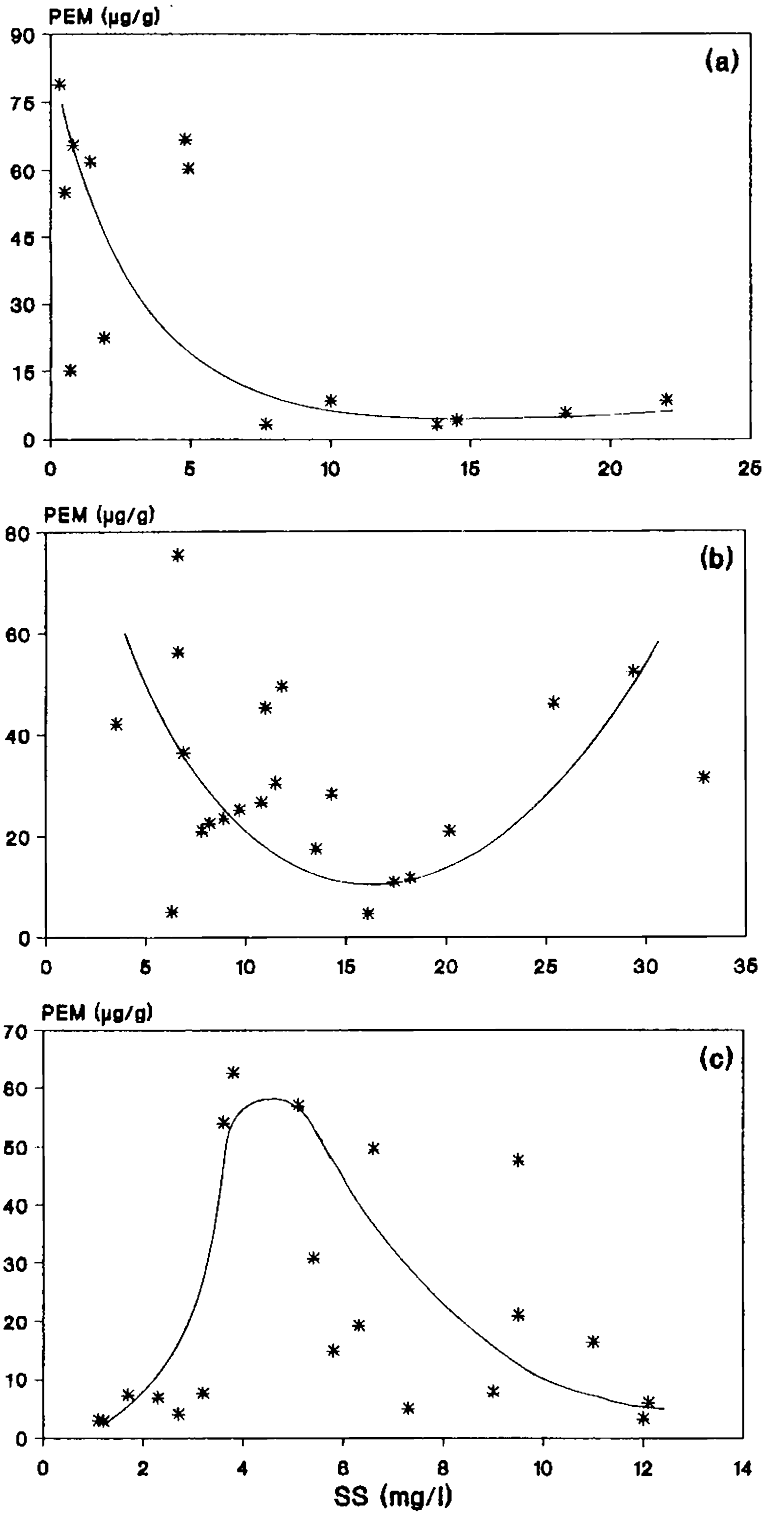


Fig. 3.6 Suspended solids - PEM plots
a) premonsoon b) monsoon c) postmonsoon

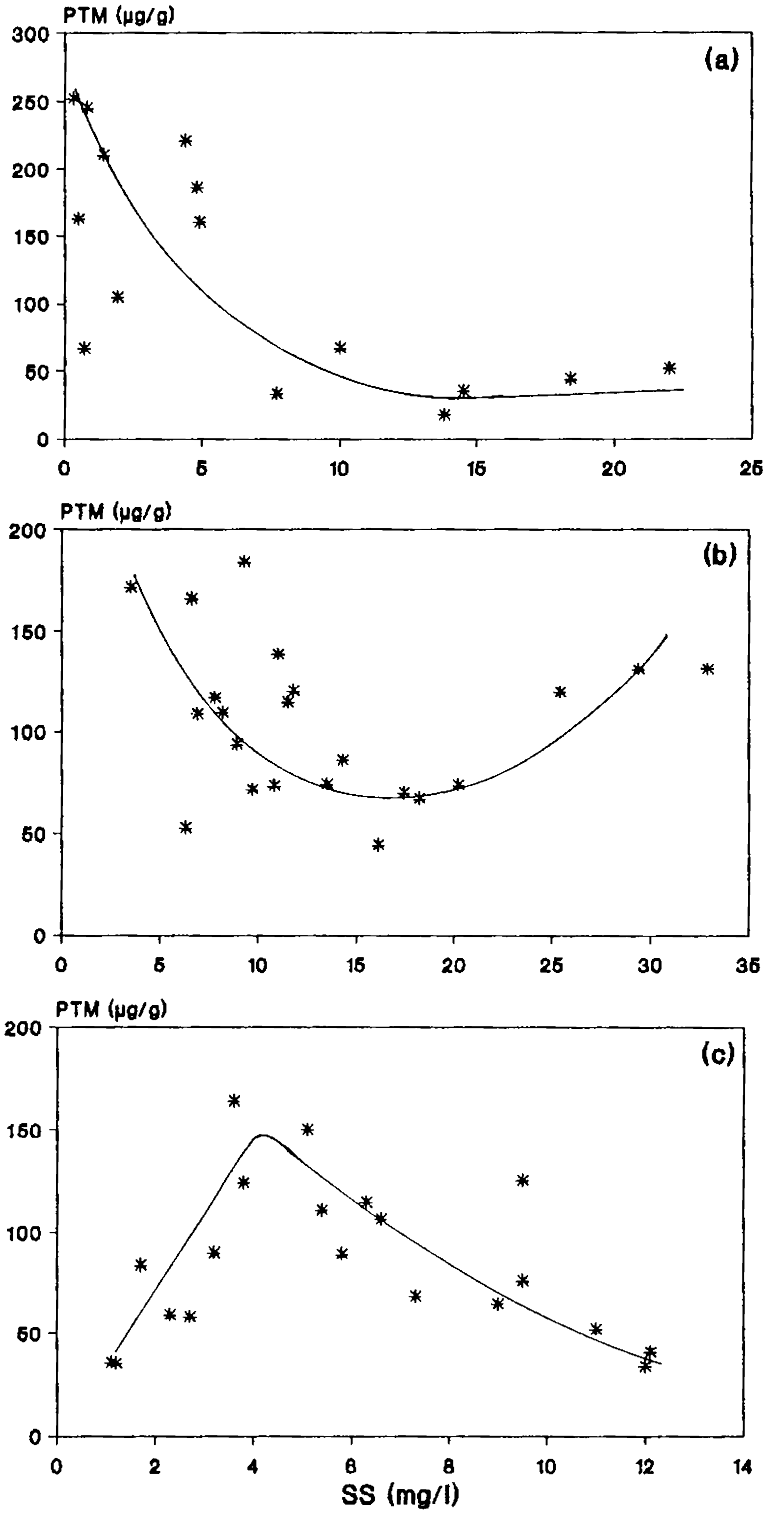


Fig. 3.7 Suspended solids - PTM plots
a) premonsoon b) monsoon c) postmonsoon

the postmonsoon season during which period both the particulate fractions initially (PEM increases to about 15 times and PTM to about three to four times) in the low turbidity zone (< 4 mg l^{-1}); this is followed by a gradual decrease to the initial value of the metal fractions as SS content increases to more than 12 mg l^{-1} during postmonsoon. The complex but obvious seasonal variability with respect to SS in the behaviour of particulate metal is only a reflection of the metal reactivity under estuarine conditions. The features exhibited in this tropical estuary differ widely from those of subtropical types, which however do not contribute to increase or decrease of metal levels. Within this estuary, the premonsoon season signifies longer residence time for the particulates in the highly saline waters. Presumably particulate reactivity occurs only in low salinities and is independent of increases in the amount of SS. Considering the decrease of particulate metal during monsoon, the higher amounts of SS are observed in lower salinity regions under which conditions the particulate related reactivity is more pronounced. This brings about a decrease in the PEM and PTM. In this context, shorter residence times coupled with resuspension of previously sedimented material from the lower estuarine reaches due to enhanced turbulance bring about only mild variations. Postmonsoon is a time of transition within the estuary in respect to hydrographical conditions which gives rise to an initial increase of SS (a `stepped-up ' enhancement) and follows a gradual decrease thereafter under conditions of occurrence of particulates in low salinities; and thereafter, the SS load increases with increase of salinity. This feature too highlightens the nongradation in the variation of particulate metal involved under conditions of changing hydrography.

Another important parameter which influences the particle associated metals is the content of POC. The amount of POC can be considered as a measure of the binding capacity of the particulate matter (Jouanneau *et al.*,1983). The POC was also found to decrease with increasing salinities in the Cochin estuary. The relations between POC and PEM & PTM are shown in Figs. 3.8 a b & c and 3.9 a b & c. The regression analysis

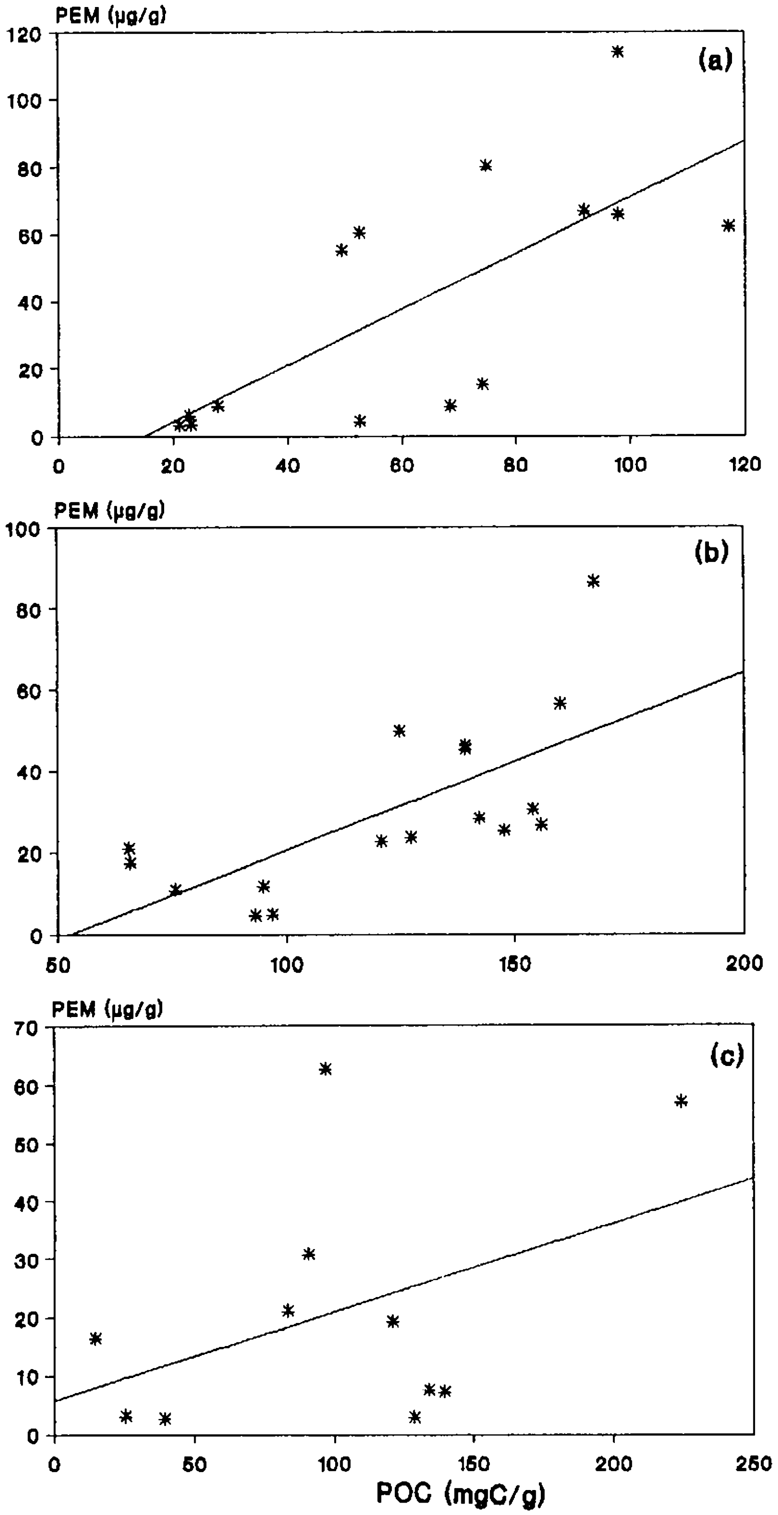


Fig. 3.8 POC - PEM trend plots

a) premonsoon b) monsoon c) postmonsoon

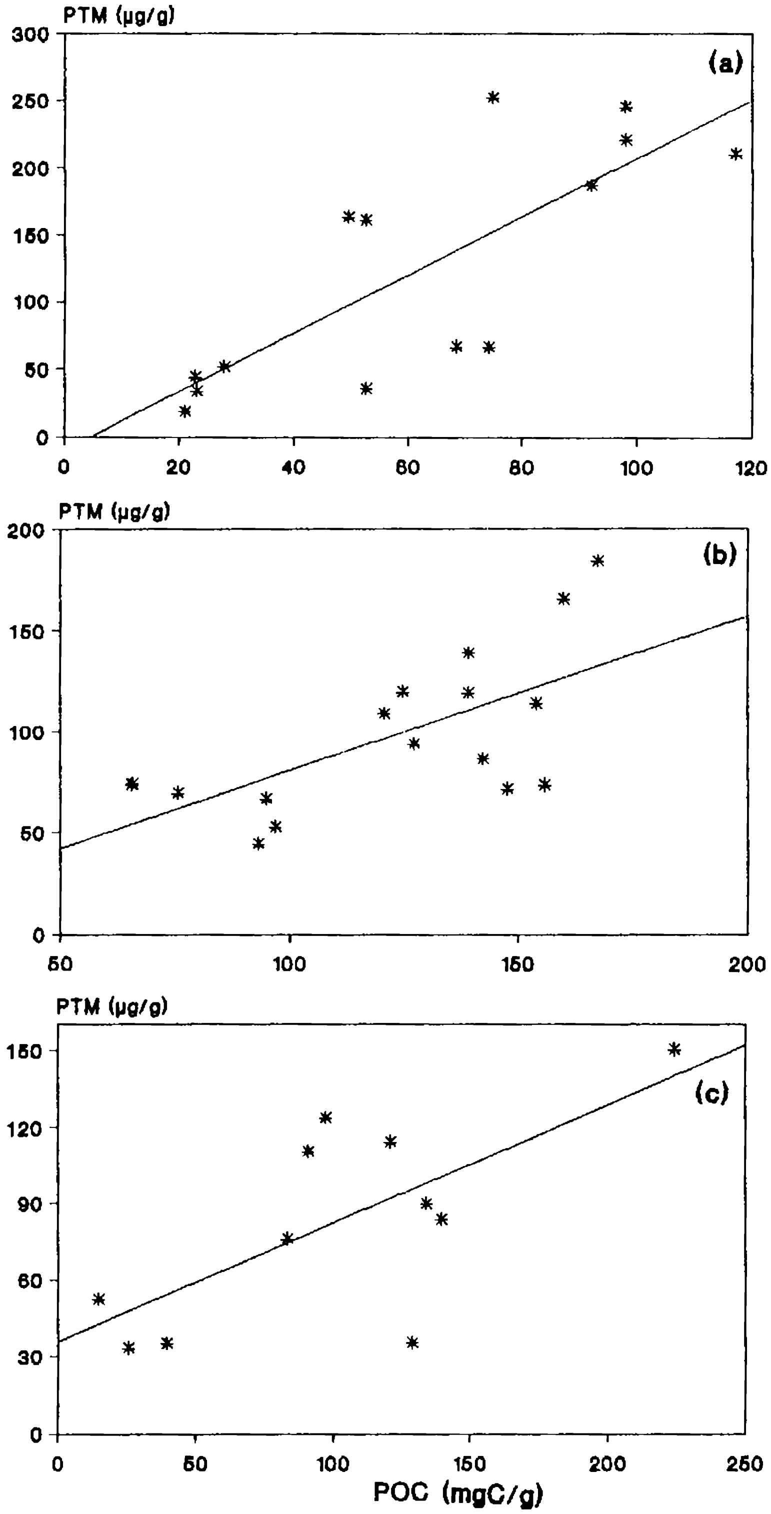


Fig. 3.9 POC - PTM trend plots

a) premonsoon b) monsoon c) postmonsoon

shows an excellent positive correlation for POC and PTM ($r = + 0.64$, $p < 0.001$). The importance of POC estimations in determining the extent of changes in particulate associated metal has been reported elsewhere (Jouanneau *et al.*, 1983; Windom *et al.*, 1988; Kuwabara *et al.*, 1989). It may well be inferred here that the decrease associated with the particulate metal towards the lower estuary is a combined effect of desorptions due to salinity changes and decrease of POC.

IV. Transport and Species Transformations

The transport of anthropogenic pollutants by rivers into tidally influenced estuaries and coastal waters has frequently been discussed. But inspite of considerable research efforts, the features are not yet satisfactorily understood (Koske, 1990). On an average, 40% of the total (CLM + OBM + PTM) copper in the Cochin estuary is transported via the particulate (PTM) phase (of which 14% is in the exchangeable form) which is in good agreement with the results of Mc Duffie *et al.*, (1976) in the Susquehanna river, U.S.A and no where near to results from Amazon and Yukon rivers, 97% and 82% respectively (Gibbs, 1977). In the Cochin estuary, during premonsoon the contribution of particulate phase to the total transport is about 37.5%, in postmonsoon it is about 26% and in monsoon, it is about 57% (Table 3.1). Available reports show that about 25% of copper is transported in the particulate phase in the Yarra river system during low discharge conditions and 63.5% during high discharge (Hart and Davies, 1981) and it is 65% during high discharge in the Elliot Bay (Paulson *et al.*, 1989).

Table 3.1

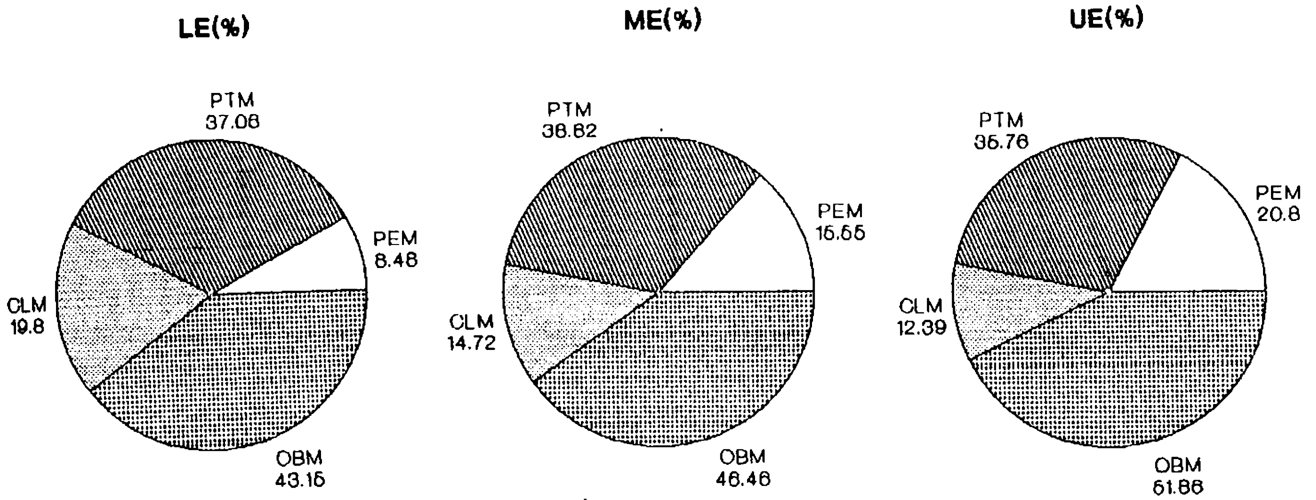
Season	CLM %	OBM %	PEM %	PTM %
Premonsoon	14.79	43.38	16.12	37.50
Monsoon	14.52	28.08	17.64	57.40
Postmonsoon	19.83	54.36	07.34	25.81
Annual Average	16.38	43.38	13.70	40.24

Another important observation in the transport of copper in this estuary is that the organically associated metal is high during premonsoon and postmonsoon (≈ 48% and 54%). On an average ≈ 60% of the total copper (CLM + OBM + PTM) is transported in the dissolved phase(CLM + OBM), out of which ≈ 73% is in the organic phase and 27% in the labile phase. The annual average of copper transport in the OBM fraction is ≈ 43% which maximises during postmonsoon (≈ 54%) and minimises during monsoon (≈ 28%). A high percentage of non-labile copper has been reported from the Newark Bay (Luther *et al.*, 1986) and the authors attributed this to the high oranic concentrations in the bay resulting from sewage outfalls. It is important to note that the complexation of copper by dissolved organic ligands tends to decrease their co-precipitation with other solids as well as their sorption onto organic solids and coagulated organic phases (Bernhard *et al.*, 1986).

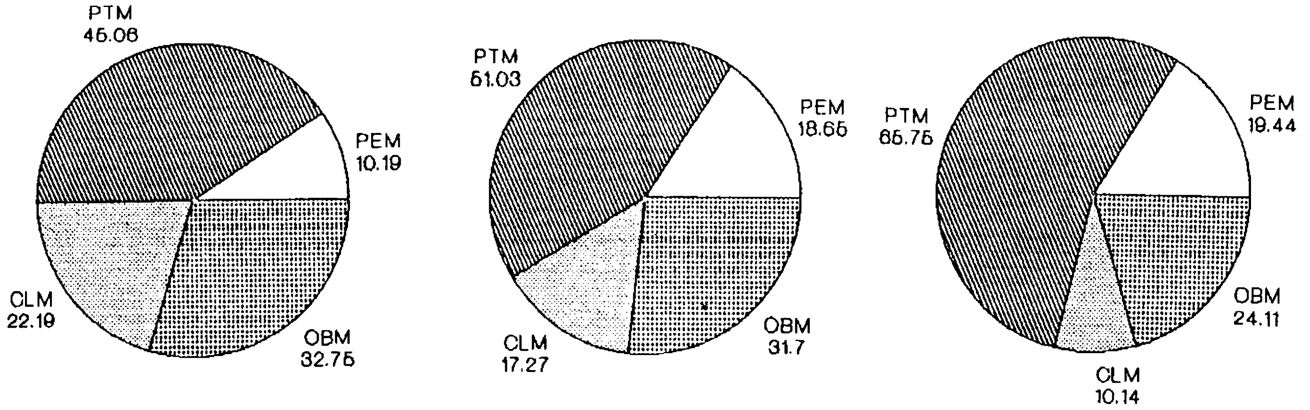
In order to have a better understanding of the species transformations during copper transport, the study area has been divided into three: Lower estuary (LE), Middle estuary (ME) and Upper estuary (UE). The percentage of each species in the three sections of the estuary are in Fig. 3.10. During premonsoon, the PEM fraction decreases sharply from 20.8% in the UE to 8.5% in the lower estuary. On the other hand the PTM does not undergo any appreciable variation (35.76 - 38.82 - 37.06%). Of the dissolved fractions, the CLM fraction increases (12.39 - 14.72 - 19.8%) towards the lower estuary while the OBM fraction decreases in the same direction (51.86 - 46.46 - 43.15%).

During monsoon, both PEM and PTM decreases towards the marine side (19.44 - 18.65 - 10.19% and 65.75 - 51/03 - 45.06%, respectively). The decrease in the PEM and PTM are compensated by a considerable enhancement of CLM (10.14 - 17.27 - 22.19%) and OBM (24.11 - 31.7 - 32.75%) contents.

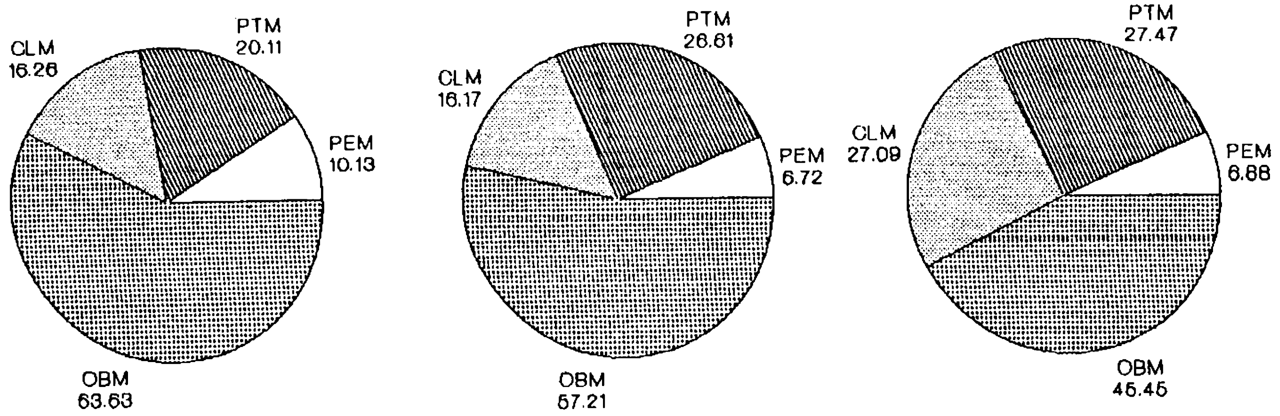
During postmonsoon, the PEM and PTM fractions decrease marginally (6.88 - 6.72 - 10.13% and 27.47 - 26.61 - 20.11%



premonsoon



monsoon



postmonsoon

Fig. 3.10 Seasonal Species transformations during estuarine transport
LE-lower estuary ME-middle estuary UE-upper estuary

respectively). The dissolved fractions undergo significant transformations during this period; CLM decreases sharply (from 27.09 - 16.17 - 16.26%) while OBM recorded a reverse trend (45.45 - 57.21 - 63.63%). It may be concluded that PEM undergoes considerable seasonal variation during premonsoon and monsoon; PTM during monsoon only. OBM also shows fluctuations only during postmonsoon while CLM varies widely during monsoon and postmonsoon.

The net result of species transformations of copper during estuarine mixing are summarised below.

Fraction	Premonsoon	Monsoon	Postmonsoon
PEM	Decreases	Decreases	Increases
CLM	Increases	Increases	Decreases
PTM	Increases	Decreases	Decreases
OBM	Decreases	Increases	Increases

V. Stochastic Mass balance of Copper in the Cochin Estuary

The northern part of the Cochin estuary was subjected to critical mass balance studies under stochastic conditions. The mass balance calculations for this part of the estuary involved a three box model similar to the model suggested by Klinkhammer and Bender (1981). The model is shown below:

Station 1 is eliminated from this calculation since it is influenced by discharge from the Muvattupuzha river on the southern part. The barmouth box contains all the samples (salinity > 20%.)
analysed in the present study; the estuary
box contains all samples with salinity 1%. < 20%. and the river box, samples with salinity < 1%..
The terms defined are:

Q_B- The input of seawater into the estuary
Q_R- The freshwater discharge from Periyar river
Q_E- Quantity of water leaving the estuary
S_B- Average salinity in the barmouth box
S_E- Average salinity in the estuary box
C_R- Average concentration of total metal in the river water (Dissolved + particulate)
C_E- Average concentration of total metal in the estuary box
C_B- Average concentration of total metal in the barmouth box

The model and the terms used here are also used for calculations in chapters 4, 5 & 6.

The freshwater discharge from Periyar river
(PWD, 1988 & 1989)

$$Q_R = 5.192 \times 10^{12} \ 1 \ Yr^{-1}$$

The average concentration of copper in the Periyar river

$$C_R = 2.58 \ \mu g \ 1^{-1}$$

Input of copper from the river

$$= 13.4 \times 10^3 \ Kg \ Yr^{-1}$$

There are essentially only two sources of water to the estuary - Q_R and Q_B
Therefore, water leaving the estuary would be

$$Q_E = Q_R + Q_B \text{-----} \ (1)$$

Since the time averaged salinity is a conservative property,

$(Q_R \times \text{zero}) + (Q_B \times S_B) = Q_E \times S_E$

Therefore $Q_E = Q_B \times S_B/S_E$ --------- (2)

Combining equations (1) and (2)

$$Q_B = \frac{Q_R}{\left(\frac{S_B}{S_E} - 1\right)}$$

The average salinity in the barmouth box,

S_B = 25.93%.

The average salinity in the estuary box,

S_E = 6.63%.

Therefore $Q_B = 1.78 \times 10^{12}$ l Yr^{-1}

The average concentration of copper in the barmouth box,

$C_B = 4.09$ µg l^{-1}

Flux in from the barmouth box,

$= 7.28 \times 10^3$ kg Yr^{-1}

The total copper flux into the estuary,

$= (13.4 + 7.28) \times 10^3$ kg Yr^{-1}

$= 20.68 \times 10^3$ Kg Yr^{-1}

$Q_E = Q_R + Q_B$

$= 6.97 \times 10^{12}$ l Yr^{-1}

The average concentration of copper in the estuary box,

$C_E = 3.22$ µg l^{-1}

Flux out from the estuary $= Q_E \times C_E$

$= 22.45 \times 10^3$ Kg Yr^{-1}

Mass balance of copper:

Flux in $= 20.68 \times 10^3$Kg Yr^{-1}

Flux out $= 22.45 \times 10^3$Kg Yr^{-1}

Flux in - Flux out $= \underline{-1.77 \times 10^3 \text{ Kg Yr}^{-1}}$

This result indicates that the total copper input and output are nearly balanced in this estuary. Some excess copper removed from the estuary may be accounted for by the input from sewage outfalls which do not figure in the above calculations. To conclude, this part of the estuary does not act as a sink for copper.

CHAPTER-4
CADMIUM

I. Introduction
II. Results
III. Discussion
IV. Transport and Species Transformation
V. Mass balance

I. Introduction

Cadmium occurs in the earth's crust at concentrations between 0.1 and 0.5 μg g^{-1} whereas the average level in natural waters is 0.4 μg l^{-1}. Also it has been well documented that Cd is closely associated with the behaviour of Zn in its geochemistry (Alloway, 1990). Cadmium is a byproduct from the smelting of zinc sulfide ore minerals, (0.2 - 0.4 % Cd is present in sphalerite and wurtzite, substituting for some amount of the Zn.) The world production of Cd increased considerably from 11,000 tonnes in 1960 to 19,000 tonnes in 1985 (Nriagu, 1988). The FAO / WHO recommended maximum human intake of Cd as 70 μg day^{-1} (Fassett, 1980). The United States Environmental Protection Agency has recommended a maximum allowable concentration of Cd(II) as 6.3 μg l^{-1}in freshwater and 59 μg l^{-1}in marine waters. Toxicologically, excess of this metal in potable waters may cause hypertension. In the human body, the critical organ is the kidney where one third of this metal is found to accumulate. There is no known mechanism for controlling Cd levels in humans, which may therefore accumulate following intake. This fact together with its relatively longer half-life (10-30 days) in biological systems makes Cd one of the most toxic metals (Craig, 1986). It is also now known that the itai-itai disease in Japan was directly linked to excessive cadmium exposure.

Considerable evidence is now available on the behaviour of Cd in the aquatic environment (Duinker and Nolting, 1978; Jouanneau *et al*, 1983; Elbaz-Poulichet *et al*., 1987 ; Huynh-Ngoc *et al*., 1988; Windom *et al*., 1988 & 1991; Paulson *et al*., 1989; Kuwabara *et al*., 1989; George, 1989; and Forstner *et al*., 1990). All these studies revealed the preference of Cd to remain in the dissolved phase (75 to 90 %) rather than in the particulate phase. In this context, the low charge density of Cd and that the concentration of Cd in the environment being controlled by weak ion-exchange reactions, this metal is significantly enriched in the water column (Martin and Whitfield, 1983). In freshwater, 90% of the cadmium appears as Cd(II) cationic species, but in the marine zones, anionic and neutral chlorocomplexes predominate. The stability of Cd-humic complexes has been reported to be far less compared to Cd-Chlorocomplexes and hence the very little organophilic nature of cadmium. Unlike copper, the particulate - associated Cd is found to be replaced by Na^+ ions when it comes into contact with seawater. In order to have a better insight into the behavioural picture of Cd during estuarine mixing, a speciation approach has been adopted in the present study.

As far as the Cochin estuary is concerned, the major point sources are the zinc smelter and a fertilizer industry on the banks of Periyar river; urban runoff from vast agricultural expanse of Periyar river basin contributes significantly to non point inputs.

II. Results:

Chelex 100 Labile Metal (CLM)

The monthly distribution of different fractions of Cd is shown in Fig. 4.1; on an average 29% of the total cadmium is

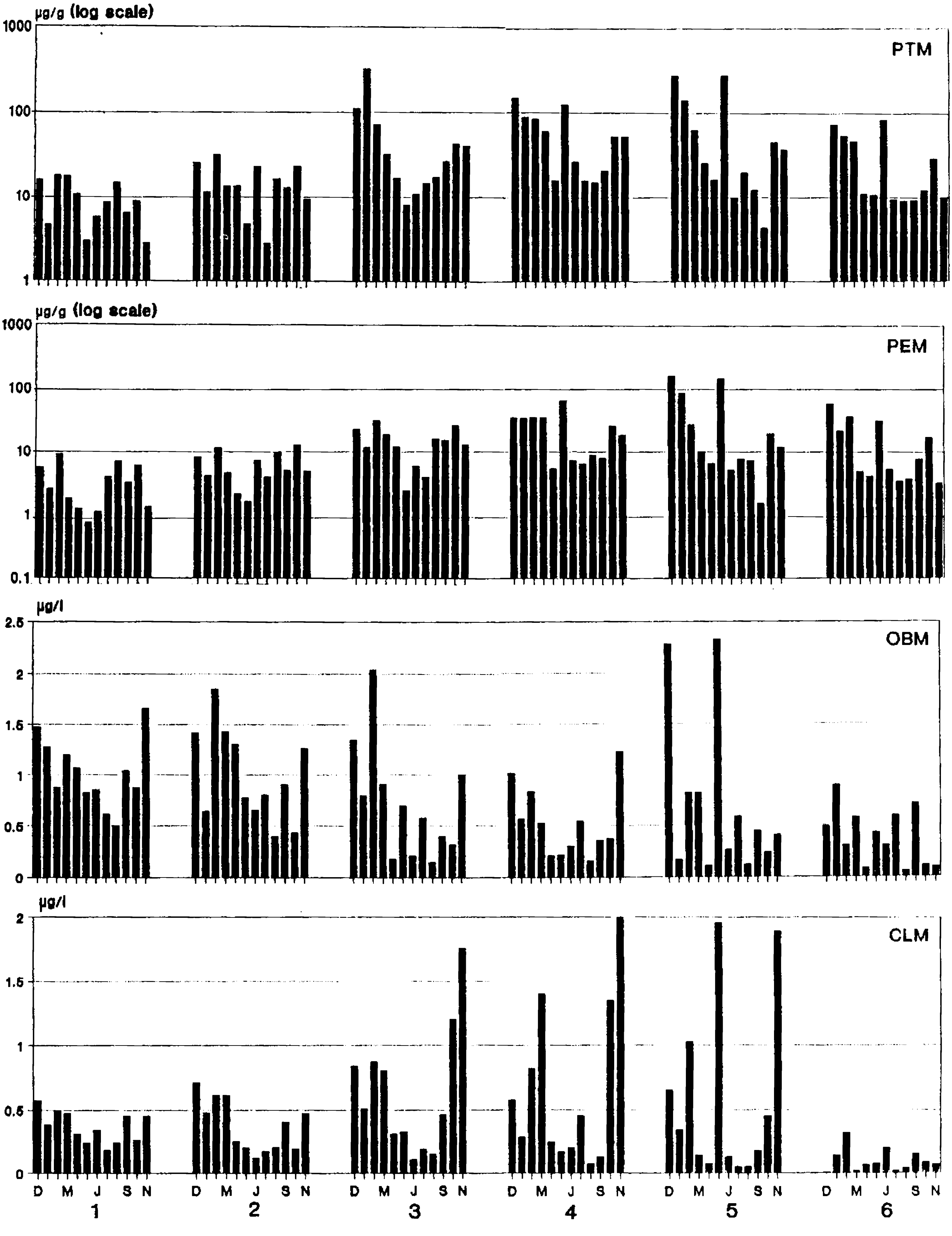


Fig. 4.1 Monthly distribution of cadmium fractions at Stations 1 to 6 (D-December 1988 to N-November 1989)

found to be present as the CLM form. In freshwater, the content of this metal was negligibly small and indicated low terrestrial inputs. Similar are the values at other downstream Stations during times of high river discharge. Analysing the features at Stations 4 & 5, binodal peaks have been noted. This feature is also translated further downstream (Stations 1 to 3) albeit with lower magnitude. Content-wise, the CLM fraction varied from near detection limit in July 1989 at Station 6 to 1.99 µg l^{-1} in November 1989 at Station 4. Exceptionally high values were recorded in November 89 at Stations 3,4 & 5 and in May 1989 at Station 5. Considerably low concentrations occurred during monsoon and was the highest during postmonsoon at all Stations except at Station 6, where it was high during premonsoon (Fig. 4.2a). The seasonal changes showed a gradual decrease towards the marine side. The premonsoon period coinciding with predominant tidal excursions define conditions conducive for sustainable concentrations within the estuary, longitudinally.

Organically Bound Metal (OBM)

The OBM fraction generally showed an increase in content towards the saline region . The minimum concentration observed was 0.1 µg l^{-1} at Station 6 in October 1989 and maximum was 2.33 µg l^{-1} at Station 5 in May 1989 (Fig 4.1). Yet another high value was also recorded at Station 5 in December 1988. Here too the metal levels were comparatively low at Station 6 in the freshwater zone , which is relatively free of pollution. The bound metal in association with the organic phase retains one half or more of Cd than the CLM fraction. Quantitatively this refers to more abundance (increasing down estuary), consistent with higher biological activity in the estuarine zones. This phase of the metal revealed 1) that through December 1988 to August 1989, the relative proportions at each Station was on the decrease and 2) that coinciding with the times of higher biological productivity, the OBM content also simultaneously peaked. The magnification in the content was 2 to 3 times more between values in July- August to those in February-March. From Fig. 4.2a it can be observed that the

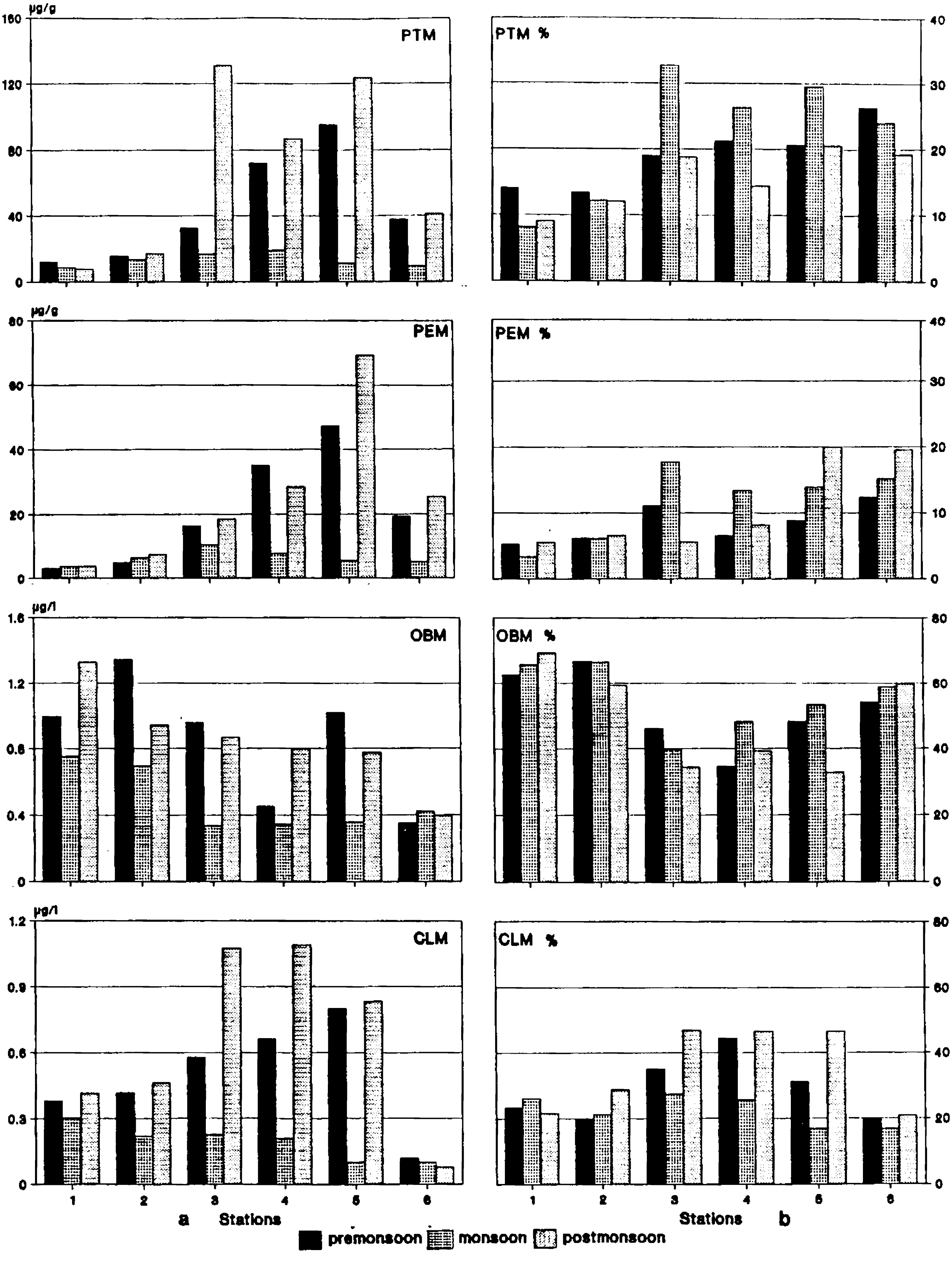


Fig. 4.2 Seasonal variation of cadmium fractions
a) absolute values b) percentages

seasonal OBM fraction was comparatively low during monsoon at all Stations except Station 6 where it was almost uniform during all seasons. Additionally, the monsoonal OBM values were similar at Station 3, 4 ,5 & 6 but enhanced at Stations 1 & 2. During postmonsoon, the values were increasing steadily from Station 6 to Station 1 (freshwater to seawater), but this feature was inconsistent during premonsoon.

Particulate Exchangeable Metal (PEM)

The distribution of particulate exchangeable metal (depicted on a logarithmic scale) for the year 1988-89 is shown in Fig.4.1. The general trend of PEM was a decrease towards the lower estuarine regions (from Station 5 to 1). The values of the PEM fraction varied in the range 0.73 $\mu g\ g^{-1}$ in May 1989 at Station 1 and 160.49 $\mu g\ l^{-1}$ at Station 5 in December 1988. The lower values of PEM were detected in May at Stations 1, 2 & 3 and relatively high values at Stations 4, 5 & 6 again in May 1989. The monthly distribution observed at Station 4 showed recurring values during the first four months of collection and thereafter, except May, the next 5 collections recorded similar, but lower, values compared to the previous collections. Noticeably, peak concentrations occurred in the month of May as stated above. Yet another feature was the gradually decreasing values at Stations 1, 2 & 3 from February to May and increasing values from May to August. Stations 1 & 2 exhibited values ranging from $\approx$ 1.0 $\mu g\ g^{-1}$ to $>$ 10 $\mu g\ g^{-1}$ which is a marginal change compared to changes in the upper reaches of the estuary (Station 4, 5 & 6 - 3.5 $\mu g\ g^{-1}$ to 160.5 $\mu g\ g^{-1}$). The PEM levels were low during monsoon and indicated the presence of a mid-estuarine maximum (Fig. 4.2a). During premonsoon and postmonsoon, a sharp decrease was noted from Station 5 to Station 1. An exceptionally high averaged value was recorded at Station 5 during postmonsoon. The seasonal changes presented in the figure revealed, remarkable Station-wise variation - quantitatively a ten times decrease towards the marine region. The exchangeable Cd in the particulate phase hence tended to diminish progressively in its spatial distribution than in its systemized temporal variation.

Total Particulate Metal (PTM)

The total particulate-associated cadmium was estimated by strong acid treatment and it revealed significant contributions from the terrestrial regions to the aquatic environments. At Station 6, since March 1989 to the end of the study, the inputs detected were ≈ 10 µg g^{-1} with an exceptionally high value in May 1989. The commencement of the study in December 1988 followed by analyses in January and February 1989 indicated marginal content of this fraction in the freshwater zone. The adjacent downstream Stations (Stations 4 & 5) contained appreciably high quantities with values, at times, more than 100 µg g^{-1}, mostly related to influence of anthropogenic inputs. There has been considerable reduction in the concentration in the distributional trends towards the saline regions; values at Stations 1 & 2 varied from a minimum of 2.8 µg g^{-1} to slightly more than 11 µg g^{-1}. Station 3 in the mid-estuarine region indicated a gradual decrease from the start of the year upto May and thereafter recorded a progressive increase. The overall behavioural pattern, irrespective of season, was a general decrease towards the lower estuarine region.

However the seasonal results presented (Fig 4.2a) illustrates, more explicitly the decrease in the content of total particulate cadmium from Station 5 to 1. Station 6 in the freshwater zone exemplified the true character of a terrestrial waterway in that the content of not only this fraction but other species estimated in this study also exhibited low metal values. Similar to the distribution of PEM, PTM values too were low at Stations 1 to 6 during monsoon whereas the decrease during premonsoon season commenced from Station 5 onwards. The profile of postmonsoon distribution was not smooth because of the hike at Station 3.

Percentage Abundance of Cd Species

The seasonal Station-wise abundance of metal species is shown in Fig. 4.2b. The percentage abundance of CLM fraction varied between 18 and 48% . The Stations 2, 3, 4 & 5 indicated a higher Cd-CLM abundance during postmonsoon period. Remarkably the end member Stations (Stations 1 & 6) showed no seasonal variation in the relative percentages. The premonsoonal behaviour of CLM, percentage-wise, exhibited a higher abundance at Station 4, which smoothened off to either sides of the river. Considering the contribution of OBM fraction, this form of dissolved metal predominated the other two fractions in this estuary. In contrast to the CLM fraction, the OBM percentages maximised at the end member Stations whereas the mid-estuarine abundance is about two-third's that of Stations 1 & 6. Within the seasons, none of the Stations showed any significant variations. The PTM percentage contribution was mainly noticed at Stations 3, 4, 5 & 6. The content was appreciably lower in the lower estuarine reaches and seasonally these two Stations besides, Station 6, exhibited only mild variations.

Station 6 in the riverine zone proportionally contained more OBM fraction followed by PTM and CLM. The Stations downstream of Station 6 were manifested by rather three equally contributing fractions with the OBM fraction alone being slightly on the higher side. The seasonal differences were explicitly significant during post monsoon period. Within Stations 1 & 2 the OBM fraction appeared to be the principal form of the metal (60 to 70%) followed by the CLM fraction (22 to 26%) and to a lesser extent the PTM fraction (8 to 14%). The fourth fraction PEM which is represented here as a part of the total metal estimated (accounted within the PTM fraction analytically) exhibited predominance at Stations 5 & 6 (12 to 20%). At both these locations, the postmonsoonal abundance far surpassed the premonsoon contribution.

Correlation Studies

The results of the intercorrelation studies among the four fractions of cadmium as well as between these fractions and various environmental parameters studied are given below.

Among the different fractions of cadmium the PEM and PTM showed excellent positive correlations with each other (r = 0.78). The CLM fraction showed positive correlations with OBM (r = 0.43), PEM (r = 0.34) and PTM (r = 0.34). Against environmental parameters, the OBM fraction showed significant positive correlation with salinity (r = 0.51) and DOC (r = 0.35). The PEM fraction showed significant negative correlation with salinity (r = -0.52),pH (r = -0.52) and suspended solid load (r = -0.49). The PTM frtaction too showed similar negative correlations with pH (r = -0.39) and SS (r = -0.44).

III. Discussion

The behavioural patterns of cadmium species during estuarine mixing are dealt with in detail hereunder. Available literature on the behaviour of cadmium (Windom *et al.*, 1988; Jouanneau *et al.*, 1990, Elbaz- Poulichet *et al.*, 1991) highlights the hydrophilic nature in the environment but a comprehensive analysis of the various fractions of cadmium was lacking in earlier studies.

i. Spatial and Seasonal Variation.

From Figs. 4.1 and 4.2a it was observed that all the four fractions of Cd studied were considerably low in amounts at Station 6. This sampling site is in the freshwater zone and relatively unpolluted since all the industrial effluent outfalls are downstream of Station 6. Noticeably all fractions of Cd indicated a rapid increase in concentration at Station 5. This is because of the anthropogenic inputs from the fertilizer industry and the zinc smelter factory situated 200m upstream of Station 5. Craig (1986) and Alloway (1990) have reported that both these industries are potential sources of Cd contamintion. Paul and Pillai (1983a) also have reported higher values of Cd in the industrial zone of Periyar river. The mid-estuarine region of this tropical water body is a very active zone in modifying the fractions of metals. The absolute values of these fractions are subjected to high variability giving rise to interspecies transformations. In the case of cadmium this aspect is well defined for OBM and PTM fractions. A direct reasoning for the above variability would be dependent on two important aspects - the tidal excursions and the bioactivity resulting from the ecosystem manifestations. The behaviour of Cd-CLM fraction appears to be influenced by estuarine ionic conditions whereas Cd-OBM was influenced more by organic detritus. The general diminution observed for Cd-PEM and Cd-PTM in the lower estuary points to a decrease in the metal adsorptivity or in the ability to retain the metal by interfacial processes. The real time variability is hence subjected to environmental modifications arising mainly out of chemical processes.

The seasonal features depicted in Fig.4.2a indicate an overall decrease towards the lower reaches of the estuary (Stations 5 to 1) with the exception that OBM fraction of Cd behaves oppositely. As far as Cd behaviour in estuaries is concerned, it is generally accepted that the mobilization processes from the particulate matter occur when river water mixes with seawater leading to the formation of highly stable and soluble Cd-chlorocomplexes (Elbaz-Poulichet *et al.*, 1987). Similar results have been reported in the lower part of the Scheldt estuary (Salomons and Kerdijk, 1986); in the Elbe estuary (Duinker *et al.*, 1982) and in the Changjiang estuary (Edmond *et al.*,1985). In the case of Cochin estuary, seasonal or otherwise, the PEM and PTM fractions decrease towards the seaward end . Hence, if the net mass has to be balanced, an increase on the Cd-CLM and Cd-OBM may have to be visualized. Relatively, only the OBM fraction exhibits this feature whereas CLM does not. The diminution in the content of CLM is appropriately compensated by the increase of values in the OBM fraction. However mass balance compensation and decompensation need not be strictly adhered to. The complexation of the mobilized Cd-CLM by free organic ligands in the estuarine region is well documented (Jouanneau *et al.*,1990; Bilinski *et al.*, 1991).

The seasonal features indicate generally lower values in monsoon for the PEM and PTM fractions. In this context, the suspended particulate matter consists of two types of particles, one is the finer texture with high metal content (in suspension) and the other consists of coarser particles with higher settling velocity and lower metal content. The exchangeable and the total particulate Cd values were plotted against the suspended solids (SS) load seasonally (Fig. 4.3a, b & c and 4.4a, b & c). These plots indicate that the metal content varies inversely with increase in the amounts of the SS load. The premonsoon decrease is sharp for the PEM fraction as the amount of SS increased to near 20 mg l^{-1} and there was low association of PEM at values greater than this. The monsoonal pattern show no consistent trend but may be surmised as a general decrease in moderately changing conditions of suspended loads. During postmonsoon, the values of PEM and PTM are limited to around 30 $\mu g\ g^{-1}$ and 160 $\mu g\ g^{-1}$ respectively at SS content < 5 mg l^{-1} which gradually lowers to values <10 $\mu g\ g^{-1}$ in turbid waters (> 10 mg l^{-1}). During monsoon, the high energy inputs due to increased river discharge cause a resuspension of bottom sediments with low metal content and the percentage of this resuspended particles will be cosiderable, accounting for the observed lower values in PEM and PTM fractions during monsoon. Alternatively the decrease in content towards the high salinity region for PEM and PTM are sharp during both premonsoon and postmonsoon. This relates to the high residence time of particles in the estuary during the low discharge condition by which time particulates undergo physical and chemical changes resulting in species transformations.

ii. Estuarine Metal Reactivity

The tropical estuaries are regions of high energy transformation sites not only in physical terms but chemically and biologically. Within this subsection the different fractions of Cd which undergo modifications are (re)viewed to identify the important mechanisms causing the above mentioned changes. As far as the particulate fractions are concerned it has already been reported that the most important mechanism

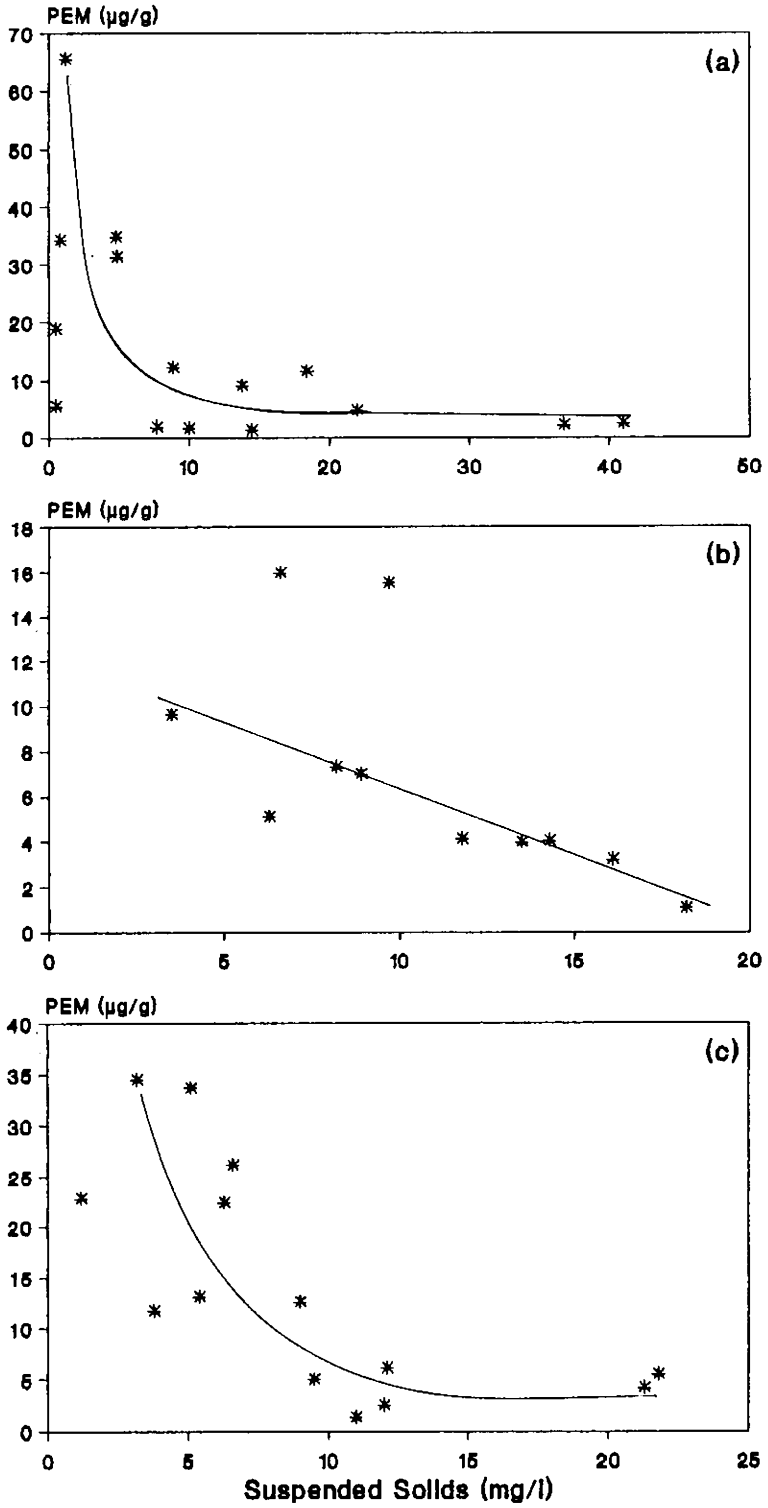


Fig. 4.3 Suspended solids - PEM plots
a) premonsoon b) monsoon c) postmonsoon

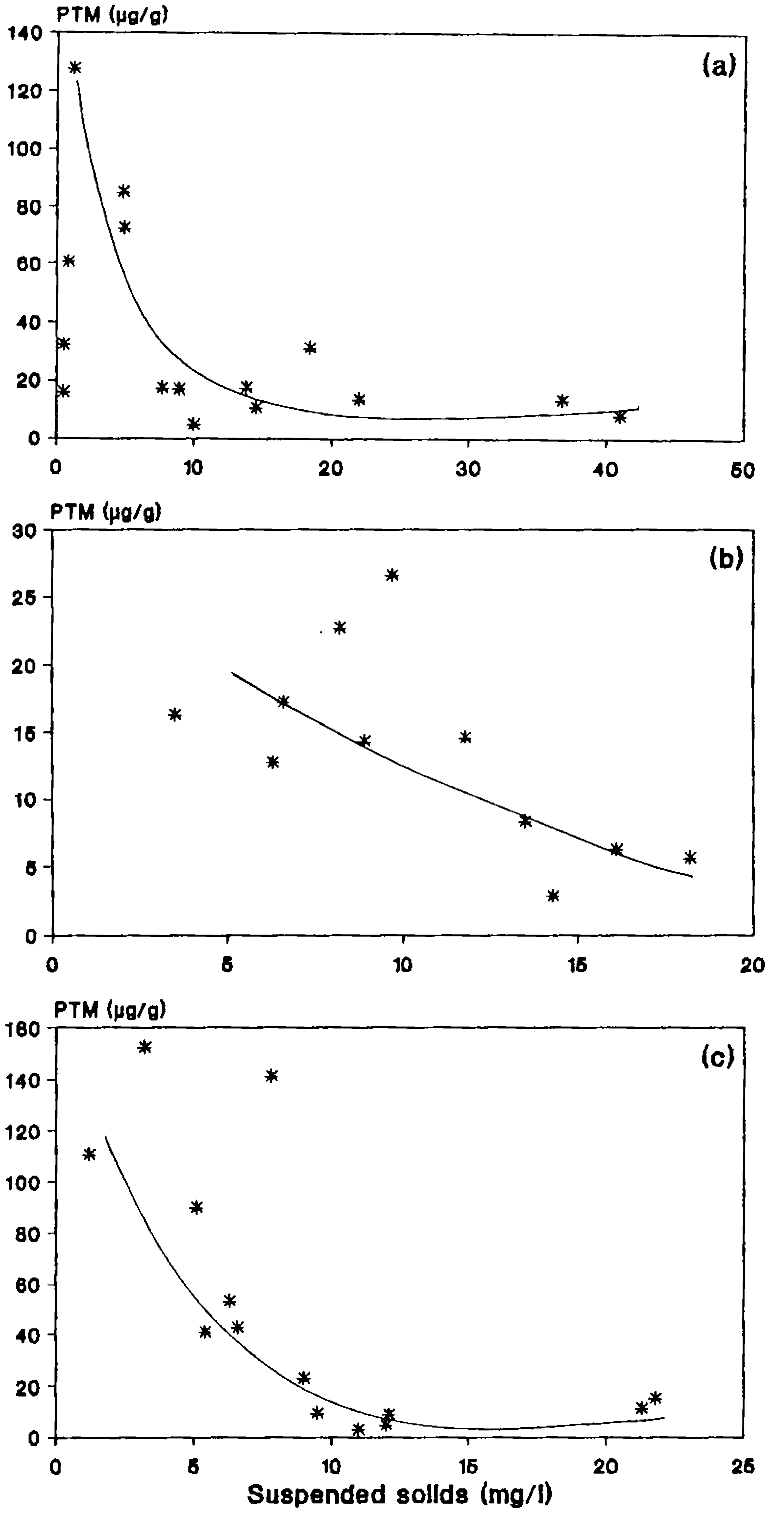


Fig. 4.4 Suspended solids - PTM plots
a) premonsoon b) monsoon c) postmonsoon

identified to be operating in the Cochin estuary is desorption (Shibu *et al.*,1990,). To illustrate the features more clearly the salinity - PEM plots and the salinity - PTM plots for premonsoon and postmonsoon are provided in Figs. 4.5 a & b and 4.6 a & b respectively. The Figures indicate a sharp removal of particulate associated metal in the low salinity regions (< 5‰.). Unlike copper, the cadmium associated with particulate matter is susceptible to exchange by Na^+ ions (Bourg, 1983) or Mg^{2+} and Ca^{2+} ions (Forstner *et al.*, 1990). Reports from South San Fransisco Bay (Kuwabara *et al.*, 1989) and Gironde estuary (Jouanneau *et al*, 1990) also show a similar removal of particulate-Cd with salinity. They attributed this to the desorption followed by a stable chlorocomplex formation. In Mandovi and Zuari estuaries, George (1989) also has observed the decrease of particulate associated Cd which was accounted as "particle dilution". He also reported an increase in the two forms of dissolved Cd (labile and bound) in higher salinity regions and proved experimentally that the desorption from particulate phase cannot quantitatively account for the observed increase. The various factors such as dredging, shipping and mining activities along with remobilization from the sedimentary phase was attributed to the above result by George (1989). Forstner *et al.*, (1990) explained the increase of dissolved Cd versus salinity gradient as a result of the formation of stable chloro-complexes and competition of alkaline earth metal ions (Ca^{2+} & Mg^{2+}) for sorption sites on solid substrates. Recently Elbaz-Poulichet *et al.*, (1991) also have reported similar behaviour of addition of Cd to the dissolved phase during etuarine mixing. In the present study, however, the CLM fraction was found to decrease towards the saline regions. This aspect is summarised as due to the high productivity in this area as revealed by the detailed seasonal studies of Gopinathan *et al.*,(1984) and Joseph (1989). Cadmium which gets transformed from the CLM phase to the OBM phase may finally end up (partially) in the sediments during the settling of organic detritus particles. Similar processes have been reported elsewhere too (Sharp *et al.*, 1984 ; Zwolsman and Van Eck, 1990). The laboratory experiments of Slauenwhite and Wangersky (1991) also testify to the operation of the above

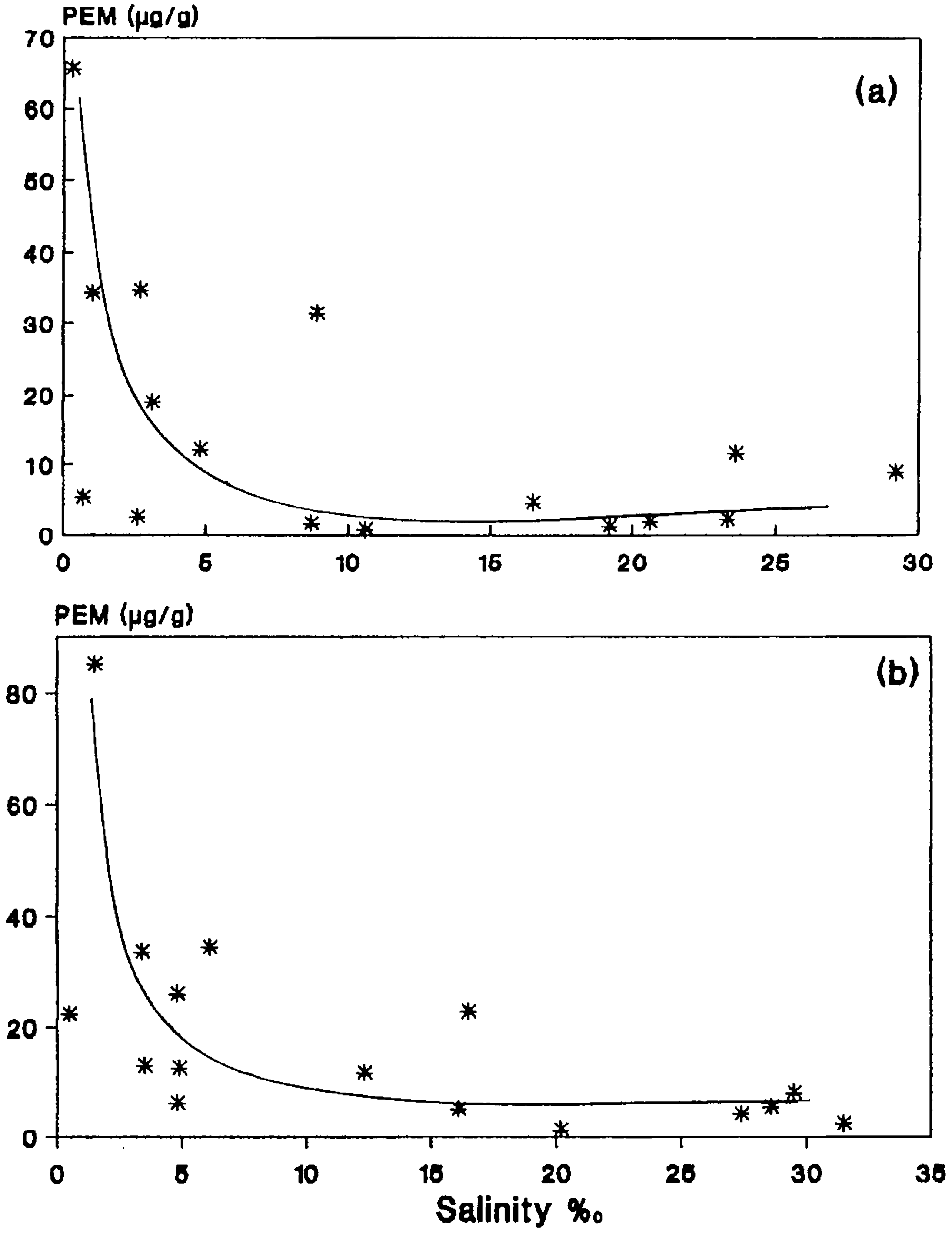


Fig. 4.5 Salinity - PEM plots
a) premonsoon b) postmonsoon

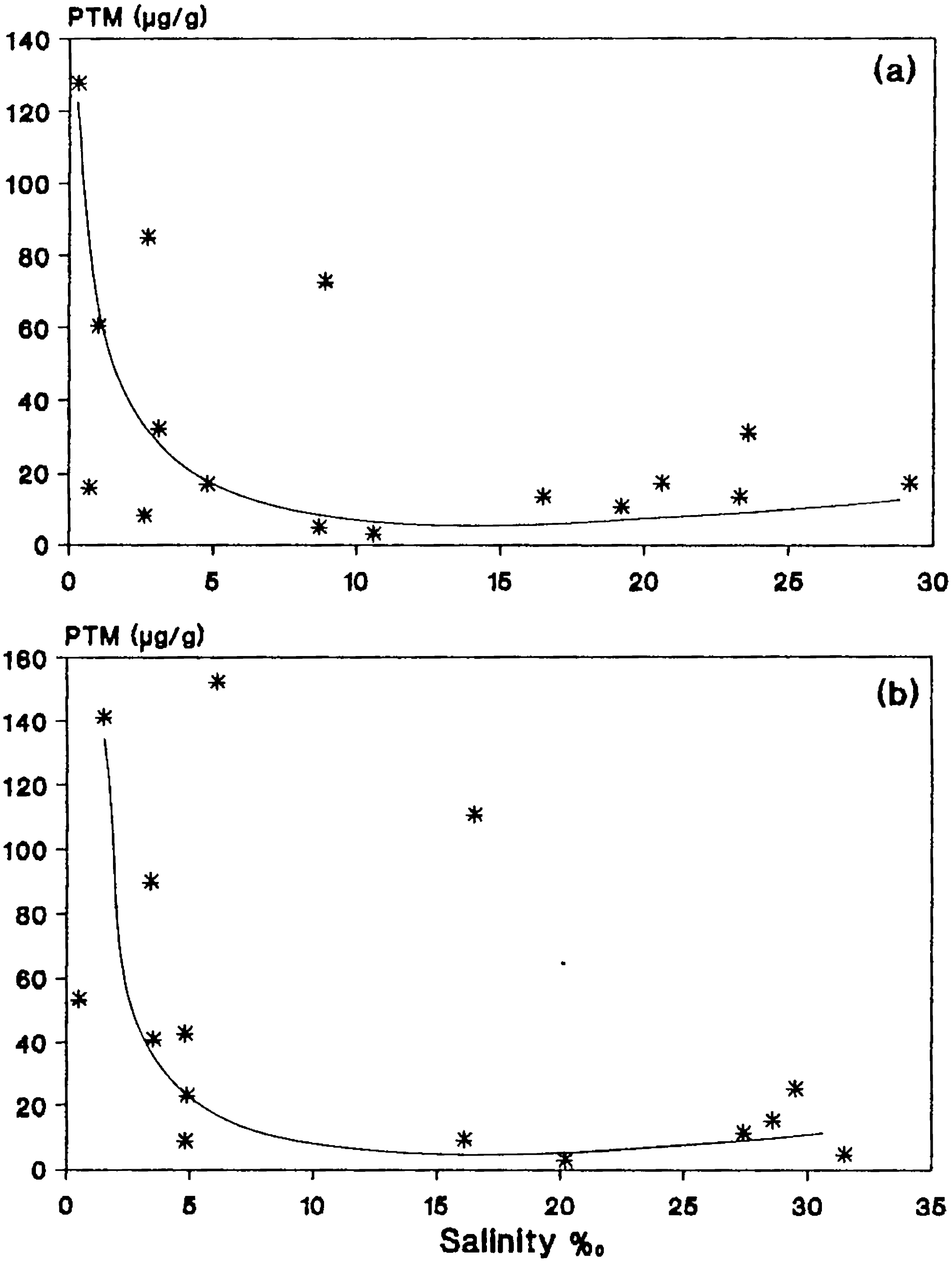


Fig. 4.6 Salinity - PTM plots
a) premonsoon b) postmonsoon

process. Furthermore, the increase in the OBM content in the present study supports the above proposition. Additionally the increase in OBM fraction can also be due to the remobilization from the sediments as a result of microbial activity stimulating Cd release by a complex process of substrate decomposition and potential organic ligand liberation and/or formation as also reported by Forstner *et al.*, (1990) in the Elbe estuary. They also observed that the distribution patterns of total and partitioned-Cd in a sediment profile to suggest the release of metals from particulates into the water media and further transfer to the biota to be controlled by the frequent downward flux of oxidized surface water by tidal action. Windom *et al.*, (1991) did identify biological regeneration as an important process which could affect the behaviour of Cd in estuaries.

From the documented evidence (Forstner *et al.*, 1990), it was expected that long term removal of upto 50% of the cadmium from the sediment subsurface would take place from the anoxic sedimentary sinks located a few centimeters below the sediment-water interface. This factor would be helpful in explaining the negative mass balance of Cd in this estuary which will be discussed later. The model experiments of Bilinski *et al.*, (1991) also have shown that Cd was released from inorganic solids, into the water column at higher salinities. Kuwabara *et al.*, (1989) found an increase of dissolved Cd with increase in suspended solids and considered the suspended particulate matter as a source for Cd in the saline region. In the present study, the CLM fraction was found to decrease sharply with increases of SS load . It may be assured that any increase in dissolved Cd is surmounted by equally vibrant increase in OBM fraction supported by remobilization from the sedimentary phase. Kuwabara *et al.*, (1989) also found that dissolved Cd is highly correlated with POC; but in the present study no such relation was observed. The salinity-OBM plots (Fig 4.7a & b) show a broad maximum at higher salinities (20-25‰). Similar broad maximum for dissolved Cd has been reported elsewhere (Elbaz-Poulichet *et al.*, 1987; Windom *et al.*, 1991). They attributed this to the

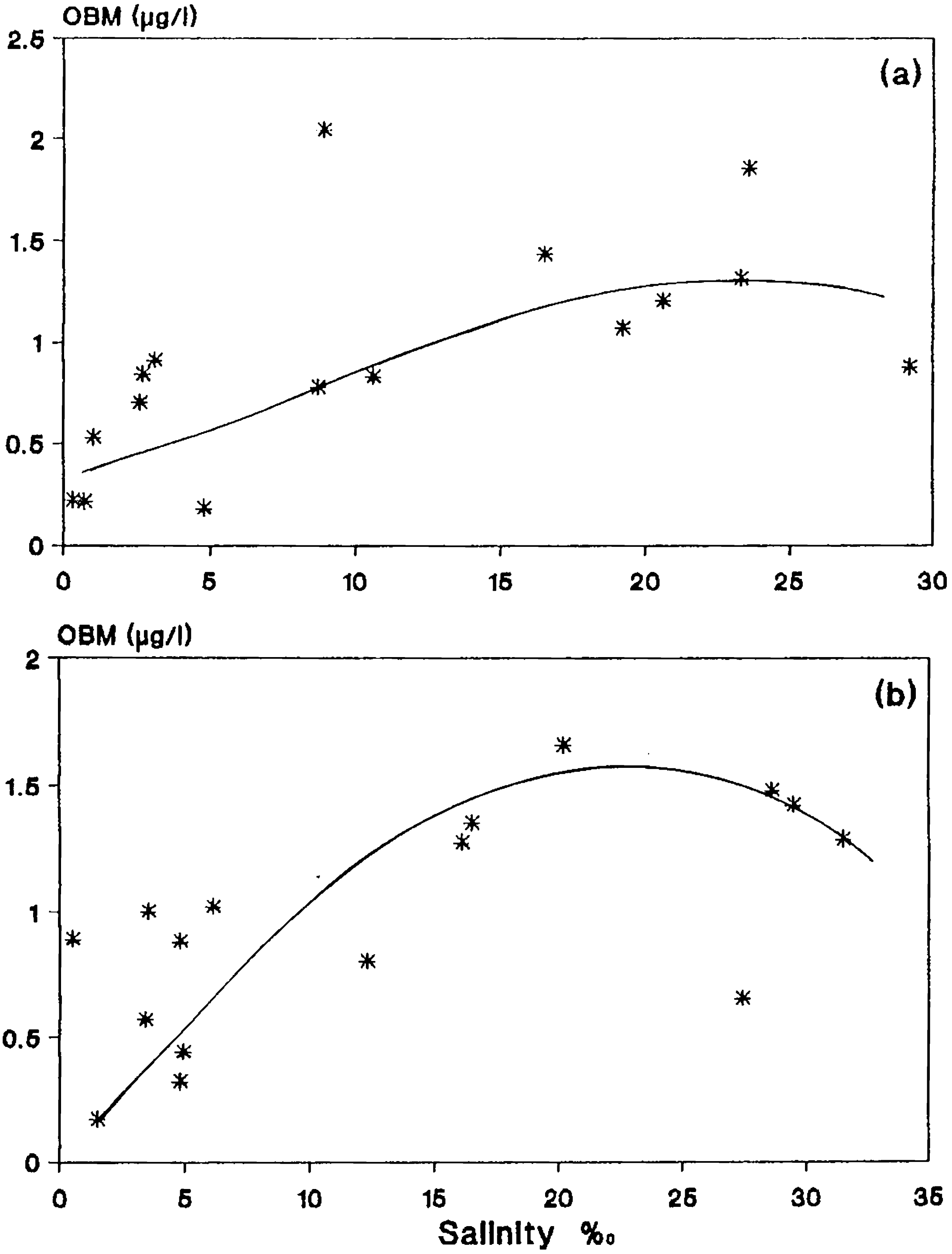


Fig. 4.7 Salinity - OBM plots
a) premonsoon b) postmonsoon

desorption followed by complexation with Cl^- ions in estuarine waters. But CLM fraction did not exhibit any such maximum in the present study. So it can be concluded here that the broad maximum observed at higher salinities in the Cochin estuary may be the result of desorption followed by complexation with organic ligands. The increase in OBM also coincides with an increase in the DOC content (Fig 4.8 a, b & c). Significant positive correlation exists between DOC & OBM ($r = 0.35$ $p < 0.001$) considering the complete data set. Concurrently, there are other speciation studies in which only very little organic association has been reported for Cd (Florence, 1977; Hart and Davies, 1981; George, 1989).

IV. Transport and species transformations

The transport of Cd in different seasons is shown in Table 4.1. Similar to the observations of Hart and Davies (1981) in the Yarra river system; Windom *et al.*, (1988) in the Bang Pakong estuary, Kuwabara *et al.*, (1989) in the San Fransisco Bay and Jouanneau *et al.*, (1990) in the Gironde estuary, here in Cochin estuary too, Cd is transported mainly in the dissolved phase. The data analysis indicate that on an average about 19% of the total Cd is transported in the particulate phase (out of this 19% , about 54% is in the exchangeable form subjected to increase upto 70% during postmonsoon) and 81% is transported in the dissolved phase. Similar metal transport was reported from CSF and RG rivers (89% dissolved & 11% particulate; Lacerda *et al.*, 1987), Rhine estuary (72% and 28%, de Groot *et al.*, 1976), Yarra river system (75% and 25% , Hart and Davies, 1981). Out of the 81% dissolved cadmium transported in Cochin estuary 35% is in the CLM form and 65% in the organic form. Generally the metal transport is highly dependent on climatic conditions and associated river discharges. In the case of Cd transport, the seasonal variations in relative proportions of different fractions are not very significant.

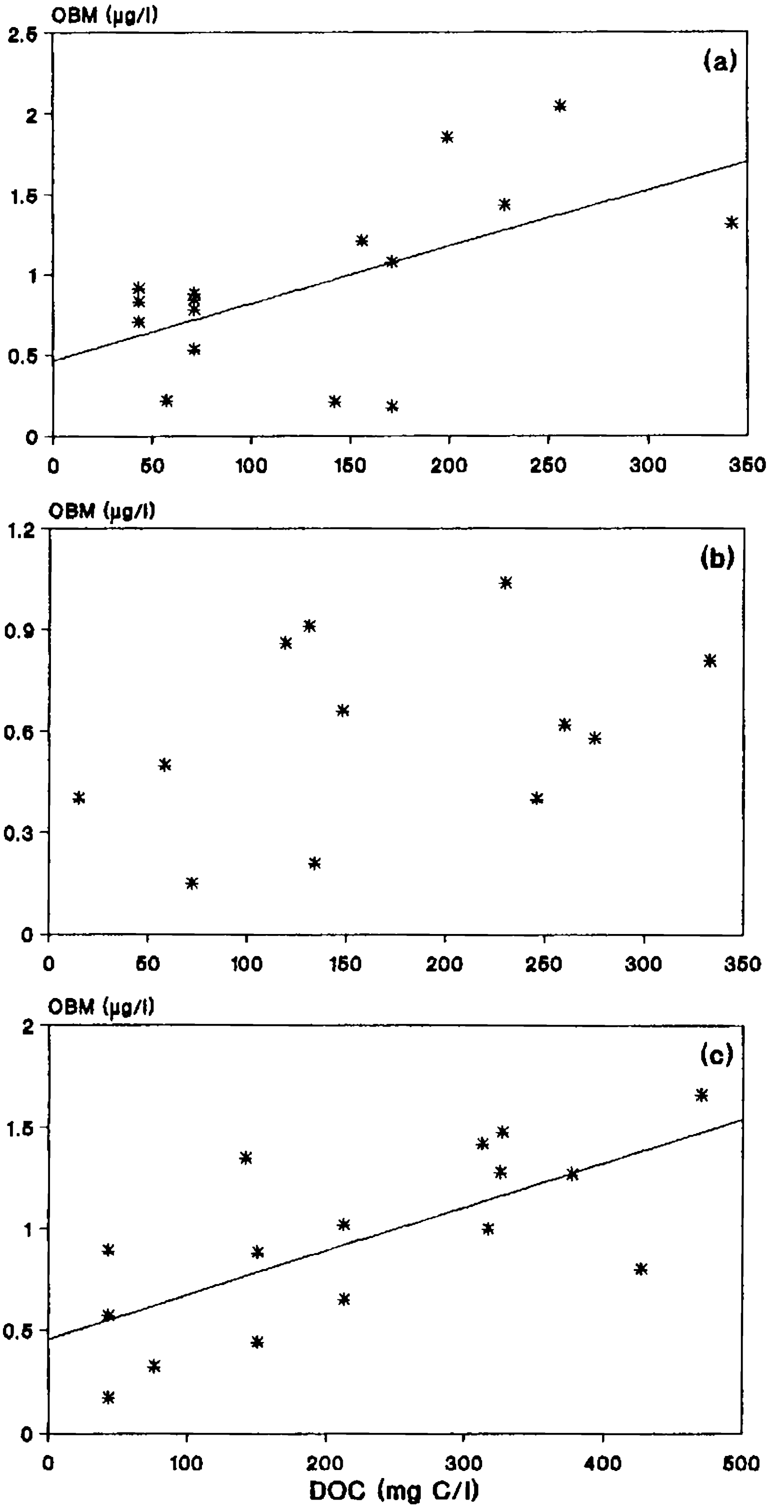


Fig. 4.8 DOC - OBM trend plots
a) premonsoon b) monsoon c) postmonsoon

Table 4.1

Season	CLM %	OBM %	PEM %	PTM %
Premonsoon	28.88	52.04	08.38	19.09
Monsoon	22.41	55.46	11.64	22.14
Postmonsoon	33.15	49.19	10.95	15.66
Annual average	28.81	52.23	10.33	18.96

The transformations that are taking place in each species on transport from the UE - upper estuary (freshwater) through ME - mid estuary to the LE - lower estuary during the three seasons are shown in (Fig 4.9). Both the particulate fractions (PEM and PTM) decreased considerably from the upper estuary to the lower estuary during all the seasons. The CLM fraction showed a mid-estuarine maximum during premonsoon and postmonsoon while it increased steadily during monsoon. In premonsoon and postmonsoon the net result of estuarine mixing was a decrease of CLM fraction in the LE and during monsoon this fraction steadily increased with repect to other fractions. During postmonsoon, the decrease of CLM was considerable (33.68% - 40.65% - 21.58%). On the other hand, sharp increase of OBM fraction during postmonsoon (46.36% - 44.32% - 69.49%) was observed. During all the seasons the percentage OBM fraction was comparable in the upper and mid estuary but increased sharply in the lower estuary.

V. Mass balance

Given

$C_R = 1.08\ \mu g\ l^{-1}$

$C_B = 2.11\ \mu g\ l^{-1}$

$C_E = 1.67\ \mu g\ l^{-1}$

Flux in from the river $= Q_R \times C_R$

$= 5.61 \times 10^3\ Kg\ Yr^{-1}$

Flux in from the barmouth $= Q_B \times C_B$

$= 3.76 \times 10^3\ Kg\ Yr^{-1}$

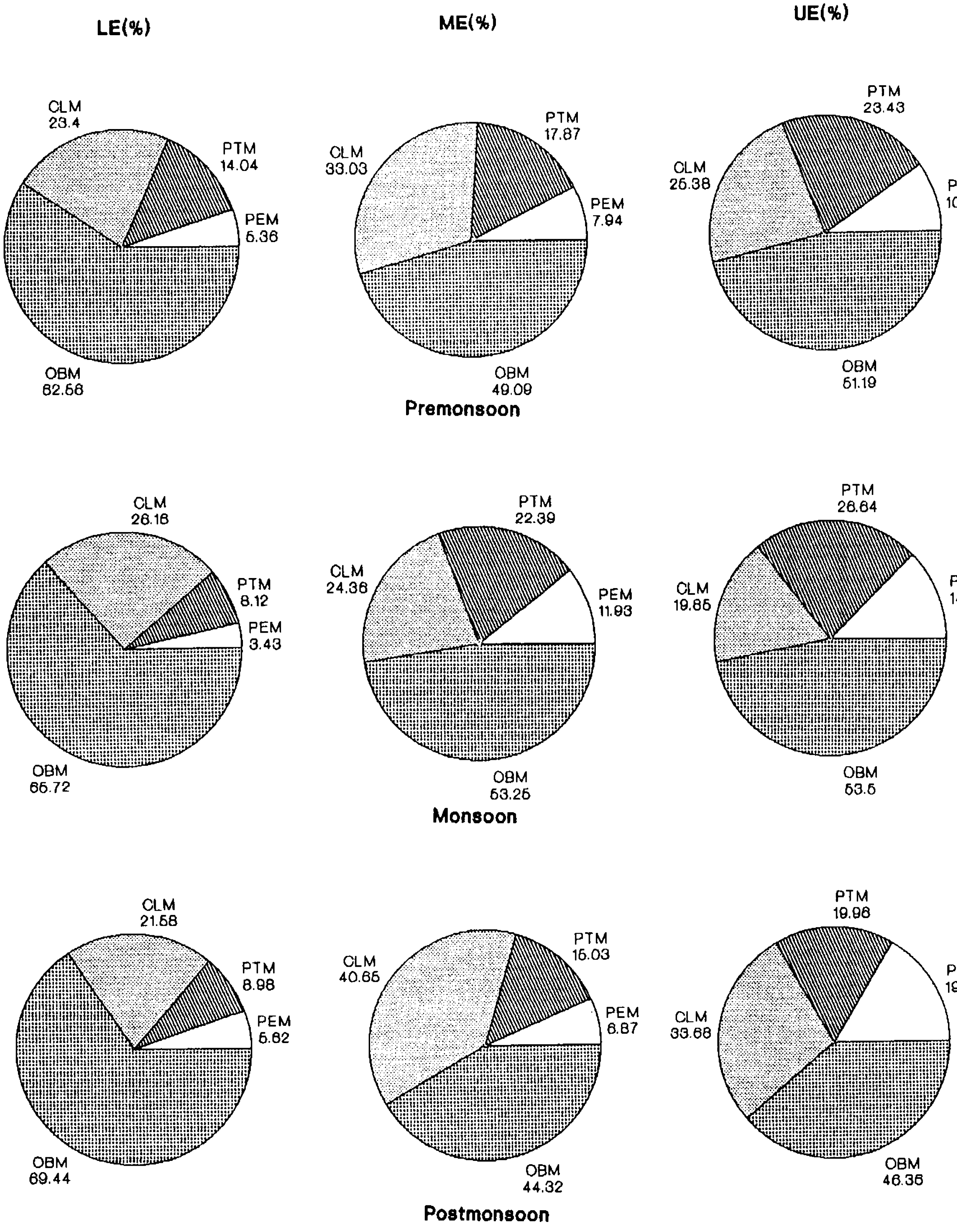


Fig. 4.9 Seasonal Species transformations during estuarine transport
LE-lower estuary ME-middle estuary UE-upper estuary

Total Cd flux into the
estuary = $(5.61 + 3.76) \times 10^3$ Kg Yr^{-1}

= 9.37×10^3 Kg Yr^{-1}

Flux out from the estuary = $Q_E \times C_E$

= 11.64×10^3 Kg Yr^{-1}

Mass balance for Cd = $(9.37 - 11.64) \times 10^3$ Kg Yr^{-1}

= $- \underline{2.27 \times 10^3 \text{ Kg } Yr^{-1}}$

The mass balance of Cd in the Cochin estuary showed an excess of 2.27×10^3 Kg Yr^{-1} indicating some sources of Cd. This may be the result of sewage discharges and desorption/remobilization from the sedimentary phase, both of which were not taken into account in this calculation. Windom *et al.*, (1976), evaluated the transport of metals and concluded that estuaries did not serve as sinks for Cd and Hg but that these two metals were transported ultimately to the coastal waters. The computations performed here attributed to a source factor of about 25% added to input flux to be discharged to the nearshore waters.

CHAPTER 5

LEAD

I. Introduction

Lead mainly exists as Pb (II) carbonate, sulfide or oxide in the earth's crust and has an average concentration of ≈ 13 $\mu g\ g^{-1}$ and in uncontaminated soils it is ≈ 10 $\mu g\ g^{-1}$ (Craig, 1986). Uncontaminated open ocean and fresh surface waters may contain 0.1 $\mu g\ l^{-1}$ and 0.5 $\mu g\ l^{-1}$ respectively. But rivers flowing adjacent industrialized centres may contain levels upto ≈ 100 $\mu g\ l^{-1}$. Considerable atmospheric addition of Pb has also been reported from various parts of the world (Alloway, 1990). The high enrichment of Pb may be a direct contribution from vehicle exhausts. Lead, one of the most abundant toxic pollutants in the environment, becomes a real concern as a contaminant because of its constant and continuous release into the air, water and soil in appreciable amounts (Branica, 1980). Lead toxicity appears to cause brain damage, mental deficiency and serious behavioural problems generally known as "Plumbism". Another consequence of lead poisoning is the kidney trouble known as `nephritis'. Several studies have demonstrated a strong positive correlation between blood lead levels and drinking water concentrations (Sherlock *et al.*, 1982; Pocock *et al.*, 1983). In appreciation of the public health risk, the USA, Canada and the European community have restricted the total Pb concentration in tap water to be 50 $\mu g\ l^{-1}$ (de Mora *et al.*, 1987). So far there is no evidence that Pb plays any essential role in metabolism.

The widespread and general use of lead is due to its high ductility and low corrosiveness. Ever since the introduction of tetra alkyl lead (TAL) as an antiknock additive in fuels used in the internal combustion engines , Pb contamination has become a major problem in the environment. The TAL species are sparingly soluble in water and saturation solubilities in freshwater are probably about 15 mg Pb l^{-1} for tetra methyl lead (TML) and 0.1 mg Pb l^{-1} for tetra ethyl lead (TEL) (Grove, 1980). A major pathway of lead is the organo metallic form whereas many other metals are released in the inorganic form (eg. Zn, Cd, etc.). Lead also shows great affinity to particulate phase retention (Windom *et al.*, 1988; Paulson *et al.*, 1989). It has been proved that Pb is unique among trace metals in the marine environment, because of its short residence time in the water column (Klomp, 1990). This feature makes the distribution of Pb respond quickly to input changes and the profile being perturbed because industrial lead inputs to the marine lead cycle have increased considerably beyond natural inputs (Schule and Patterson, 1981). It appears that most of the fluvial lead is removed over the continental shelves near the coasts by rapidly settling particles which sequester metals like Pb (Turekian, 1977). Wilhelmy and Flegal (1991) observed a separation of Pb from the cluster of nutrients and other trace metals, indicating that the source and transport processes affecting the distribution of Pb are considerably different from those for other metals. They also suggested that Pb distributions are most likely to be dominated by atmospheric inputs.

Available data on lead in estuarine waters are limited and include those of Danielsson *et al.*, (1983); Elbaz-Poulichet *et al.*, (1984 & 1991); Windom *et al.*, (1985 & 1988); George (1989), Paulson *et al.*, (1989); Forstner *et al.*, (1990) and Harper (1991). All of them have reported considerable particulate association for Pb. So far, the only data available for the Cochin estuary are those of Ouseph (1987); Nair *et al.*, (1990) and Nair *et al.*, (1991) on the sediment associated lead. In the Cochin estuary, the major source of Pb contamination has been identified as being the industrial and sewage effluents, shipping lines and atmospheric fall-out.

II. Results

In the Cochin estuary, the dissolved form of lead accounts for about 75% of the total metal. The other forms studied, principally total particulate Pb, though less in magnitude, exhibited significant features. Equally important was the exchangeable particulate form observed in this estuary which varied both seasonally as well as spatially. The results have been used to compare the abundance of the metal fractions on a percentage basis during the three seasons.The monthly distribution of the different Pb fractions is presented Station-wise in Fig. 5.1, averaged seasonally in Fig. 5.2a and as percentage abundance in Fg. 5.2b.

Chelex-100 Labile Metal (CLM).

The Chelex-100 eluted AAS read dissolved lead exhibited low content in fresh water and higher amounts towards the seaward side. The CLM values ranged from near detection limits at Station 3 in July 1989 to 9.64 $\mu g\ l^{-1}$ at the same Station in December 1988. Intermediate Stations lying in the estuarine zone were composite in nature but evidently pointed to an increase of this fraction progressively from the freshwater zone. During the entire survey consistantly ranged but varying values were observed for this fraction but for the three lone values observed at Stations 1, 3 & 6 in December 1988 and September 1989. The amount of Pb-CLM fraction as pointed out earlier was generally low at Station 5 & 6 except during the postmonsoon months at Station 5 (Fig. 5.2a). Elevated levels were noticed at Stations 3 & 4 during two seasons, the premonsoon and the postmonsoon. During the months from June to September, the above Stations (Stations 3 & 4) were characterized by low to very low amounts of dissolved CLM-lead. The values at Station 2 indicated some amount of scatter during the early part of the survey. The location at the barmouth (Station 1) showed considerable abundance even during the intervening period of themonsoon while during other periods of

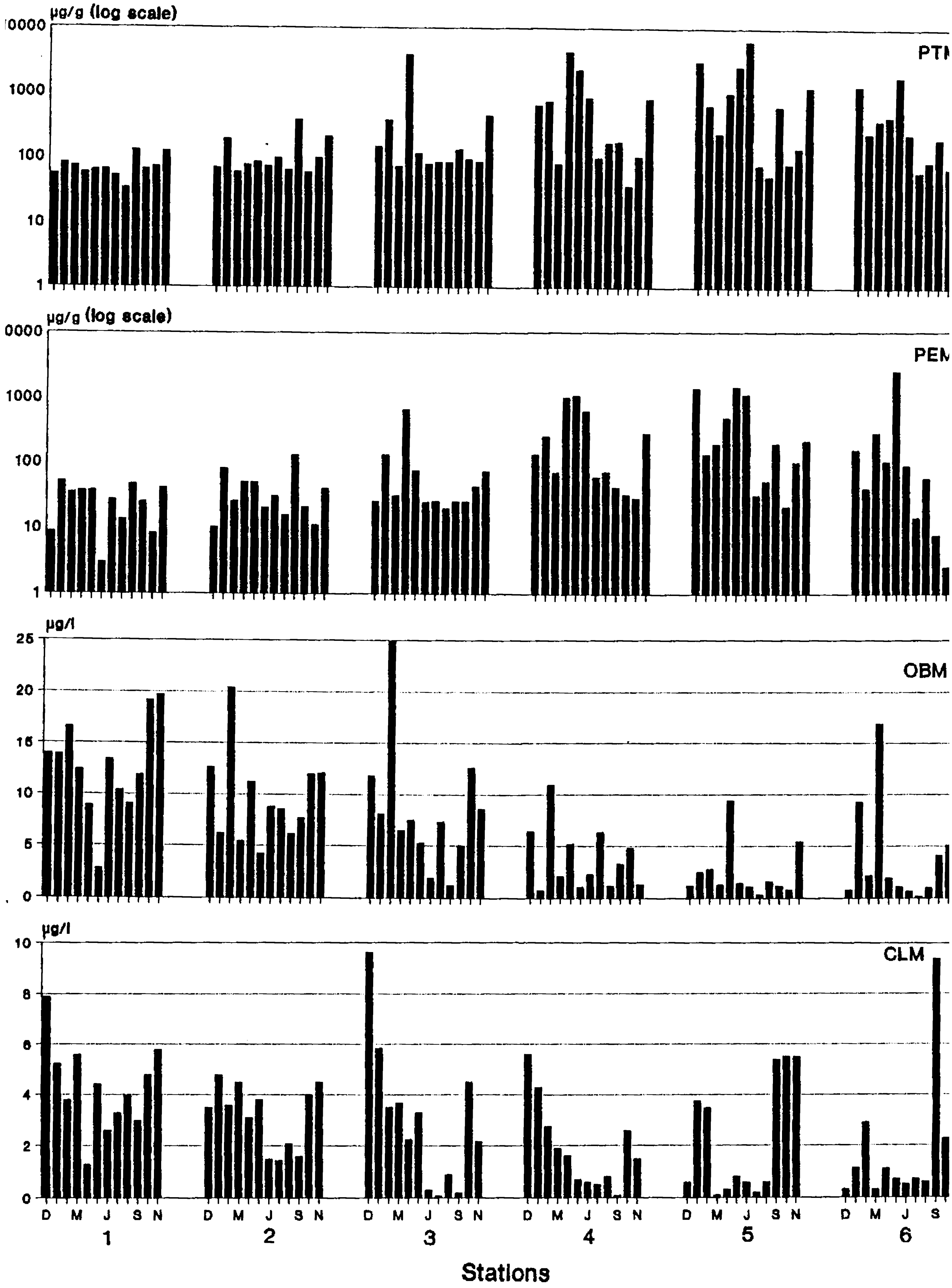


Fig. 5.1 Monthly distribution of lead fractions
at Stations 1 to 6
(D-December 1988 to N-November 1989)

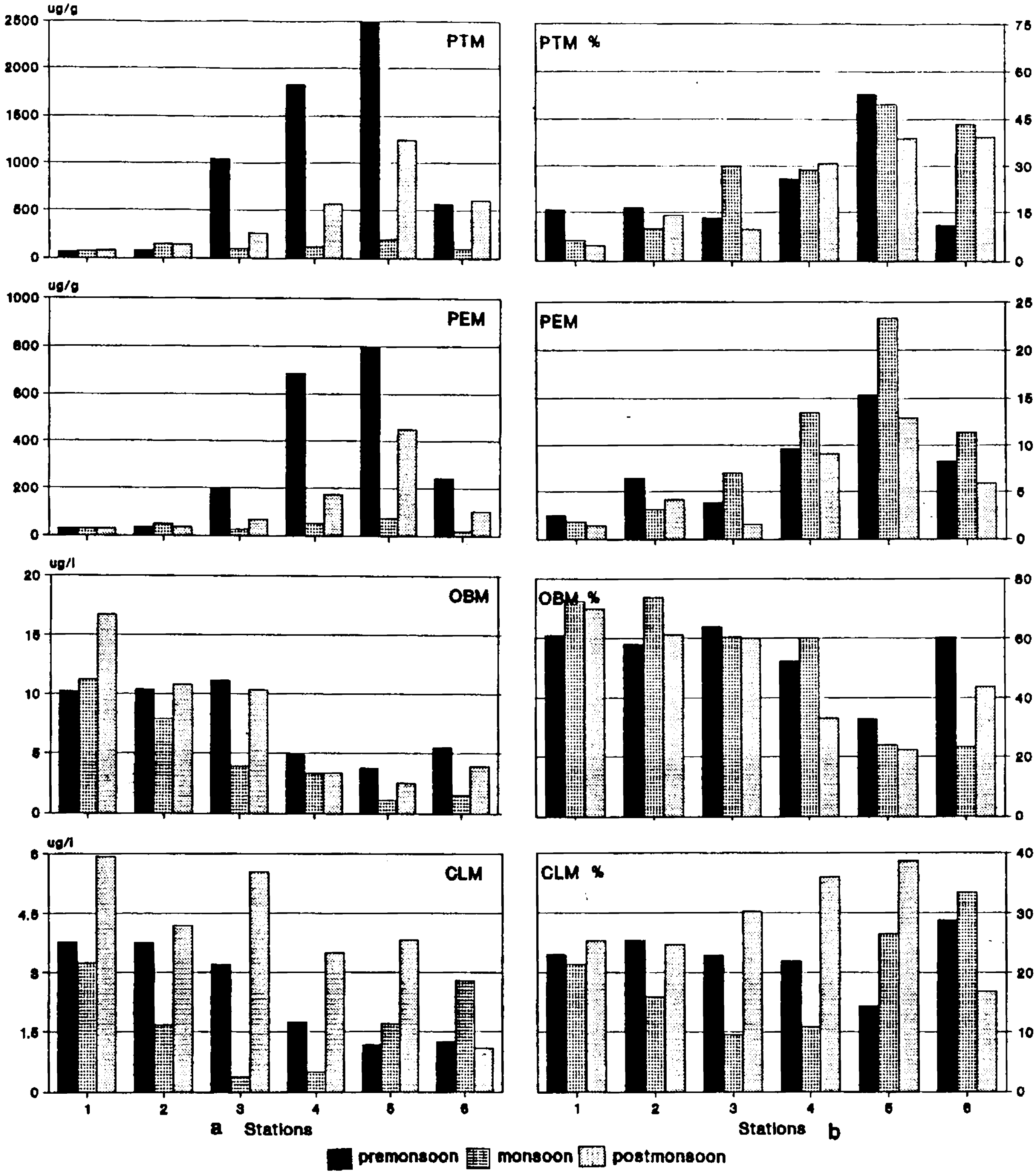


Fig. 5.2 Seasonal variation of lead fractions
a) absolute values b) percentages

the year the values were still higher. Thus the general distribution trends pointed out to an increase of this metal fraction longitudinally from upper estuarine reaches to the lower estuary.

The seasonally segregated feature (Fig.5.2a) exhibited a steady increase of this metal fraction both during premonsoon and postmonsoon from Station 6 to Station 1 i.e. from upper estuarine reaches to the lower estuarine reaches. The monsoon season was characterised by a mid-estuarine minimum. The range of values in monsoon was lower than the values during the other two seasons. This figure also helps to point out the occurrence of higher amounts of this fraction of the metal during postmonsoon season except at Sation 6 where the averaged monsoonal value predominates.

Organically Bound Metal (OBM).

Results on the studies of the organically bound metal in the lead fractionation scheme delineated two areas of the estuary, one in which the content was considerably low (freshwater to low saline - Stations 6, 5 & 4) and the other with marginal to high values in the lower estuary (Stations 3, 2 and 1). The contribution of OBM - Pb by the river as observed from the data at Station 6, varied from near detection limits to ≈ 5 $\mu g\ l^{-1}$. Exceptionally high value were recorded in January and March 1989 at this Station. The adjacent downstream Stations (Stations 5 & 4) too contained only low amounts of the bound metal while the features drastically changed at Station 3. The trend at Station 3 was a gradual decrease from premonsoon period to monsoon months followed by a recovery to the initial levels. At this Station too a single peak was encountered in February 1989. The distribution feature at Station 2 was no different from that of Staion 3 except that during monsoon the level of metal was enhanced at this Station compared to Station 3. A more equitable distribution was observed at Station 1 during the initial four months of the survey as well as towards the end of the survey. Considerable variation was noticed in the metal levels between

April and October 1989. To generalise the OBM profile, Stations 1 to 6 may be segmented into the upper estuary (Stations 4 to 6) with comparatively low content and the lower estuary (Stations 1 to 3) with high OBM content. Fig 5.2a analyses both seasonal as well as the spatial abundances. The behaviour of Pb associated with organics hence have to be viewed more critically in their spatial variation than inter-seasonal. A marked seasonal increase was observed at Station 1 during postmonsoon and Stations 2 & 3 incorporated low monsoon values compared to the higher values in the preceeding and succeeding seasons.

Particulate Exchangeable Metal (PEM)

The content of PEM varied between2.55 $\mu g\ g^{-1}$ at Station 6 in September 1989 and 1425 $\mu g\ g^{-1}$at Station 5 in April 89. It has not been possible to derive any major feature in the distribution of PEM from Station 1 to 6. However it may be generally stated that the freshwater Station (Station 6) contained intermediate values which increased sharply at Staiton 5 and then gradually decreased towards the lower reaches of the estuary. It was also noted that the content of PEM fraction was generally high during postmonsoon with still higher values in premonsoon followed by a fall during monsoon season. This fact was quite evident in the three uppermost Stations (Stations 4 , 5 & 6) than at Stations 1, 2 & 3 in the lower estuary. There was always a likelyhood that this fraction of Pb was found in abundance at any Station irrespective of the month / season. The pattern of variability indicated that:

a) the monsoonal values were very low at all Stations to produce any appreciable trend in the distribution

b) in the freshwater region the premonsoon and the postmonsoon value were higher than during the monsoon and the difference was still further enhanced at Stations 4 & 5. However at Stations 1 & 2 no seasonal differences were noted when the abundance of PEM was at the minimum. The large peaks at Stations 4 & 5 indicative of premonsoonal enrichment mainly referred to the high single value observation made in the month of April.

Total Particulate Metal (PTM)

The trends and abundance of Pb - PTM were more or less the same as that of Pb - PEM. The PTM values ranged between 34.24 µg g^{-1}at Station 4 in September 89 and 6194 µg g^{-1} at Station 5 in May 89. Once again during April 89 Station 5 exhibited ananomalously high value. The range of PTM values was more susceptable to changes during premonsoon and postmonsoon whereas no such variations could be observed during monsoon. PTM and PEM distribution profiles closely resembled each other except that the obseved values were scaled an order higher.

Percentage Abundance of Different Fractions

The results of this analysis serve to bring out the relative proportions of seasonal abundance in percentages among the four fractions in which the PEM has already been included in the PTM fraction. Fig.5.2 b indicates sharp variations in the seasonal abundance of the three fractions at Station 6. The content of OBM far exceeded that of CLM and PTM during premonsoon but occurred as the least during monsoon when either of the other species (PTM & CLM) were equitably distributed. It was the PTM and OBM fractions which dominated in content during postmonsoon season. However these inter-seasonal variability gradually minimised to a well graded and near uniformly patterned difference as the analysis was extended to Stations nearer the seaward side. e.g. at Station 3 exhibited an OBM content of ≈ 60% during all seasons whereas 20 to 30% of CLM was followed by 10 to 15% of the PTM lead in two seasons namely premonsoon and postmonsoon. In the case of changes observed during monsoon CLM and to some extent the PTM also showed consistent fall from Station 6 to Station 3 compensated by the enhancement in the OBM fraction. Noteworthy were the changes of trends in the case of CLM and PTM at Stations 1, 2 & 3 during monsoon when the former tended to increase towards the lower estuary and the content of PTM decreased. At the same instance the proportion of OBM fraction in monsoon remained a constant. As recorded in Fig.5.2a, the pattern of changes in PEM , a true replica of variations of Pb - PTM, the seasonal abundance on a percentage basis also followed simialr and identical changes. On the whole, comparing percentages of all the four fractions, Pb-associated with organic matter was found to play an important role followed by PTM in deciding the relative proportions of Pb abundance within the Cochin estuary.

Regression Analyses

The results of the regression analyses showed significant positive correlations between CLM and OBM ($r = 0.40$, $P < 0.001$). With different environmental parameters CLM and OBM showed significant positive correlations with salinity ($r = 0.51$ and $r = 0.60$); pH ($r = 0.3$ and $r = 0.32$) and only OBM showed a positive correlation with DOC ($r = 0.39$, $p < 0.001$). The particulate fractions PEM and PTM showed significant negative correlations with salinity ($r = -0.30$ and $r = -0.35$); pH ($r = -0.35$ and $r = -0.37$); SS ($r = -0.54$ and $r = -0.46$) and with POC only the PEM showed significant positive correlation ($r = 0.41$). (For all the above cases $p < 0.001$ and $n = 72$)

III. Discussion

i. Spatial and Seasonal Variation

The behaviour of Pb fractions in Cochin estuary highlights distinct features with regard to each of the estimated species. Between species themselves and between Stations too, variations though existent, were found to be within a rather uniform range of values. To start with, Pb in the freshwater zone (Station 6) contains low amounts of all the four fractions during all the seasons when compared to low saline Stations. The values at this location may be taken to represent aquatic environments which are relatively unpolluted and clean. The fractions of Pb surveyed at Station 5, which is downstream of the cleaner location, gave rise to enhanced amounts of particulate Pb attributable to the anthropogenic inputs at this region. This observation is no exception as elevated levels of many other metal fractions are being distinctly noted at this site. Since the initial months of the study (January to May), both the particulate fractions showed enhanced values at Stations 4, 5 & 6. The elevated levels occur during the period of low river discharge when effects of industrial effluents, if any, will be noticeable and the possibility of high to very high values cannot be ruled out.

The Stations 3 & 4 in the intermediate salinities and Sations 1 & 2 in the lower estuary exhibit two different trends: one of increasing amounts in the dissolved fractions and the other of decreasing contents in the particulate fractions. The decrease of the particulate fractions may be either due to the dilution of the metal-rich limnic particles with metal depleted oceanic particles or to the desorption of Pb from the particulate phase in the presence of water with higher ionic strength. The non-conservative behaviour of PEM and PTM discussed later negates the possibility of particle dilution. On the contrary the dissolved fractions were observed to increase towards the saline region. Analogous to this increase, the labile Pb has been reported to magnify quantitatively towards the seaward side in the Gironde estuary (Elbaz-Poulichet *et al.*, 1984). This feature may be attributed to factors like desorption from the particulate phase, remobilization from sediments, eolian inputs as industrial Pb, shipping activities and dredging operations. It is certain that all or some of these factors will be operative in the Cochin estuary too. Surveys performed in the Brazos river estuary is a pionter of lead cycling between dissolved and particulates (Keeney - Kennicutt and Presley, 1986). It has been observed as well as experimentally proven in the laboratory that increase in the dissolved phase, has been accounted more by the remobilization from the sedimentary phase, than the dissolution of the metal from the particulate phase. This gives rise to the situation of low riverine values and high estuarine values which has been true in the Cochin estuary too. Another causitive factor for the high dissolved Pb in the estuarine Stations is the dredging activities in the harbour area. Amongst many heavy metals Pb in its labile form has been shown to be released into the water column during dredging operations (De Groot *et al.*, 1976; Luther *et al.*, 1986). Within the dissolved fractions the relative enhancement occurs to the OBM fraction of Pb in the lower estuary. The occurance of this feature is more associated to extensive motorised watercraft plying in this region giving rise to introduction of TAL compounds.

On focussing attention on the seasonal behaviour of Pb fractions, the CLM fraction which indicated a mid estuarine minimum during monsoon specified a condition of higher riverine inputs associated with higher river discharge but on mixing with seawater in the estuarine region nearer to the seaward side, rapid desorption from other phases do occur to cause the increase in CLM lead. The lower values occur in a region where particulate precipitation is maximum (low salinity region) bringing down the concentration of CLM-Pb. The seasonal variations (Fig. 5.2 a.) also indicate a progressive increase of the OBM fraction in each of the seasons, in the down estuary. Relatively the enhancement occurs mostly during postmonsoon followed by monsoon and the least in premonsoon for which the causitive factors have already been discussed. The trends with regard to two other fractions within the particulate is surmised, for premonsoon as due to low river discharges (alternatively this affects the dilution of effluents discharged) coupled with settling of coarser particles (containing depleted amounts of metals) leaving the finer texture in suspension. The differential settling of particles have accounted for the higher values of particulate metals in the studies conducted in the Rhine estuary (Duinker, 1983).

ii. Estuarine Metal Reactivity

In the Cochin estuary, the CLM fraction was found to increase towards the estuarine region (Stations 6 to 1). This may be attributed, among various factors, to the salinity induced desorption from particulates and sediments. The salinity - CLM plots for premonsoon and postmonsoon are given in Figs. 5.3 a & b. No presentable features are available for dissolved fractions (CLM and OBM) versus salinity in monsoon.

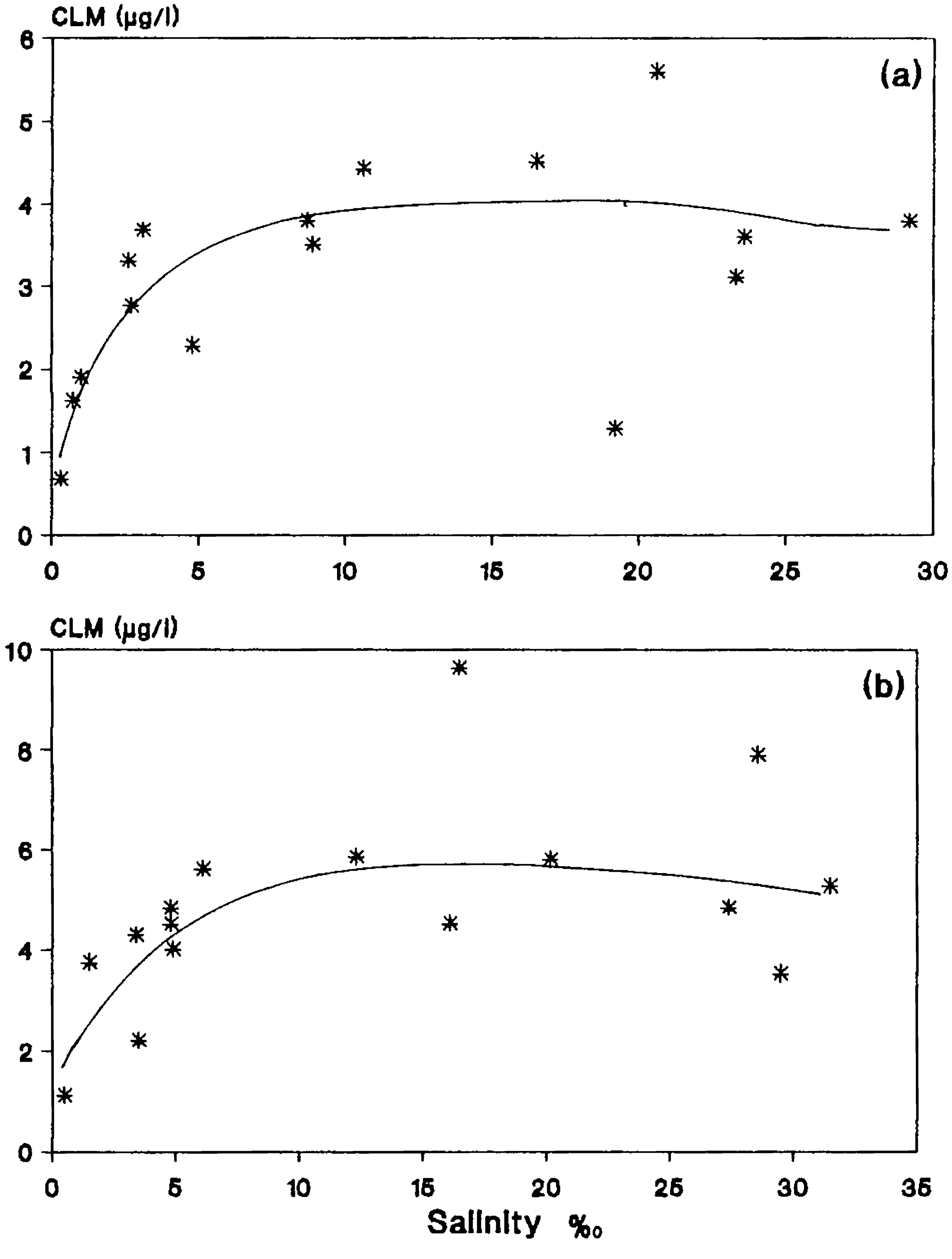


Fig. 5.3 Salinity - CLM plots
a) premonsoon b) postmonsoon

In both premonsoon and postmonsoon the CLM increases sharply upto salinity 5%. and then maintains a steady state with increasing salinities. The distribution of CLM as well as OBM with respect to salinity changes in the Cochin estuary is significantly different from those reported elsewhere (Duinker, 1983 in the Rhine estuary and Windom *et al.*, 1988 in the Bang Pakong estuary). The enrichment of dissolved Pb in the low salinity region is a major finding in the estuarine behaviour of element lead in Cochin estuary.

The major source of organic lead in the aquatic environment has been identified as the atmospheric fallout (Windom *et al.*, 1985). They also postulated that the fluvial contribution to the total lead concentrations are insignificant compared to atmospheric inputs. In Cochin estuary too, atmospheric fallout may be in reasonable amounts due to the proximity of metropolis of Cochin and the extensive water traffic in the adjoining backwaters. This additional source may be a reason for anegative mass balance of Pb in this estuary. The attempt to understand the behaviour of Pb-OBM with respect to salinity changes (Figs. 5.4 a & b) seasonally reveals two distinct behavioural patterns. In the first case, during premonsoon the organic lead is enriched in the low salinity (5%.) region followed by its depletion upto salinity 12%.. In salinities > 12%. a well marked increase was observed in the distribution of OBM. In the second case during postmonsoon, initially the Pb-OBM fraction gets enriched upto salinity 6%. and thereafter gradually levels off to a constant value in higher salinities. The characteristics emerging from these two figures are concomittant with those of the Pb-CLM fraction except for the decrease of OBM in the low / intermediate salinities of the Cochin estuary during premonsoon. With available data on the organically bound Pb at the above specified salinities, it has not been possible to categorise the perturbations quoted above. Similar analysis on the behaviour of organically bound metals with respect to salinity changes in the Cochin estuary does not however give rise to a similar situation. A closer inspection may reveal sharp discontinuities in the association of Pb with organic matter or a major influencing factor on organo-lead

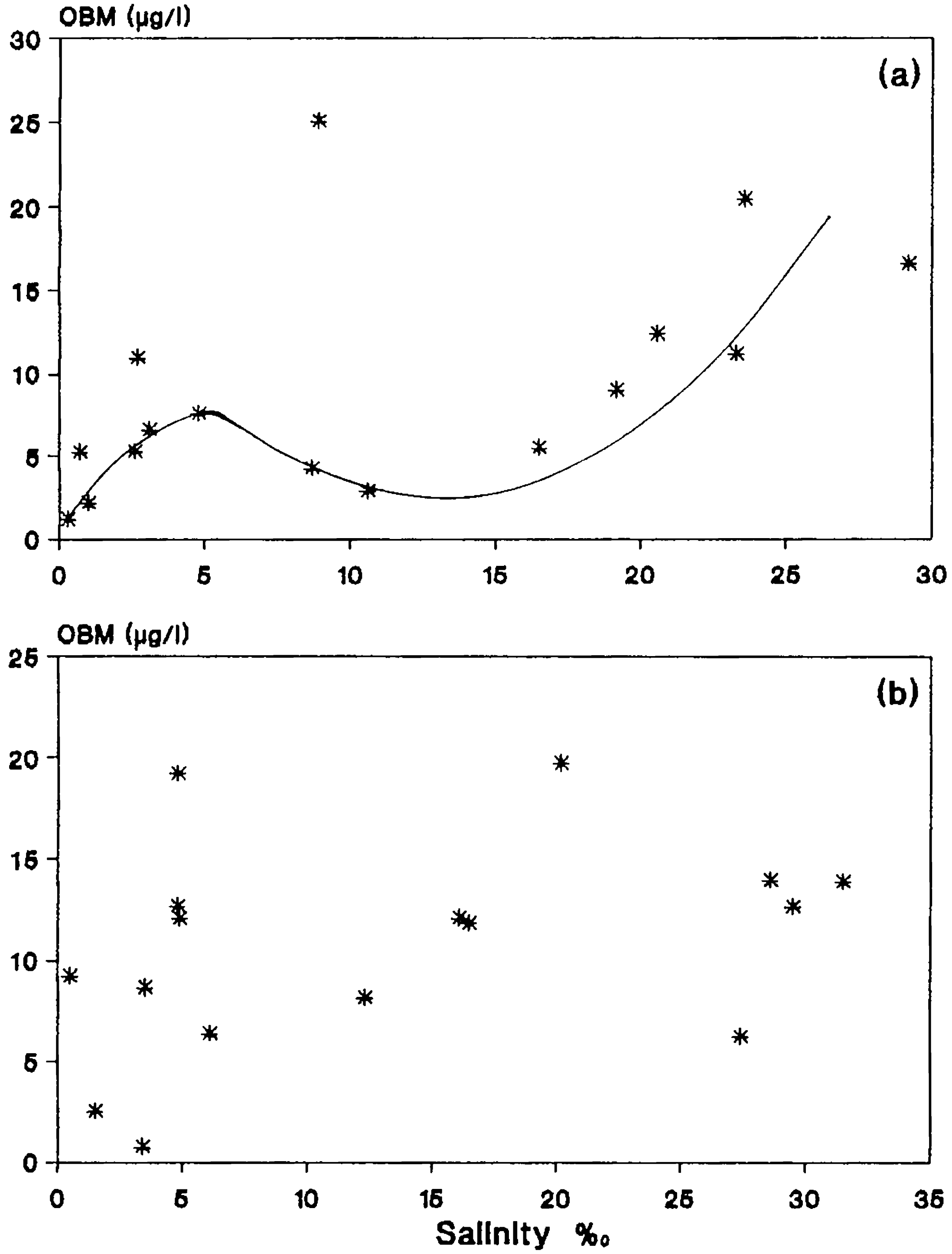


Fig. 5.4 Salinity - OBM plots
a) premonsoon b) postmonsoon

compound by the ionic behaviour of seawater. On an average, 51% of the total Pb (CLM + OBM + PTM in $\mu g\ l^{-1}$) is in the organic form (OBM). Higher quantities of non-labile Pb have been reported from elsewhere, 12 to 58% (Luther *et al.*, 1986); 16 to 45% (Nilsen and Lund, 1982) and 45 to 70% (Batley and Florence, 1976 a & b.)

As reported by Chau and Wong (1980), methylation mechanisms can play an important role in the transport of Pb from sediment to the aqueous layer. This fraction of Pb shows another significant positive correlation with DOC ($r = 0.39$ $p < 0.001$). The co-variance of organic lead with DOC (Figs.5.5 a, b & c for premonsoon, monsoon and postmonsoon) suggests a natural relationship between the two and indicates that Pb is transported primarily in chemical association (complexed or adsorbed) with dissolved organic substances or as Pb concentrates in highly weathered organic rich drainage basins. A peculiarity of organic Pb in the environment compared to other metals is that Pb is predominantly added in the organic form, while other metals are usually added in the labile form and later get organically associated in the environment. It is also reported that "organic-rich" rivers contain the highest Pb concentrations (Windom *et al.*, 1985).

From Figs. 5.1 and 5.2a it was noted that both the particulate fractions decreased towards the saline region. The non-conservative behaviour of PEM and PTM for premonsoon and postmonsoon is shown in Figs. 5.6 a & b and 5.7 a & b. In monsoon no such trend could be observed. During premonsoon and postmonsoon these fractions undergo a sharp removal in the very low salinity region (salinity < 5‰). This is due to the turbulance aided coagulation processes followed by desorption caused by seawater with high ionic strength. The process of coagulation has been shown to occur at salinities even as low as 0.3 ‰ in the Delaware Bay (Gibbs *et al.*, 1983) and the Gironde estuary (Gibbs *et al.*, 1985). Duinker (1983) also has suggested that in most of the estuaries, the fine grained river-borne material would be flocculated in the early stages of mixing. In the Elbe estuary also the Pb content of

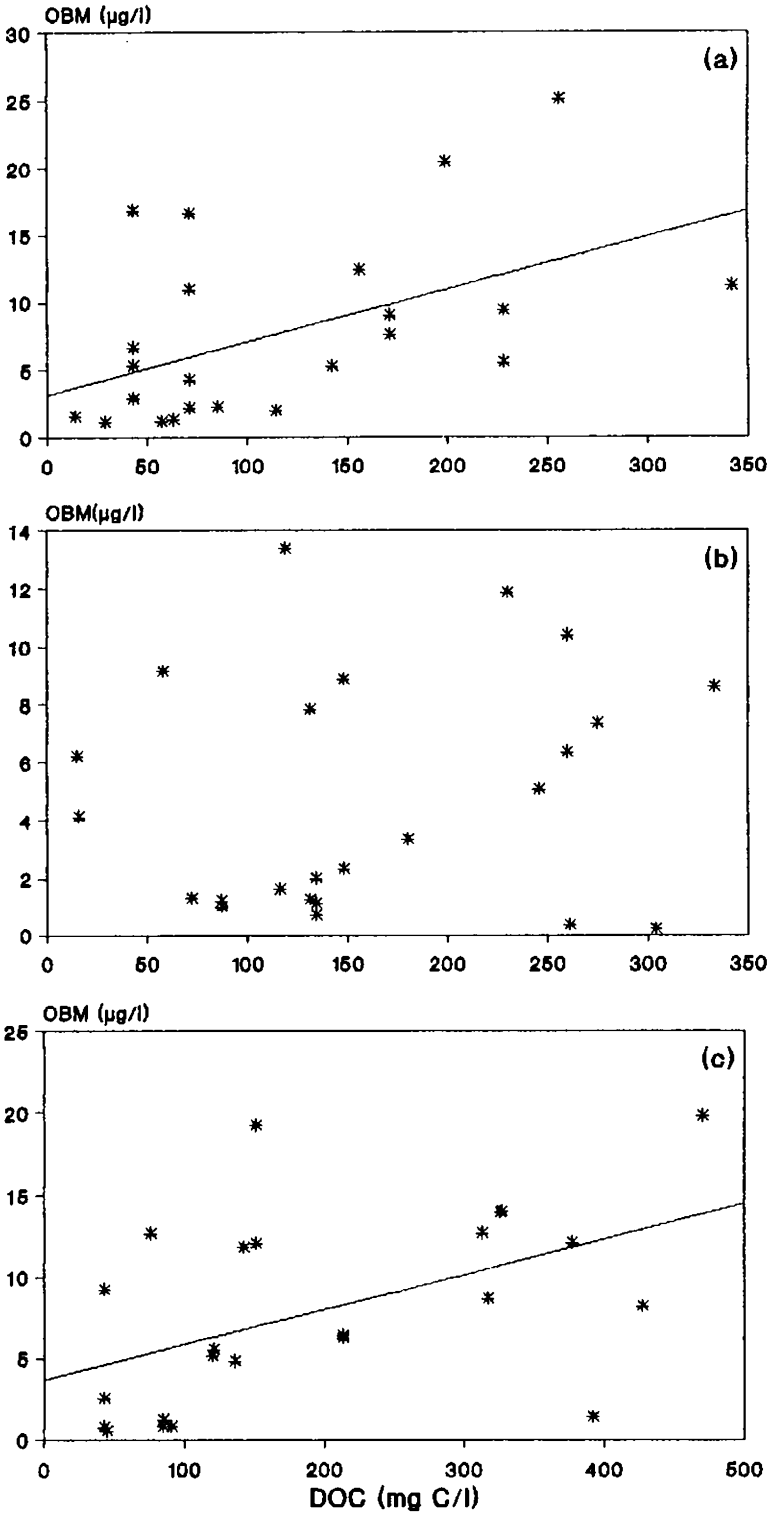


Fig. 5.5 DOC - OBM trend plots
a) premonsoon b) monsoon c) postmonsoon

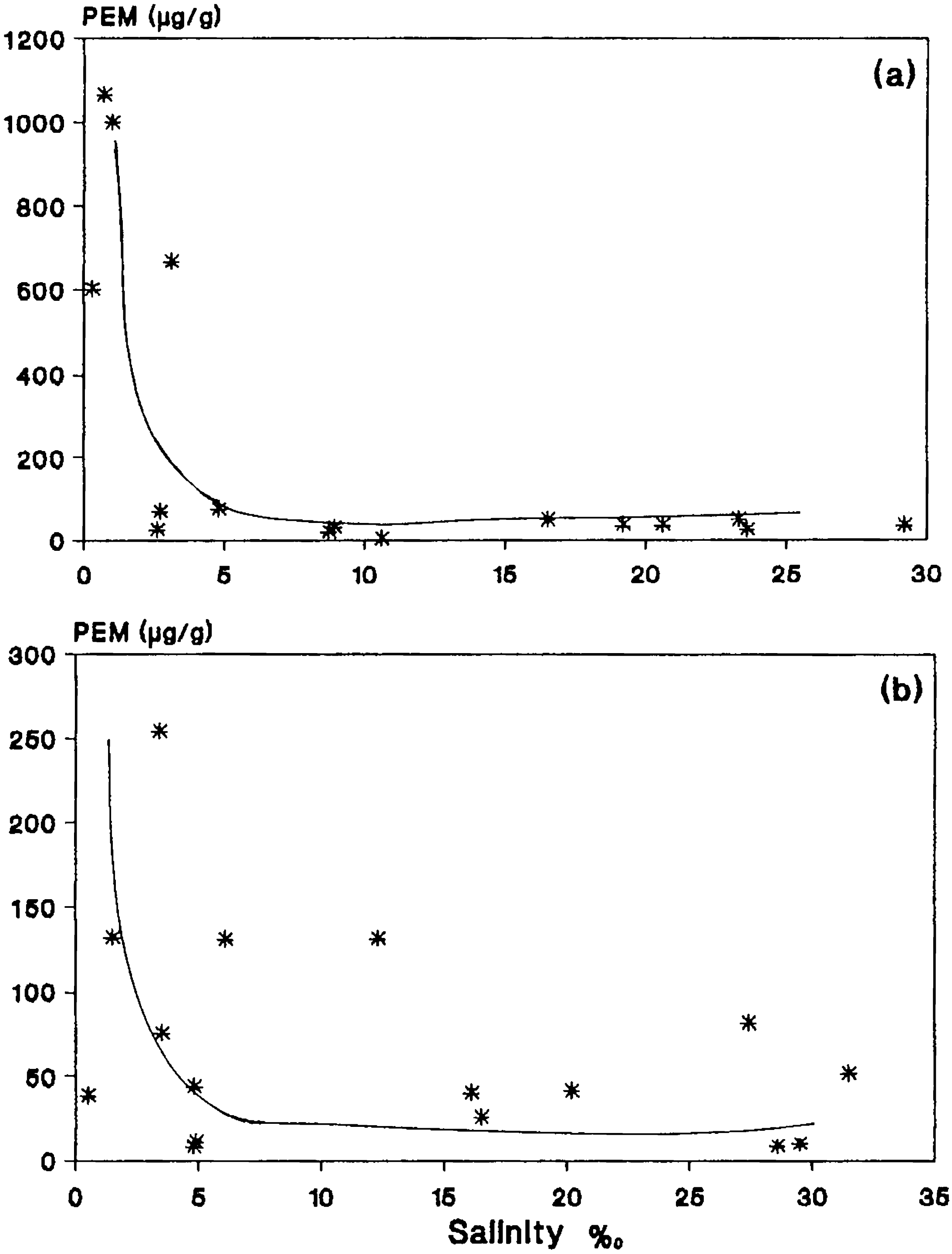


Fig. 5.6 Salinity - PEM plots
a) premonsoon b) postmonsoon

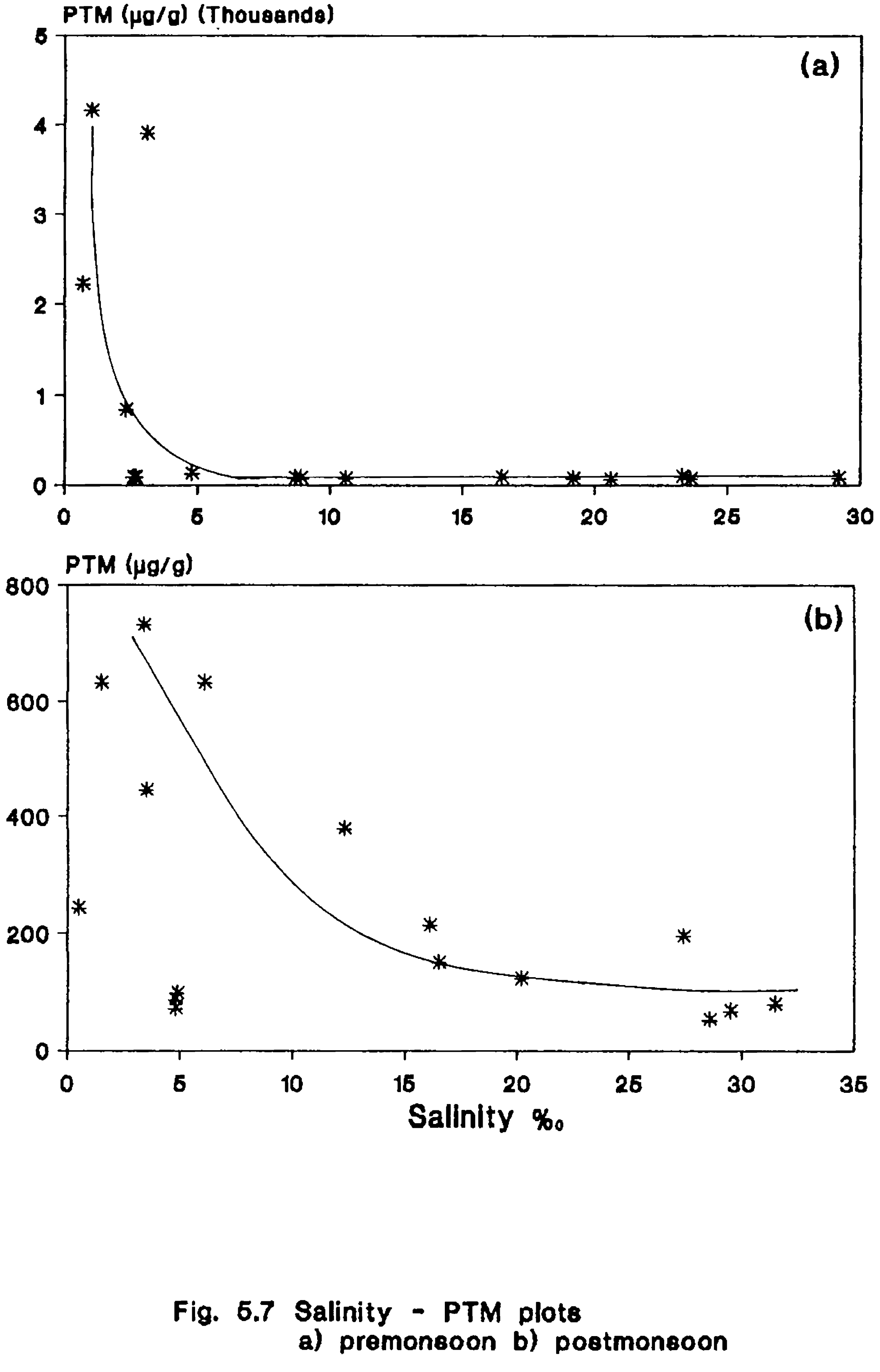


Fig. 5.7 Salinity - PTM plots
a) premonsoon b) postmonsoon

suspended particulate matter decreased considerably in the saline region during periods of low river discharge (Vollmer *et al.*, 1990) and the feature was attributed to the high sedimentation rate of SPM combined with dilution by material transported upstream. The PEM fraction shows a significant positive correlation with POC ($r = 0.41$, $P < 0.01$). Hence it may be inferred that a part of the decrease of PEM can be the result of a decrease in POC content. The PEM and PTM are also found vary inversely with suspended solids (Figs. 5.8 a & b and 5.9 a & b). The regression analysis shows $r = -0.54$ & $r = -0.46$ for PEM and PTM versus suspended solid load respectively.

IV. Transport and Species Transformations

The available reports on the transport of Pb shows that it is mainly associated with the particulate phases, ≈ 45% in the fresh water region & ≈ 69% in the estuarine region of the Yarra river system, (Hart and Davies, 1981); ≈ 47% in the Susquehanna river, (Mc Duffie *et al.*, 1976); ≈ 72% in the Rhine estuary, (de Groot *et al.*, 1976) and ≈ 50% in the Mandovi and Zuari estuaries, (George, 1989). Contradictory to the above observations, in the Cochin estuary, Pb is found to be transported mainly in the dissolved form (≈ 75%), whereas the particulate-phase transport is only ≈ 25% of which 8% is in the exchangeable form (Table 5.1). During premonsoon and postmonsoon ≈ 23% is transported in the particulate phase and ≈ 77% in the dissolved phase. The monsoonal transport is characterised by a slightly increased particulate association (≈ 28%). The organic phase transport varied between ≈ 48% during postmonsoon and ≈ 55% during premonsoon. The transport in the labile form varied between ≈ 20% in monsoon and ≈ 29% during postmonsoon.

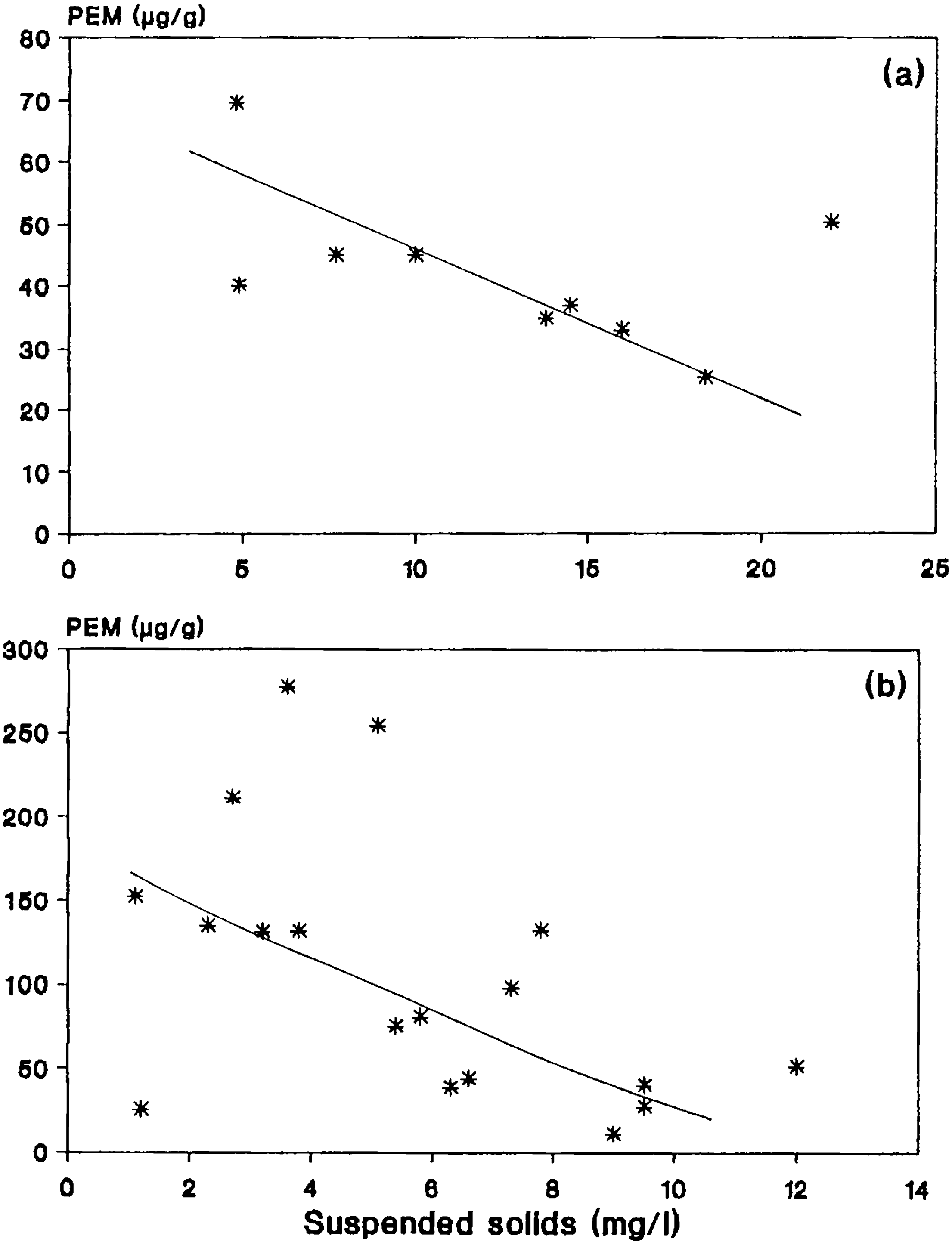


Fig. 5.8 Suspended solids - PEM plots
a) premonsoon b) postmonsoon

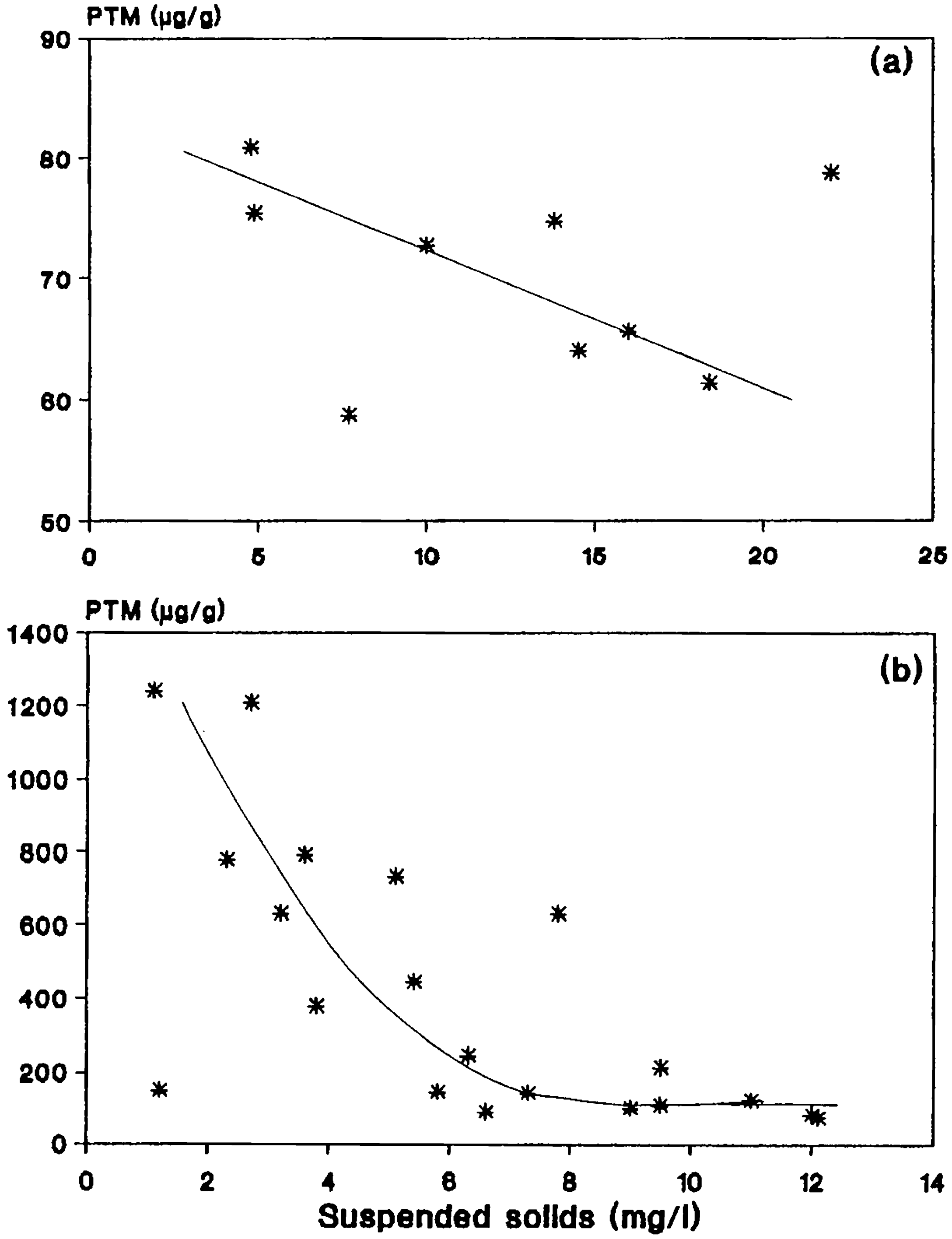


Fig. 5.9 Suspended solids - PTM plots
a) premonsoon b) postmonsoon

Table 5.1

Season	CLM %	OBM %	PEM %	PTM %
Premonsoon	22.73	54.73	07.66	22.54
Monsoon	19.58	52.41	10.02	28.00
Postmonsoon	28.65	48.39	05.85	22.96
Annual Average	23.66	51.84	07.84	24.50

The species transformations taking place during estuarine transport are shown in Fig. 5.10. During premonsoon the PEM decreases from 11.81% in the upper estuary (UE) to 2.45% in the lower estuary (LE). In monsoon it decreases from 16.04% to 1.85% and in postmonsoon from 9.42% to 1.39% . During premonsoon PTM showed a sharp decrease from 31.82% in the UE to 18.57% in the middle esutary (ME) and then gradually decreases to 15.88% in the LE. In monsoon the decrease of PTM is considerable from 40.61% in the UE to 6.16% in the LE. In postmonsoon the decrease is from 39.2% in the UE to 4.7% in the LE.

The CLM fraction marginally increases during premonsoon from 21.62% in the UE to 23.01% in the LE. In monsoon a sharp decrease was observed from 23.58% in the UE to 12.71% in the ME and then it increased to 21.35% in the LE. The postmonsoon showed a marginal decrease from 27.84% in the UE to 25.31% in the LE with a maximum in the ME (30.31%). During premonsoon the OBM fraction showed a sharp increase from 46.5% in the UE to 58.04% in the ME and then gradually increased to 61.11% in the LE.The monsoonal variation showed a sharp increase from 35.81% in the UE to 67.28% in the ME and then gradually increased to 72.49% in the LE. In postmonsoon the increase was steady from 32.96% in the UE to 70% in the LE.

The net result of species transformations of lead during estuarine mixing is given below:

The net result is a gain in the OBM content during all the seasons and a marginal gain for CLM during premonsoon. All the

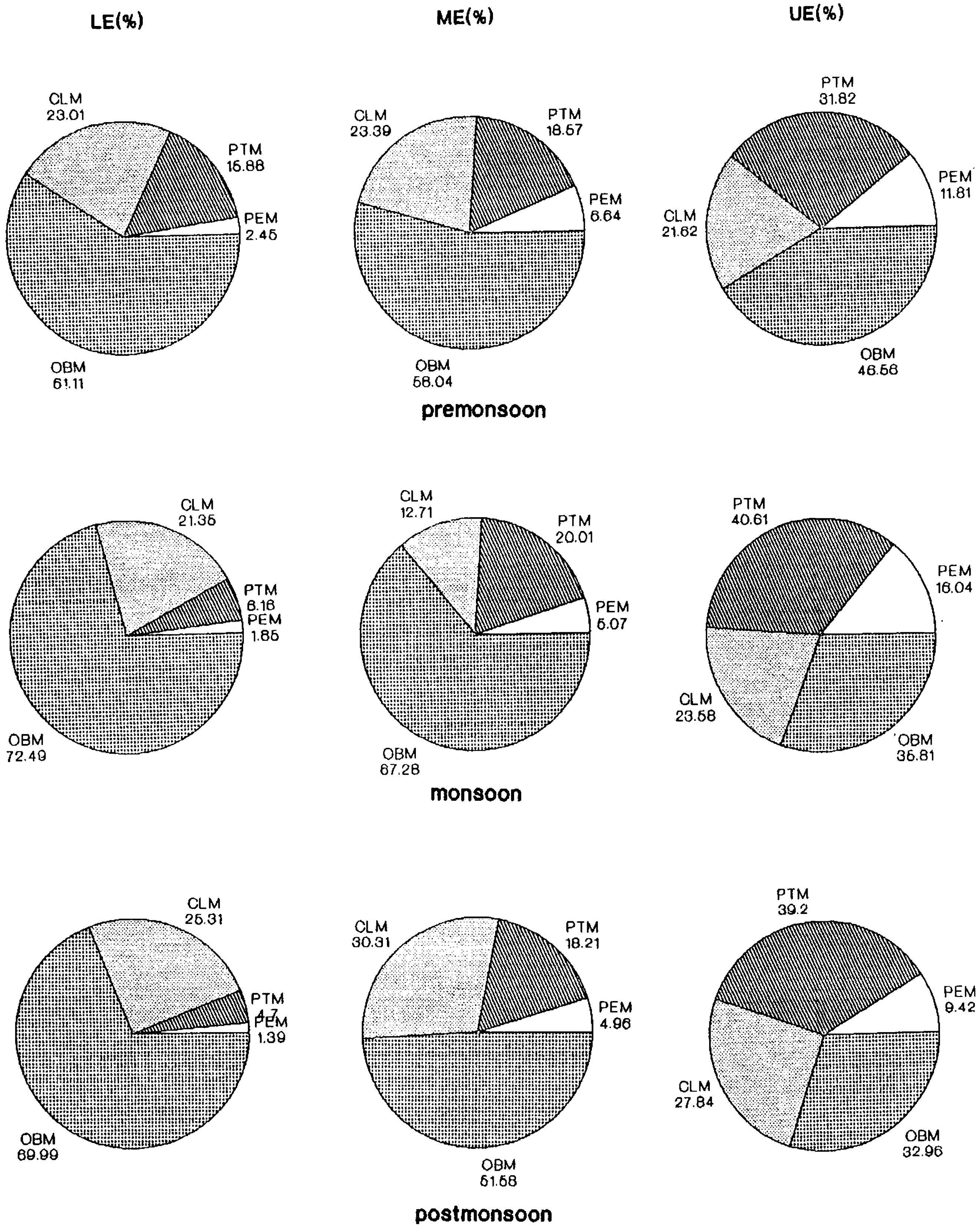


Fig. 5.10 Seasonal Species transformations during estuarine transport LE-lower estuary ME-middle estuary UE-upper estuary

other fractions experienced a net loss. In monsoon the mid-estuarine minimum associated with CLM fraction is proportionally reflected in the enhanced OBM levels.

V. Mass Balance

Given,

$C_R = 6.92\ \mu g\ l^{-1}$
$C_B = 18.78\ \mu g\ l^{-1}$
$C_E = 13.59\ \mu g\ l^{-1}$
$Q_R = 5.192 \times 10^{12}\ l\ Yr^{-1}$
$Q_B = 1.780 \times 10^{12}\ l\ Yr^{-1}$
$Q_E = 6.970 \times 10^{12}\ l\ Yr^{-1}$

Flux in from the river
$= Q_R \times C_R$
$= 35.93 \times 10^3\ Kg\ Yr^{-1}$

Flux in from the barmouth
$= Q_B \times C_B$
$= 33.43 \times 10^3\ Kg\ Yr^{-1}$

Total Pb flux into the estuary
$= (35.93 + 33.43) \times 10^3 Kg\ Yr^{-1}$
$= 69.36 \times 10^3\ Kg\ Yr^{-1}$

Flux out from the estuary
$= Q_E \times C_E$
$= 94.72 \times 10^3\ Kg\ Yr^{-1}$

Mass balance of lead:
flux in - flux out $= (69.36-94.72) \times 10^3\ Kg\ Yr^{-1}$
$= \underline{-25.36 \times 10^3\ Kg\ Yr^{-1}}$

The mass balance of lead in this estuary shows an excess of 25.36×10^3 Kg Yr^{-1}. It has been reported that fluvial contributions to the total lead are insignificant compared to atmospheric fallout in the estuaries of southern United States (Windom *et al.*, 1985). In the Cochin estuary the fluvial contribution of Periyar river is $35.93 \times 10^3 Kg\ Yr^{-1}$ and the excess lead is $25.35 \times 10^3 Kg\ Yr^{-1}$. This shows that an amount equal to about 70% of the fluvial lead is added from some other sources. A significant increase in the total lead concentrations was reported in the Yarra river system when river water enters estuarine water (Hart and Davies, 1981). Evans and Cutshall (1973) attributed this sort of increase to a possible leaching from the sediments that occur at higher salinities. The mass balance calculations of Klinkhammer and Bender (1981) for the Hudson river estuary and that by Fanger *et al.*, (1990) for the Hamburg harbour area however showed a higher input flux of lead than the output flux. The remobilization from the sediments along with atmosperic fallout, sewage effluent, shipping and dredging activities may be some of the reasons for the observed excess lead output from this estuary.

CHAPTER 6

ZINC

I Introduction

Zinc ranks fourth among the metals in its annual consumption (Nriagu, 1980) after iron, aluminium and copper. Its important uses include galvanization of iron, alloying ingredient in brass, chemical constituent in rubber and paints etc. Zinc is also an essential element for human beings, animals and higher plants. A deficient intake consistently results in an impairment of functions from optimal to suboptimal levels and supplementation to physiological levels, prevents or cures this impairment (Alloway, 1990). Zinc acts as a catalytic or structural component in many enzymes involved in energy metabolism as well as in transcriptions and in translations. Zinc deficiency symptoms in humans and animals result in dietary malfunction, severe growth depression, skin lesions and sexual immaturity. The recommented safe and adequate dietary intake for adults is around 15 mg day $^{-1}$.

The average range of concentration of Zn in the earth's crust is 65 to 80 $\mu g\ g^{-1}$, the major ores of zinc are wurtzite and sphalerite ($\approx$ 67% Zn). The average Zn level in seawater varies between 0.1 $\mu g\ l^{-1}$ at the surface and 0.62 $\mu g\ l^{-1}$ in the deep waters (Bruland *et al.*, 1978). In fresh water the average concentration is $\approx$ 10 $\mu g\ l^{-1}$ (Wedepohl, 1972)). The development of methods for the chemical speciation of Zn is especially important, because Zn is one of the most ubiquitous of the essential trace metals. Zn is also a component of many enzymes, it is involved in the synthesis of RNA and DNA and acts to diminish the biological toxicities of other metals such as Cu and Cd (Davies, 1977)). Lal (1977), Pocklington (1977) and Turekian (1977) have all presented convincing arguments supporting the theory that adsorption onto particles, both organic and inorganic, is the dominating process controlling the equilibrium concentrations of Zn in sea water. There is some controversy over the proportion of the organically complexed fraction of Zn in natural waters. Slowey and Hood (1971), Fukai *et al.*, (1973), Van den Berg *et al.*, (1987) and Donat and Bruland (1990) have reported that a considerable percentage of the Zn is organically complexed, whereas Stumm and Brauner (1975), Pocklington (1977), Florence (1977), Hart and Davies (1981), and Kuwabara *et al.*, (1989) have reported only very little organic association. There is also a considerable amount of disagreement in the literature about the types of Zn complexes present in natural waters; most investigators have found that a significant fraction of the Zn was present in other than simple ionic forms which may be either organic or not.

Behaviour of Zn during estuarine mixing has been closely investigated in the past. A conservative behaviour has been reported in the San Fransisco Bay (Eaton, 1979), the Gota river (Danielsson *et al.*, 1983), the Bang Pakong estuary (Windom *et al.*, 1988) and a non-conservative nature involving either removal or addition or both has been reported for the Fraser river estuary, (Grieve and Fletcher, 1977), the Tamar estuary (Morris *et al.*, 1978, Ackroyd *et al.*, 1986), the Elbe estuary (Duinker, 1982) and for the Cochin estuary (Shibu *et al.*, 1990).

II. Results:

Chelex-100 Labile Metal (CLM)

The monthly distribution of different Zn fractions are shown in Fig. 6.1 and the seasonal variations in Fig. 6.2 a. The concentration of CLM fraction of Zn was evenly balanced at either ends of the estuary. At Station 5, this fraction showed a sudden increase compared to Station 6. The same was true between Stations 2 and 3. The values of CLM fraction varied between 0.2 µg l^{-1} at Station 1 in January 1989 and 96.1 µg l^{-1} at Station 3 in November 1989. The higher amounts at Stations 3, 4 & 5 were an important feature in the spatial distribution of this fraction. The seasonal variation of this fraction presented in Fig. 6.2a also highlighted a higher abundance in the mid-estuarine Stations. There was also evidence of seasonal differences in the content of Zn with occurrence of lower ranges of CLM during monsoon sandwiched between the relatively higher values during premonsoon and postmonsoon. From Figs. 6.1 & 6.2a the seasonal variations in the end member Stations were hardly perceivable.

The content at Station 6 ranged between 0.65 µg l^{-1} and 16.39 µg l^{-1} and those at Stations 1 & 2 combined ranged within 14.89 µg l^{-1} (except the value in September 1989 at Station 2). In contrast, the higher amounts observed between Station 3 & 5 (2.42 µg l^{-1} to as high as 96.1 µg l^{-1}). It was noted that the metal levels are comparatively low durig monsoon except at Stations 1 & 2.

Organically Bound Metal (OBM)

Similar to the CLM, the OBM fraction also showed minimal values either end member Stations and maximal presence at Stations 3, 4 & 5. The maximum value was recorded at Station 5 (121.76 µg l^{-1}) in December 1988 and minimum value was 0.15 µg l^{-1} at Station 1 in Novemebr 1989. The monsoonal values of this fraction did not show any appreciable variation in this estuary. The OBM values showed a sharp increase at Station 5 during premonsoon and postmonsoon compared to values at Station 6 and these high values were also encountered at Stations 3 & 4. Fig. 6.2a indicated that the decrease of OBM to either sides of the mid-estuary was sharp during postmonsoon and gradual during premonsoon. The monsoonal features were subdued

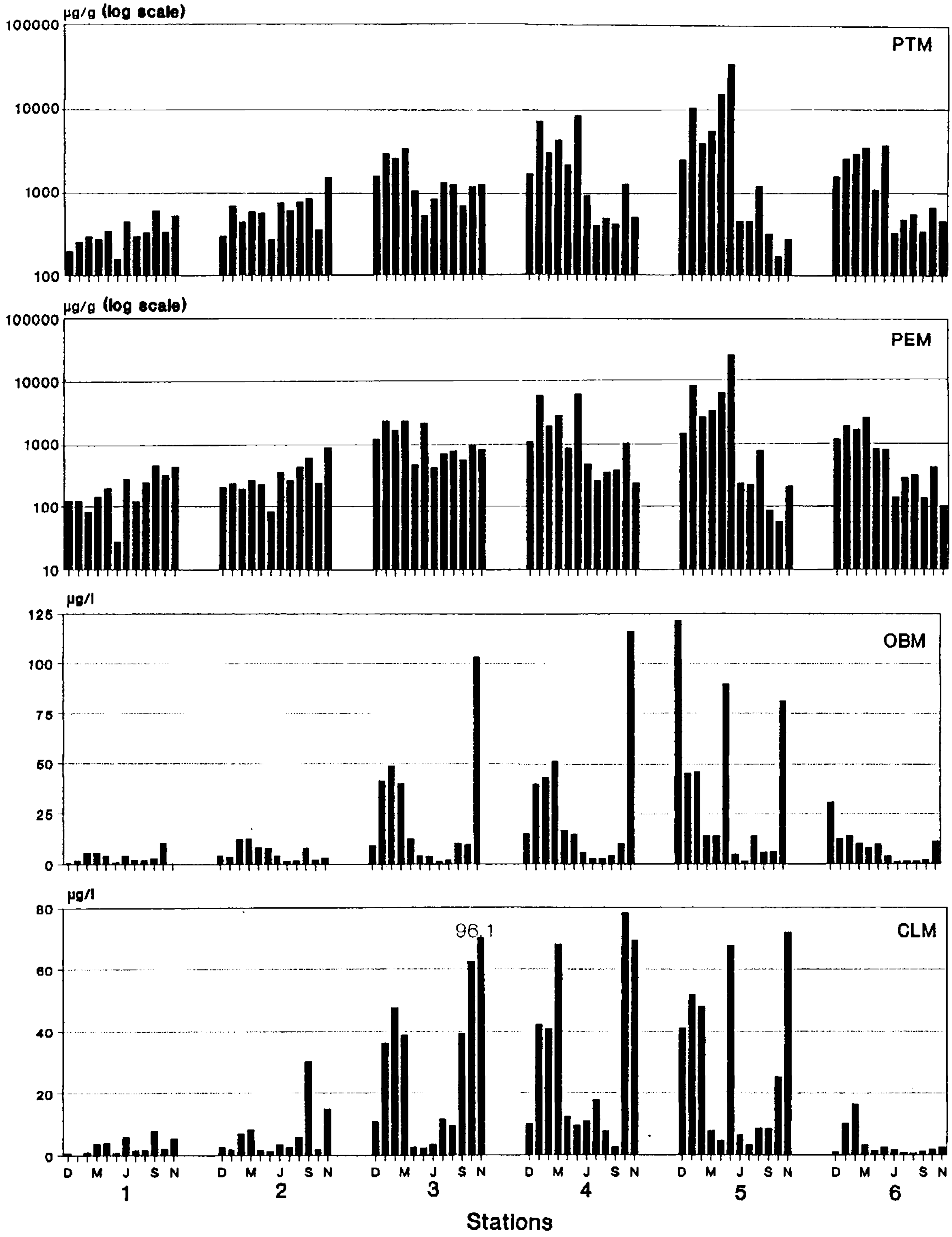


Fig. 6.1 Monthly distribution of zinc fractions at Stations 1 to 6 (D-December 1988 to N-November 1989)

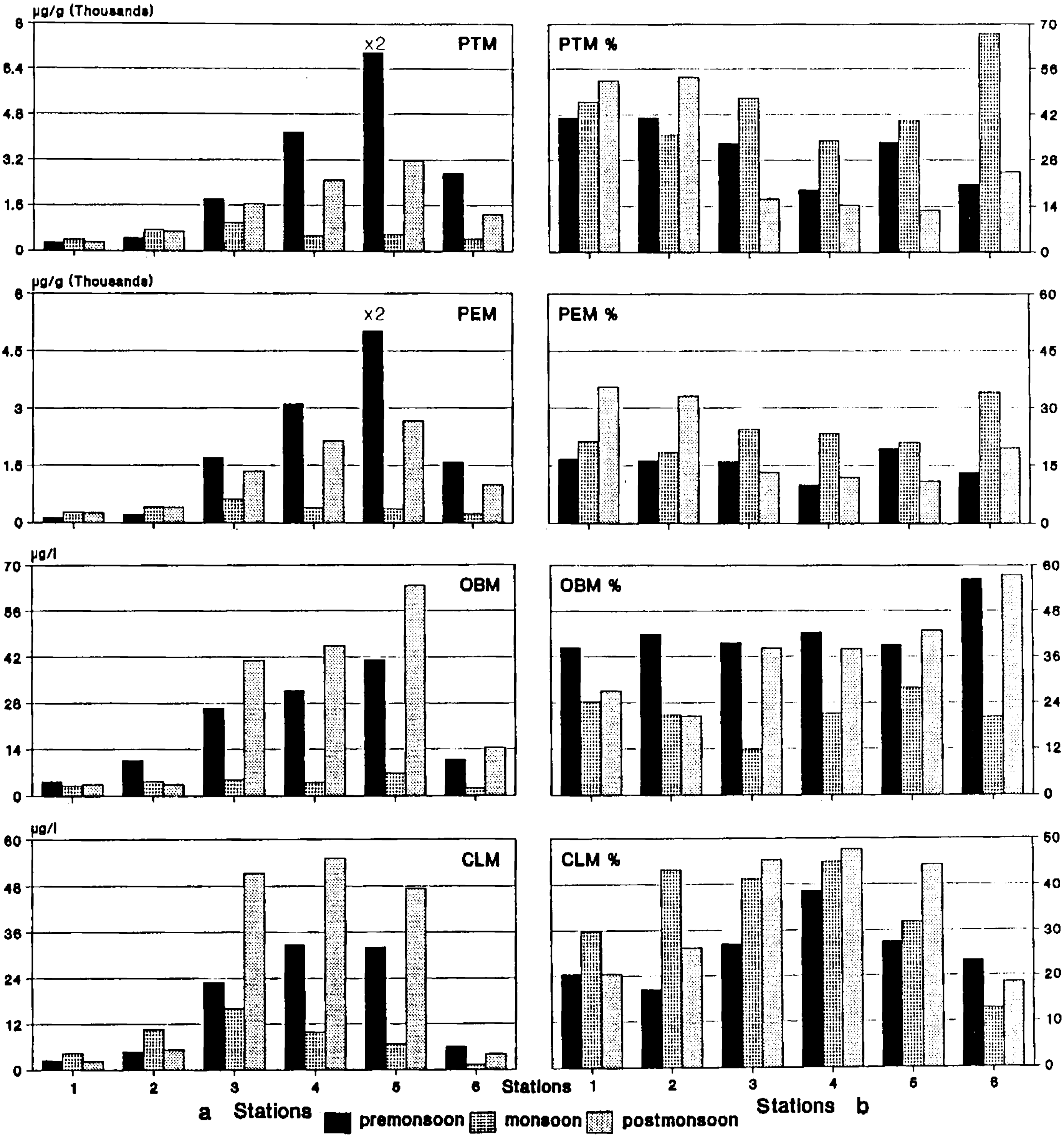


Fig. 6.2 Seasonal variation of zinc fractions
a) absolute values b) percentages

and exhibited no definite pattern.

Particulate Exchangeable Metal (PEM)

This fraction of Zn also showed a sudden increase at Station 5 and then decreased towards the lower reaches of the estuary. The highest value of PEM recorded was 26892 µg g^{-1} at Station 5 during May 1989 and the minimum was 27.04 µg g^{-1} at Station 1 during the same month and the PEM levels were generally high in the mid-estuarine Stations. The PEM could have been introduced into the Cochin estuary from the river as well as from effluent discharges. A distinct pattern of this addition is shown in Fig. 6.1. Station 6, located as the uppermost Station in the present study, gave rise to values > 1000 µg g^{-1} during Decemebr 1988 to March 1989. With the advent of the monsoon the content of PEM was lowered to the range 100 to 400 µg g^{-1}. In this set up the adjacent downstream Station exhibited still higher during the first 6 months of the study. Similar features were also obtained at Stations 3 & 4 located further downstream of the estuary. Another result obtained in this study was the relatively lower variability in the PEM values observed during monsoon. The seasonal averages plotted for Stations 1 to 6 in Fig. 6.2a showed that the highest levels were encountered during premonsoon at Station 5 followed by a decrease in the same season at all locations below Station 5. The postmonsoon season too showed this decreasing tendancy to relative average concentrations in premonsoon. The three seasonal averages were more or less the same at Stations 1 & 2. The abundance of PEM occurred as the highest in premonsoon at Station 6 followed by slightly more than the half, from that of premonsoon, during postmonsoon and came down to very low values during monsoon.

Total Particulate Metal (PTM)

The PTM also showed a trend similar to that of PEM. The maximum recorded value was 32685 µg g^{-1} at Station 5 in May 1989 and the minimum was 155.8 µg g^{-1} at Station 1 during the same month. The seasonal variation (Fig. 6.2a) showed that PTM values decreased towards the saline region to such an extent that the monsoonal values slightly exceeded that of premonsoon and postmonsoon at Stations 1 & 2. As observed for other metals selected in this study, the trends in PTM strictly followed that exhibited by the PEM. Commencing from higher amounts during the first phase of the study at Station 6, the values levelled off during monsoon at approximately half the initial readings. As observed for the PEM fraction the PTM content also shot up at Station 5 in the months of December 1988 to May 1989 followed by a gradual gradation to lower values up to the end member Station at barmouth. This fraction of Zn too exhibited relatively lesser variability during monsoon. The features of occurrence at Stations 1 & 2 were a replica of that observed for PEM fraction. Most other observations made for PEM are also true for the PTM fraction.

Percentage Abundance of Zn Fractions

The percentage distribution of dissoloved and particulate fractions of Zn in the Cohin estuary computed seasonally (Fig. 6b) exhibited mainly three features - one pertaining to that in the fresh water region (Station 6), the other in the saline regions (Stations 1 & 2) and the third in the intermediate regions (Stations 3,4 and 5). Premonsoon and postmonsoon were periods when the OBM fraction at Station 6 far exceeded that of CLM and PTM. However during monsoon it was the PTM fraction that dominated this location. This feature was altered at Stations 1 & 2 in the saline region. An abundance of OBM and PTM was prevalent at Stations 1 & 2 during premonsoon (nearly 40% each). Monsoon was characterized by the presence of higher amounts of CLM and PTM fractions and by the low amounts of the OBM fraction. However,during postmonsoon only the PTM dominated the lower part of the estuary in comparison to both the dissolved fractions. The PEM seasonal percentages closely resembled the changes of PTM.

To summarize the observations from Stations 3, 4 & 5:

a) Premonsoon and postmonsoon OBM percentages remained fairly constant.

b) Monsoon and postmonsoon CLM showed very low variations and

c) Postmonsoon PTM percentages remained constant followed by comparatively higher content with minor changes during monsoon for this fraction. The premonsoon features at Station 3, 4 & 5 for the CLM and PTM fractions brougtout the feature of balanced near equal amounts at Stations 3 & 5 whereas an increase at Station 4 in the average CLM value coincided with a low PTM at the same Station for the same season. Similar subordinate features were also noticed for the PEM fraction compared with the PTM fraction.

Regression Analyses

The regression analysis showed that a highly significant positive correlation exist for CLM with OBM ($r = 0.78$); PEM ($r = 0.35$) and PTM ($r = 0.31$). The OBM fraction showed excellent positive correlation with PTM ($r = 0.75$) and to a lesser extent with PEM ($r = 0.32$). With other environmental parameters the CLM fraction showed negative correlations with salinity ($r = -0.33$) and OBM fraction showed a negative correlation with pH ($r = -0.40$). The PEM and PTM showed significant negative correlations with salinity ($r = -0.36$ & $r = -0.35$); and suspended solid load ($r = -0.37$ & $r = -0.47$) respectively. In all the above cases $p < 0.001$ and $n = 72$.

II. Discussion

Among the various trace metals, which have been investigated extensively in the present study, Zn showed the most anomalous behaviour in this estuary. The behaviour and distribution of Zn again showed considerable difference from the features that other metals have exhibited.

i. Spatial and Seasonal Variations.

To generalise the spatial trends, all the four fractions of Zn showed the same distribution pattern in this estuary. At Station 5, the content of all the fractions were considerably high compared to those at Station 6. This is plainly because Station 5 is located just downstream of the effluent discharge point of a Zinc smelter which happens to be a potential source for Zn contamination in the Cochin estuary. Maximum concentrations were observed at this Station and a steady decrease towards the saline region was observed, which could have been the result of salinity induced solubilization of the particulate associated metal, the details about which are discussed below. A similar decrease of particulate Zn has been reported in the Rhine estuary (Duinker, 1983). Parallel to the feature in the Cochin estuary, Jouanneau *et al.*, (1983) also have reported a decrease of particulate Zn in the Gironde estuary and the authors attributed this partly to the decrease of POC content and partly to the increase of salinity.

Both the CLM and OBM fractions also decreased towards the lower reaches of the estuary. The decrease in OBM content is due to flocculation processes concurrent sedimentation / utilization of the dissolved organic matter along with the organically complexed Zn. However reports from different estuaries on organic complexation of Zn are conflicting. In some cases, only minute organic associations of Zn have been reported (Florence, 1977; Hart and Davies, 1981 and Kuwabara *et al.*, 1989), whereas in some other cases extensive organic associations (60 to 95%)have been reported (Van den Berg *et al.*, 1987; Donat and Bruland, 1990). The CLM fraction of Zn also experienced a decrease in the saline region. The salinity induced removal of dissolved Zn has been reported by many workers (Windom and Smith, 1985; Duinker, 1983, Windom *et al.*, 1991) and is discussed in more detail hereunder.

A significant observation was the high particulate fractions during premonsoon and the high dissolved fractions during postmonsoon. The high values of PEM and PTM during premonsoon may be a result of textural features in river transported material. At low discharges, the suspended matter is relatively finer, the coarser particles having already settled on the river bed far upstream and most of the metal (contaminants) would preferentially be associated with the finer particles. For a number of rivers it has been found that the concentration of the particulate metals depends on discharge (Salomons and Baccini, 1986). The reasons may be a) the proportional dilution as the discharge increases, assuming a constant load of metal into the river systems, b) a dilution as a result of increased erosion during high discharge (surface run off) leading to a mixing of contaminated fluvial particulates with predeposited soil particles and c) differences in residence times. The residence time of the particles in the river during high discharge will be low in contrast to periods of low discharge and as the amount of metal adsorbed onto the particles depends on residence time, relatively small amounts will be available for adsorption during period of high discharge.

The increase of OBM fraction during postmonsoon is a result of bilogical uptake during periods of high organic productivity. Compared to Cu, the bilogical uptake of Zn is low. Inspite of this reduced biological uptake too, Zn is sedimented more strongly than Cu (Salomons and Baccini, 1986). This may be one of the reasons for a sharp decrease of OBM during postmonsoon at Sations 1 & 2.

ii. Estuarine Metal Reactivity

The mixing curves of dissolved trace metal concentrations measured over the whole estuarine salinity range against a suitable index of mixing (end to end member relation) have been used to distinguish conservative from non-conservative behaviour of dissolved components. From Figs. 6.3 a, b & c it is deduced that the CLM fraction undergoes rapid removal in the salinity range 0 to 5. An associated phenomenone is the tendancy of removal of $Zn(OH)_2$ with increase of salinity. The model calculations by Bourg (1983) have shown that the forms $ZnCl_3^-$, $ZnCl_2$and $ZnCl^+$increase with salinity whereas, especially $Zn(OH)_2$, and Zn-humics decrease with salinity. Zirino and Yamamoto (1972), and Florence and Batley (1975, 1976 and 1977) have shown that the majority of Zn is present as $Zn(OH)_2$ which readily explains the removal of CLM with salinity. Investigation in the Maeklong and Medway estuaries (Windom *et al.*, 1991) indicated that the removal processes dominate the

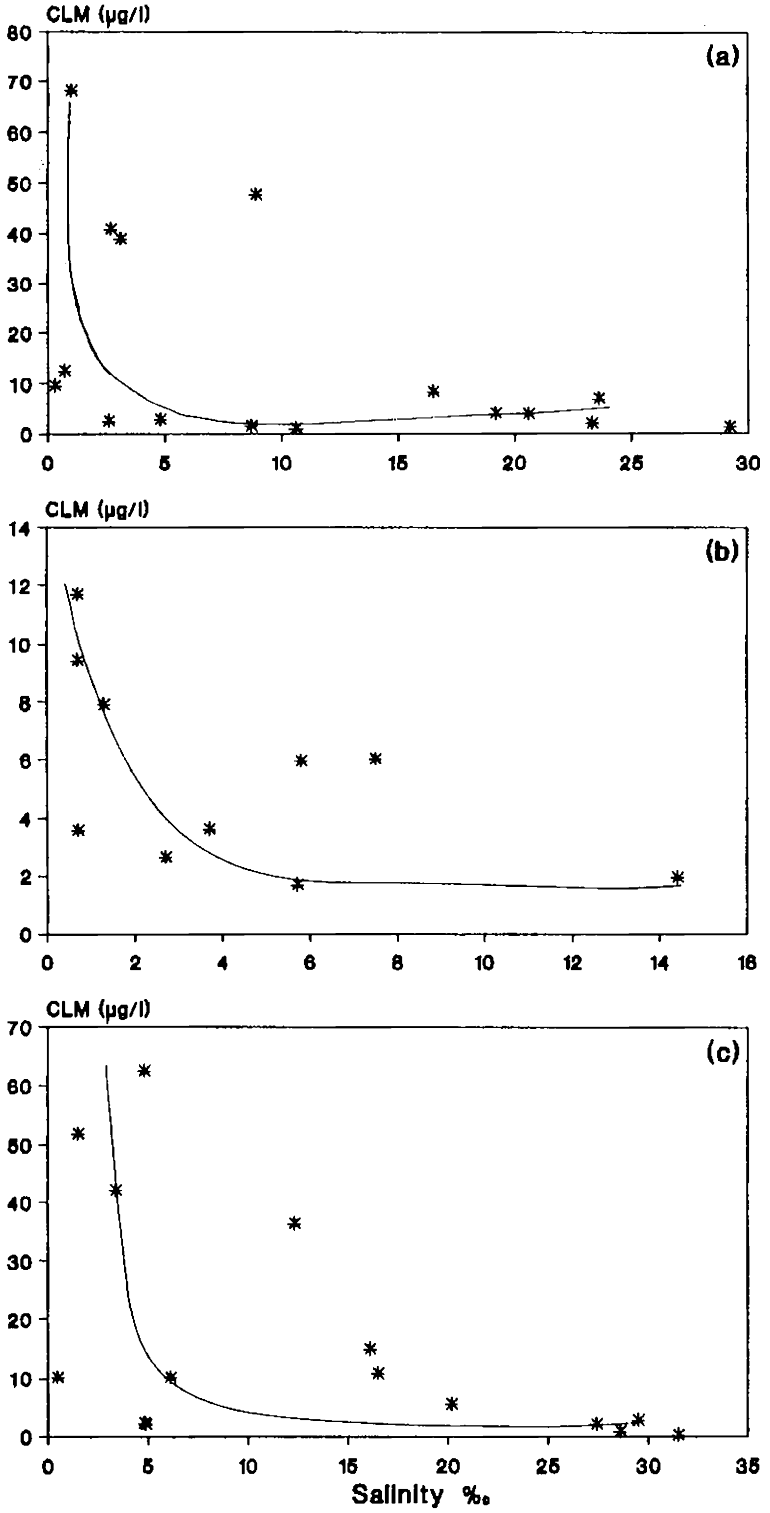


Fig. 6.3 Salinity - CLM plots
a) premonsoon b) monsoon c) postmonsoon

estuarine distribution of Zn. The removal trend therefore appears to be similar to that of Fe and the above authors suggest inorganic chemical control to modify the dissolved forms of Zn in most estuaries. Removal of Zn in the very low salinity regions (0.5%.) followed by mid-estuarine addition in the salinity region (3 - 20%.) have been reported in the Tamar estuary (Ackroyd *et al.*, 1986). In the River Rhine and the Elbe, Duinker and Nolting (1978) and Duinker *et al.*, (1982) have deduced that Zn was removed from solution onto particles at low salinity (< 5%).

Van den Berg *et al.*, (1987) have shown for the first time that the Zn concentration co-varies with the organic Zn complexing capacity in estuaries. In the Cochin estuary, the OBM fraction was found to decrease with increase of salinity and the removal was sharp in the salinity range 0 to 5%. during Premonsoon and postmonsoon (Figs. 6.4 a & c). And during monsoon, no clear features were distinguishable since the concentration of this fraction was minimal to undergo any appreciable changes. Already it has been noted that Zn-humics decrease with increase of salinity (Bourg, 1983). It is hence concluded that the removal of Zn associated with humic substances during estuarine mixing, constitutes the reason for the observed decrease of organically bound Zinc (with salinity) in this estuary. Similarly, during estuarine mixing, a considerable reduction of organic Zn has been reported in the Yarra river system (Hart and Davies, 1981). Kuwabara *et al.*, (1989) also found a negative correlation between dissolved organic zinc and salinity and a positive correlation with DOC. However in the present study, no significant correlation was observed between organically bound Zn and DOC. The highly significant positive correlation ($r = 0.78$, $p < 0.001$) between CLM and OBM and the absence of any relation between OBM and DOC confirms the argument of Windom *et al.*, (1991) that inorganic processes probably excert a major control on the estuarine behaviour of Zn.

The salinity - PEM and PTM plots are shown in Figs. 6.5 a, b & c and 6.6 a, b & c and show a considerable removal in the

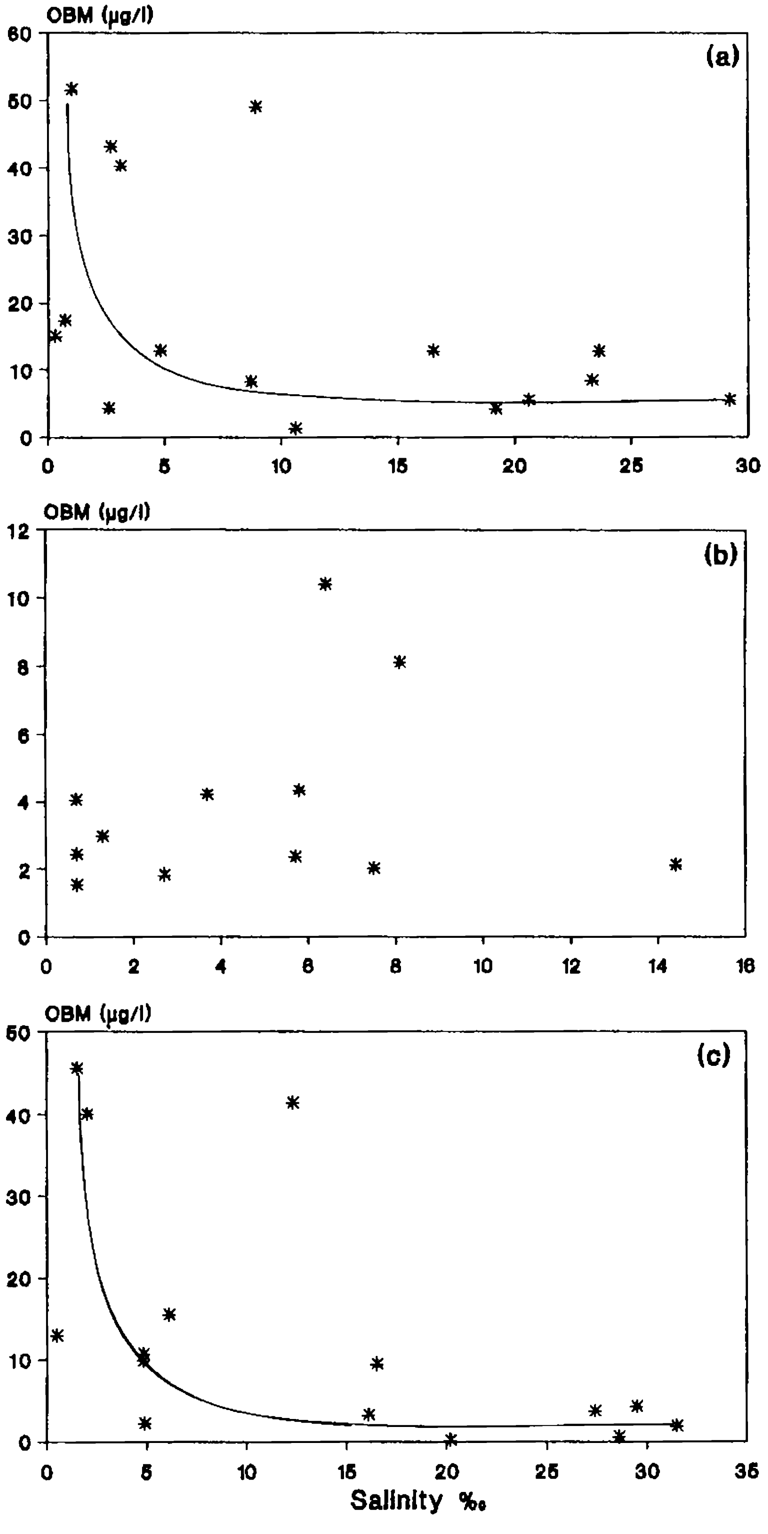


Fig. 6.4 Salinity - OBM plots
a) premonsoon b) monsoon c) postmonsoon

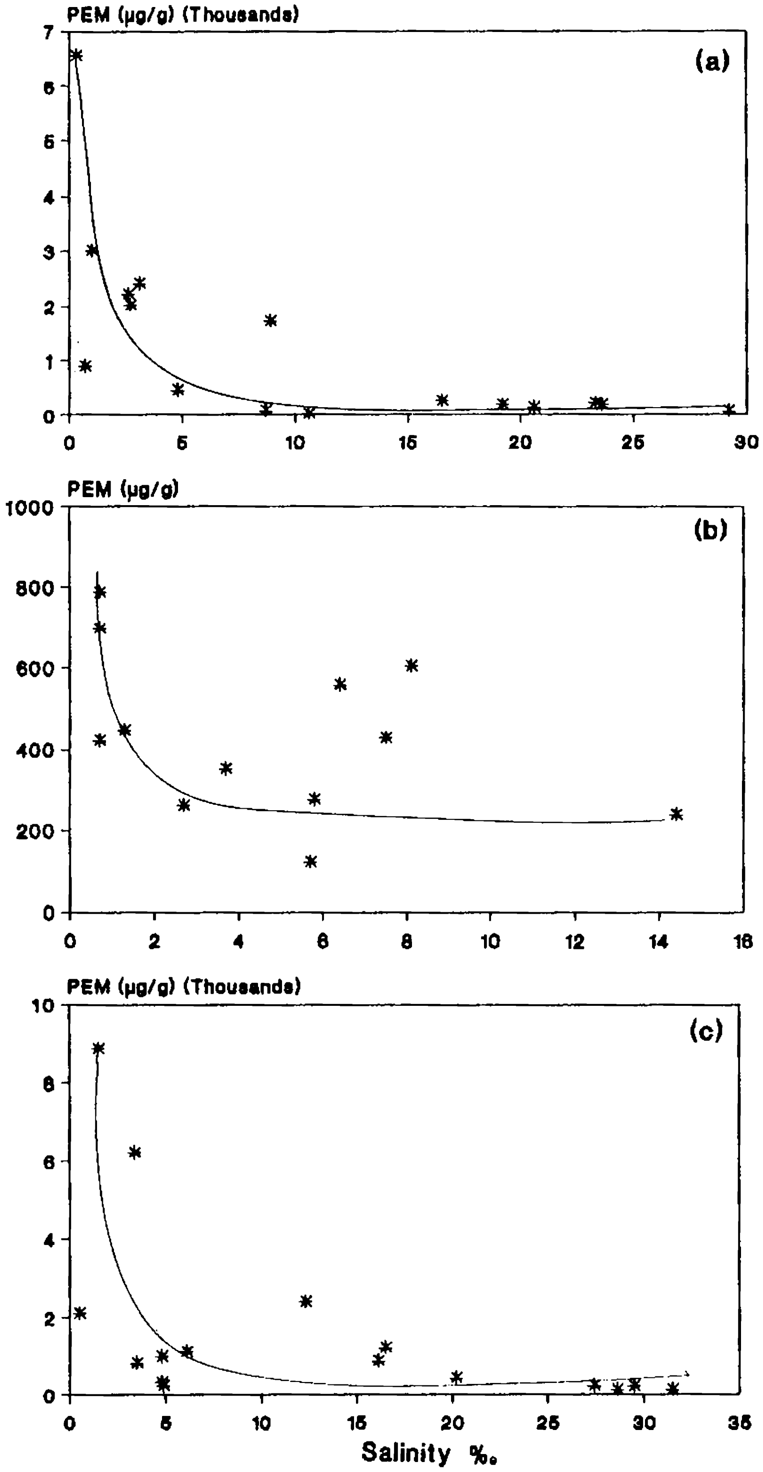


Fig. 6.5 Salinity - PEM plots
a) premonsoon b) monsoon c) postmonsoon

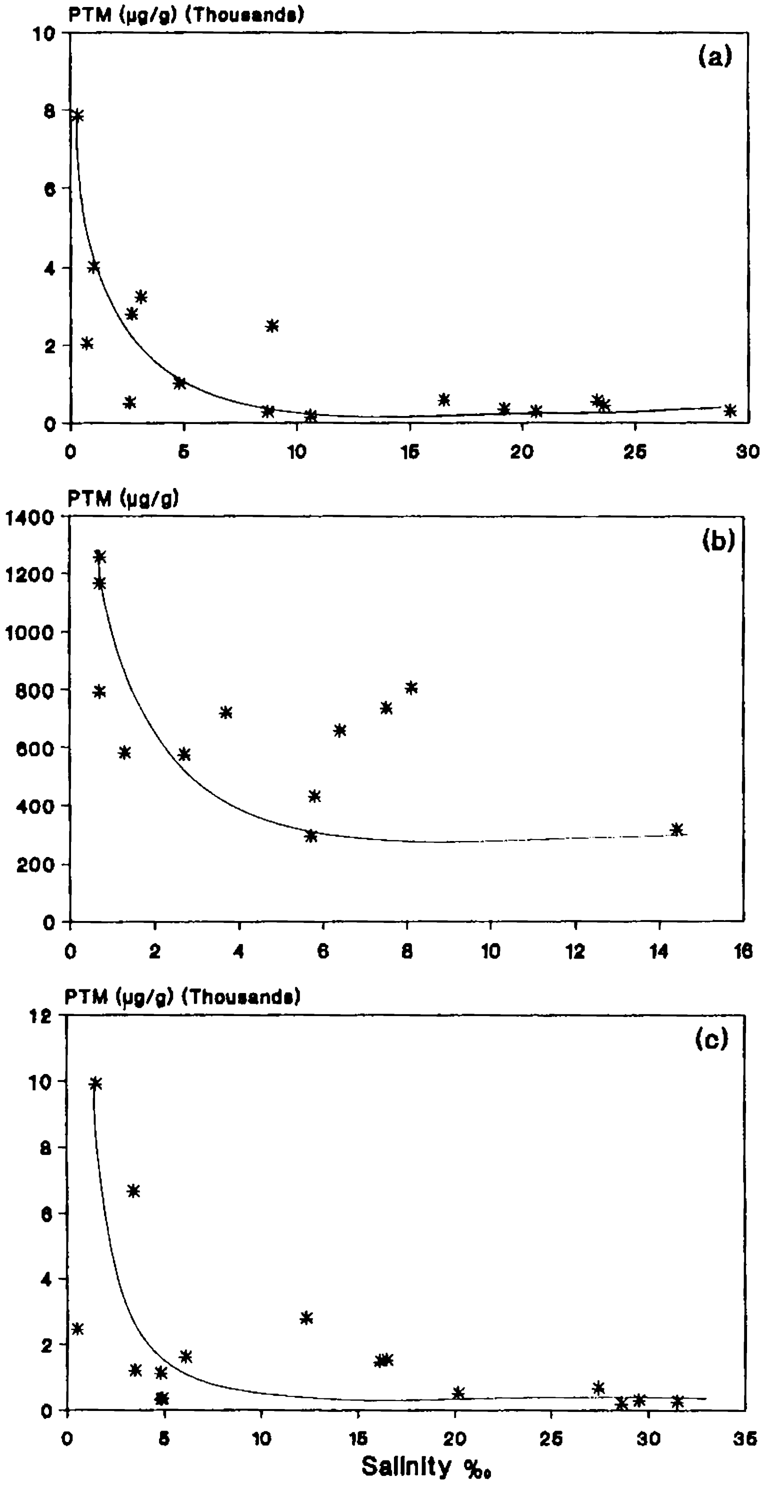


Fig. 6.6 Salinity - PTM plots
a) premonsoon b) monsoon c) postmonsoon

low salinity region (0 to 5%.). If the removal of Zn from solution was onto the particulate phase then a positive deviation from linearity should have been observed in the S%. - particulate metal plot. Instead a negative deviation is observed with a sharp removal of PEM and PTM fractions. Duinker (1983) also has reported a similar removal phenomenone in the Rhine estuary. He found the interpretation to be complicated because various sources contributed to the concentration and composition of particles in that estuary, such as 1) particles originally present in river suspension 2) particles derived from the marine environment, 3) flocs formed from smallar particles originally present in the river, including colloidal material 4) particles derived from the bottom by wind, currents and organisms and 5) components taken up from solution in the estuary. But this removal may be better explained by the desorption processes. The chloride complexation and Ca^{2+} competition for absorption sites are felt more strongly by Zn than Cu. Bourg (1983) attributed this to the low surface constants and relatively high chloro-complex constants. Similar salinity induced desorption of Zn from sedimentary phases was reported in the Fraser river estuary (Thomas and G ill, 1977). Kuwabara *et al.*, (1989) also found that partitioning of Zn onto suspended particles decreased with increase of salinity. Jouanneau *et al.*, (1983) have shown that ≈ 50% of the decrease of particulate Zn occurs at salinity < 0.5%. . The linear relationship between salinity and particulate Zn in the Elliot Bay contradicts the desorption processes (Paulson *et al.*, 1989). Additionally he found that dissolved Zn was conservative in the Bay . In this context it has been demonstrated that removal of metals from the dissolved phase by adsorption is feasible only when suspended particulate loads are high (Morris, 1986; Ackroyd *et al.*, 1986).

An investigation into the behaviour of Zn-PEM and PTM indicates a decrease in content with increase of SS load (Fig. 6.7 a, b & c and 6.8 a, b & c. The simple reason is the change in composition of the particles as a result of the resuspension of bottom materials, features of which have already been discussed in the previous chapters.

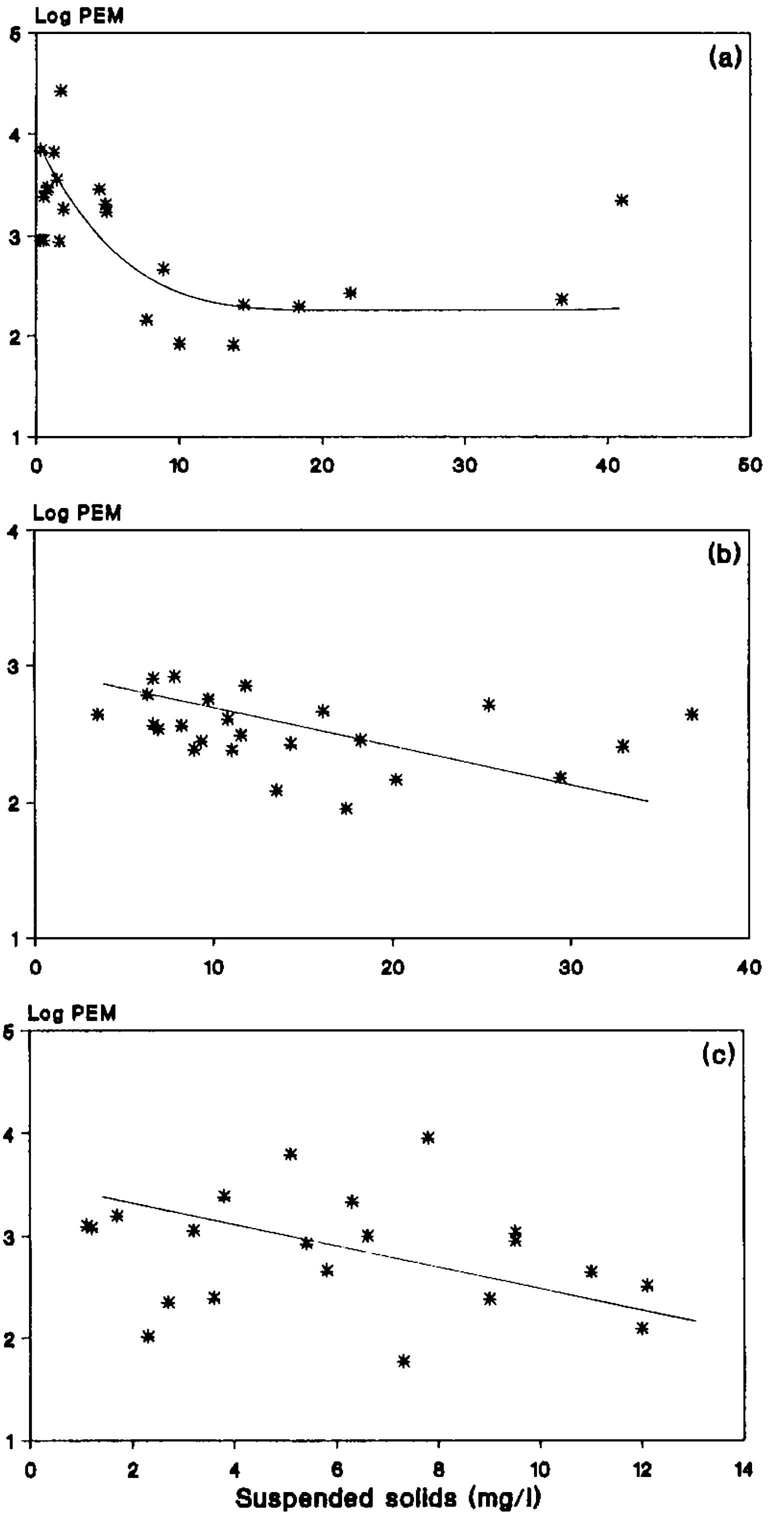


Fig. 6.7 Suspended solids - LogPEM plots
a) premonsoon b) monsoon c) postmonsoon

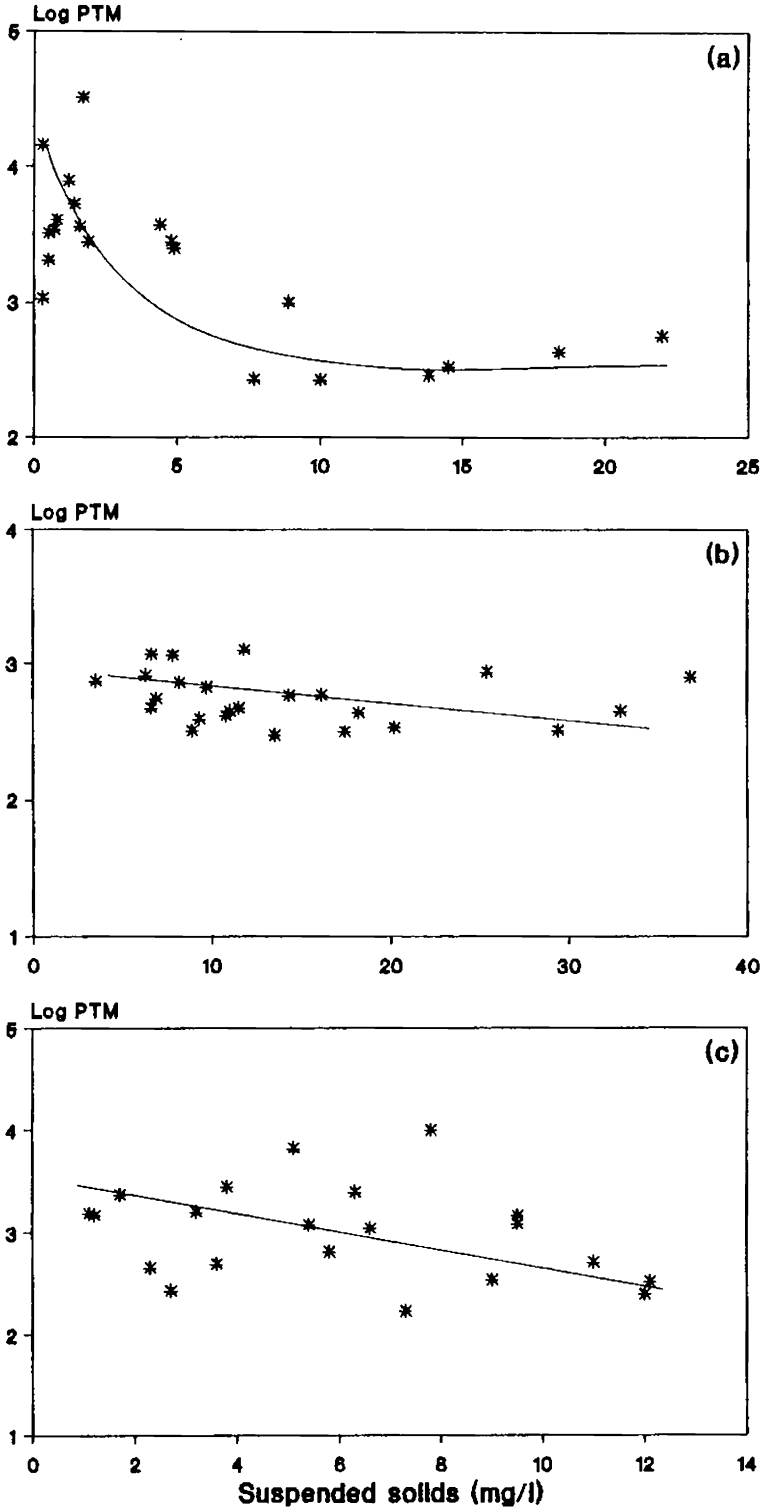


Fig. 6.8 Suspended solids - LogPTM plots

a) premonsoon b) monsoon c) postmonsoon

IV. Transport and Species Transformations

The details of Zn transport in the Cochin estuary are given in Table 6.1. In this estuary on an average 35%. of the total (CLM + OBM + PTM) Zn is transported in the particulate phase and 65%. in the dissolved phase. De Groot *et al.*, (1976) found a similar Zn transport (34% and 66% respectively) in the Rhine river. In the Elliot Bay ≈ 75% of the total Zn orginating from the riverine and anthropogenic sources was transported in the dissolved form (Paulson *et al.*, 1989). But in the Susquehanna river the major phase (62%) was the particulate Zn (Mc Duffie *et al.*, 1976). In this estuary out of the total particulate Zn, ≈ 57% is in the exchangeable form. The particulate phase (PTM) transport is maximum during monsoon (45%) and minimum during postmonsoon (29%). Of the 65% dissolved Zn, 31% constitutes in the CLM form and 34% is in organically bound (OBM) form. The CLM was minimum (25.64%) during premonsoon and OBM was maximum (43%) during premonsoon. The monsoonal transport is characterised by very low organic phase (21%).

Table 6.1

Season	CLM %	OBM %	PEM %	PTM %
Premonsoon	25.64	43.01	15.14	31.35
Monsoon	34.04	20.92	23.84	45.04
Postmonsoon	33.77	37.36	20.75	28.87
Annual Average	31.15	33.76	19.91	35.09

The details of species transformations during estuarine transport is depicted in Fig. 6.9. The PEM during premonsoon remains constant in the upper and lower estuary (16.60%) with a minimum in the mid estuary (14%). During monsoon PEM decreases from 26% in the upper estuary to 21.53% in the mid- estuary and then remains steady in the lower estuary. In postmonsoon PEM slightly increases in the ME (15.19 to 19.52%) and then falls sharply to 35.6% in the LE segment. Similarly PTM increases

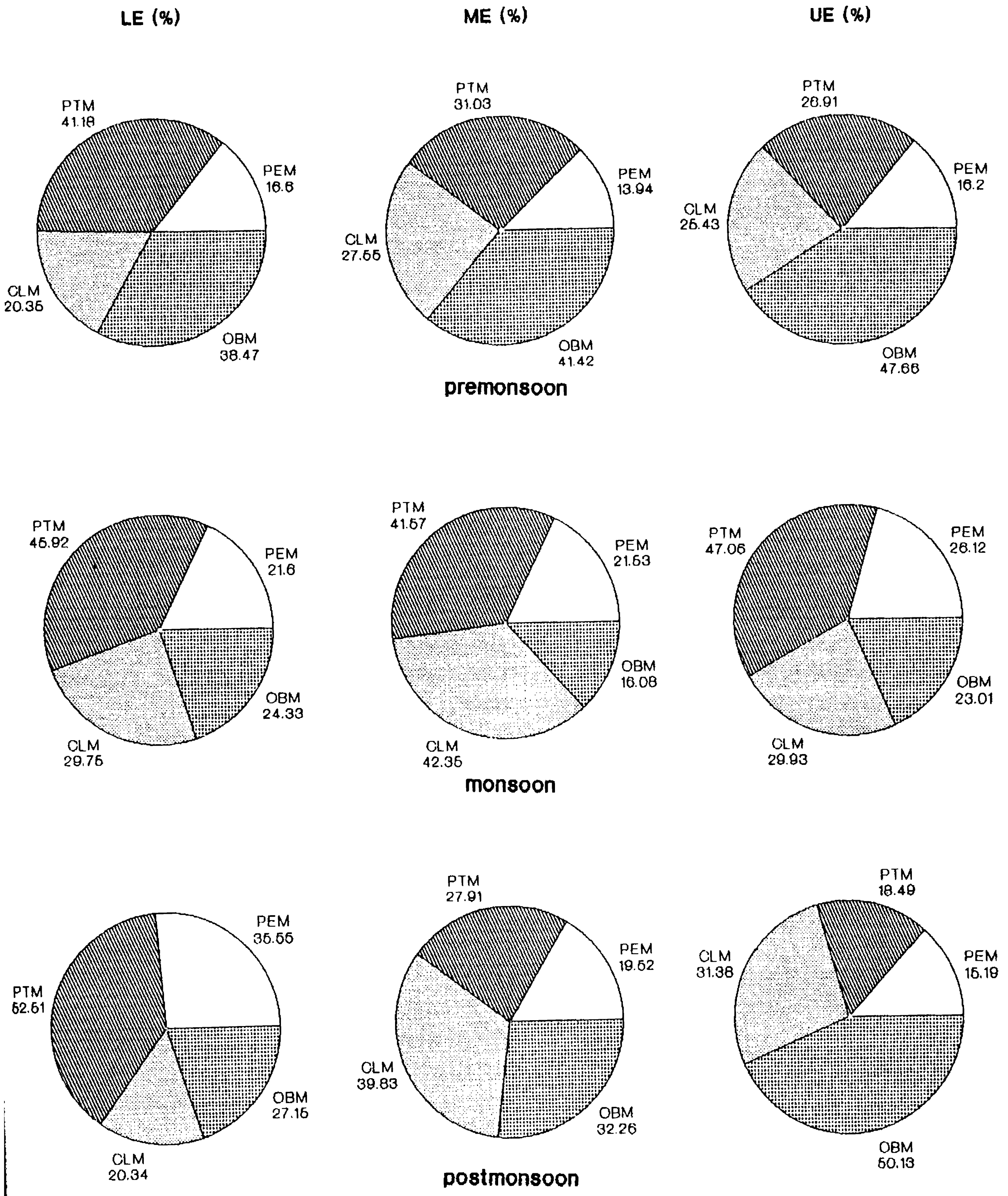


Fig. 6.9 Seasonal Species transformations during estuarine transport
LE-lower estuary ME-middle estuary UE-upper estuary

from 27% in the UE to 41% in the lower estuary during premonsoon. In monsoon PTM shows a minimum in the mid-estuary. During postmonsoon PTM increases from 18.49% to 52.5% in the lower estuary. During premonsoon the increase of particulate phase is compensated by a corresponding decrease in CLM (25.43% to 20.35%) and OBM (47.66% to 38.47%). During monsoon, the species transformations are not so significant compared to premonsoon and postmonsoon.

During postmonsoon the sharp increase of PEM and PTM are compensated by the decrease of CLM (from 31.38 to 20.34%) and OBM (from 50.13 to 27.15%). The maximum variations are observed during postmonsoon where the dissolved fractions decrease sharply and the particulate phases increase correspondingly.

V. Mass Balance:

Given,

$C_R = 66.57\ \mu g\ l^{-1}$
$C_B = 20.47\ \mu g\ l^{-1}$
$C_E = 43.40\ \mu g\ l^{-1}$
$Q_R = 5.192 \times 10^{12}\ l\ Yr^{-1}$
$Q_B = 1.780 \times 10^{12}\ l\ Yr^{-1}$
$Q_E = 6.970 \times 10^{12}\ l\ Yr^{-1}$

Flux in from the river

$= Q_R \times C_R$
$= 345.63 \times 10^3\ Kg\ Yr^{-1}$

Flux in from the barmouth box

$= Q_B \times C_B$
$= 36.44 \times 10^3\ Kg\ Yr^{-1}$

Total flux of zinc into the estuary

$= 382.07 \times 10^3\ Kg\ Yr^{-1}$

Flux out from the estuary

$= Q_E \times C_E$
$= 302.5 \times 10^3\ Kg\ Yr^{-1}$

Mass balance of zinc:

$$\begin{aligned} \text{Flux in} &= 382.07 \times 10^3 \text{ Kg Yr}^{-1} \\ \text{Flux out} &= 302.50 \times 10^3 \text{ Kg Yr}^{-1} \\ \text{Flux in} - \text{Flux out} &= (382.07 - 302.50) \times 10^3 \text{ Kg Yr}^{-1} \\ &= \underline{79.57 \times 10^3 \text{ Kg Yr}^{-1}} \end{aligned}$$

The mass balance of Zn shows that ≈ 80 x 10^3 Kg of Zn gets accumulated in this part of the estuary every year. This result is expected since all the four fractions of Zn were decreasing in the saline region in relation to addition of metal via anthropogenic inputs. Similar results are also available from the Hudson river estuary (Klinkhammer and Bender, 1981) and Seto Inland Sea, Japan (Hoshika *et al.*, 1988).

Chapter 7

SPECIATION - A CRITICAL APPRAISAL

I. Overview
   i. Intermetallic Comparison
   ii. Metal Reactivity in the Estuary
   iii. Metal Transport
   iv. Elemental Budget
II. Anthropogenic Inputs
III. Enrichment Factors
IV. Metal Cycling

I. Overview

A critical evaluation of the metal speciation in the Cochin estuary is provided in this chapter. This part of the work which serves as the summary is presented under different sub-headings.

I.i. Inter-metallic comparison

This chapter deals with the comparative behaviour of the four metals during estuarine transport. Several attempts have been hitherto made (Kuwabara *et al.*, 1988; Windom *et al.*, 1988) to categorize the metals according to their behaviour in the estuarine environment. The complexity and diversity of different estuaries along with differences in the chemistry of these metals make the proposition beyond contemplation. The studies, when enlarged to accommodate speciation aspect too, become all the more complicated. However very useful and directional results could be achieved by closely following the processes as revealed from the behaviour of each of the metals investigated in this study. Of the four metals studied, the dissolved labile fractions (CLM) of cadmium and zinc were found to decrease towards the saline region (Figs. 4.2a and 6.2a) whereas those of copper and lead showed an appreciable increase in the same direction. Notedly the CLM fraction of all the four metals showed enhancement at Station 5 compared to values at Station 6.

The organically bound fractions of copper, cadmium and lead were found to increase towards the lower reaches of the estuary, but the same fraction of zinc was found to decrease in the same direction. The OBM fraction of cadmium and zinc only showed considerable increase at Station 5 compared to Station 6.

With regard to the particulate exchangeable and total metal fractions (PEM and PTM)- all the four metals followed similar distribution patterns; elevated levels at Station 5 compared to Station 6 and thereafter a decrease towards the lower reaches of the estuary. It may be concluded at this point that the anthropogenic inputs at Station 5 (see Fig. 7.2) was mainly in the CLM and particulate fractions (PEM and PTM) for copper; all fractions in the case of Cd and Zn and only as the particulate fraction (PEM and PTM) for lead.

The results of the intermetallic correlation studies (r values) for each fractions of the four metals are given in Table 7.1. The CLM fraction of cadmium showed an excellent positive correlation (r = 0.87) with Zn and to a lesser extent with Cu (r = 0.35). This fraction of Cu vs Pb also showed significant positive correlation (r = 0.44).

In the OBM fraction lead showed significant positive correlations with Cd (r = 0.50) and Cu (r = 0.42). Cd also showed moderate positive correlation with Cu and Zn (r = 0.33 each). The exchangeable particulate fraction of Zn showed excellent positive correlations with Cu (r = 0.79) and Cd (r = 0.66).

Table 7.1

Intermetallic, interspecies
Correlation (r) values; (n=72)

Fraction	Metal	Cu	Cd	Pb
	Cd	0.35		
CLM	Pb	0.44	0.22	
	Zn	0.10	0.87	_
	Cd	0.33		
OBM	Pb	0.42	0.50	
	Zn	0.17	0.33	-0.1
	Cd	0.49		
PEM	Pb	0.26	_	
	Zn	0.79	0.66	0.26
	Cd	0.36		
PTM	Pb	0.32	_	
	Zn	0.75	0.55	0.45

Cadmium also showed a significant positive correlation with copper Cu (r = 0.49). The total particulate fraction of Zn showed excellent positive correlations with Cu (r = 0.75), Cd (r = 0.55) and Pb (r = 0.45). Also there existed significant positive correlation between Cu and Cd (r = 0.36). It may be surmised that Cd and Zn are closely similar in its behaviour in the different phases in this estuary. Alloway (1990) also reported that Cd was closely associated with Zn in its geochemistry. The behaviour of Cu and Pb in the dissolved phase was well correlated but the exchangeable fractions did not co-vary.

To generalize, Cd and Pb in this estuary show significant relationship in their organic association where as copper, cadmium and zinc are related in their particulate association.

To sum up, the order of intermetallic CLM relation would be expressed as: Cd & Zn > Cu & Pb > Cu & Cd > Cd & Pb > Cu & Zn > Pb & Zn. In the OBM fraction, the sequence would be Cd & Pb > Cu & Pb > Cd & Zn = Cu & Cd > Cu & Zn > Pb & Zn. The order for both the particulate fractons (PEM & PTM) would be as follows Cu & Zn > Cd & Zn > Cu & Cd > Pb & Zn = Cu & Pb > Cd & Pb.

I. ii. Metal Reactivity in the Estuary

Both the particulate fractions of all the metals studied in this estuary showed a sharp decrease in their content in the salinity range 0 - 5%.. Among the dissolved fractions, Cu-CLM did not exhibit any noticeable trend with salinity. The OBM fraction of cadmium showed a broad maximum in the 20 - 25%. salinity range whereas the CLM fraction of the same metal did not show any such trend. The CLM and OBM fractions of lead showed an initial increase upto salinity ≈ 5%. and thereafter, the CLM remained at a steady level. But the OBM fraction decreased within the salinity range 5 - 12%. and then increased sharply with increase of salinity. In the case of zinc both CLM and OBM fractions showed a sharp removal in the low salinity region (< 5%.). The particulate fractions (PEM & PTM) of copper was found to decrease with increasing amounts of suspended solids during both premonsoon and monsoon seasons However it increased sharply in the initial stages (of low suspended solids) and fell back to a steady state during postmonsoon as turbidity increased. Lead showed a decrease with increase of suspended load only during premonsoon and postmonsoon. In the case of cadmium and zinc the decreasing trend was consistant during all the three seasons.

In the analysis of results of metal vs organic carbon, both the PEM and PTM of copper showed excellent positive correlations with POC ($r = 0.55$ and $r = 0.64$); other metals did not show any significant correlation. The feature of decrease of particulate copper towards the lower reaches of the estuary was commented upon earlier as being due to the decrease of POC contents. The metal species discussed in relation to DOC indicates that the OBM fractions of copper, cadmium and lead showed significant positive correlations while zinc did not exhibit any such relation . Additionally the organophillic nature of the four metals studied in this estuary follows the order Cu > Pb > Cd > Zn.

I. iii. Metal Transport

The Cochin estuary, a typically tropical one, portrays interesting features on metal transport and associated phenomenon. On an annual average basis all the four metals studied (two phases - dissolved and particulate) are transported mainly in the dissolved form. This phase (CLM + OBM) accounts for Cu - 59.76%, Cd - 81.04%, Pb - 75.50% and Zn - 64.91% . Within this dissolved phase (CLM + OBM) the maximum organic association (OBM) was for Cu (72.59%) followed by Pb (68.67%), Cd (64.45%) and the minimum was for Zn (52.00%). Corresponding CLM fraction values are indicated in Table 7.2. The particulate associated transport in this estuary followed the order Cu (40.24%) > Zn (35.09%) > Pb (24.50%) > Cd (18.96%). The particulate phase accounted for the total particulate metal (PTM) of which the PEM fraction i.e., the exchangeable form was in the following order: Zn (56.73%) > Cd (54.48%) > Cu (34.00%) > Pb (32.00%). The table also provides the T - E percentage values which is the difference between the two particulate metal fractions.

Apart from calculating the annual average basis, the metal transportation was checked during the monsoon season when the amount of suspended solids in the river runoff peaks to a maximum. In this context the monsoonal transport was characterised by an increased particulate association in the order Cu (57.40%) > Zn (45.04%) > Pb (28.00%) > Cd (22.14%). This seasonal rating indicates the higher particulate associated copper (compared to dissolved) as well as other metals (compared to annual averages) to be on the greater side, which is an important feature.

Table 7.2

Phase	Metal			
	Cu	Cd	Pb	Zn
Dissolved %	59.76 CLM % OBM % 27.41 72.59	81.04 CLM % OBM % 35.55 64.45	75.50 CLM % OBM % 31.33 68.67	64.91 CLM % OBM % 48.00 52.00
Particulate %	40.24 PEM % T-E % 34.00 66.00	18.96 PEM % T-E % 54.48 45.52	24.50 PEM % T-E % 32.00 68.00	35.09 PEM % T-E % 56.73 43.27

T - E% = total particulate metal (PTM%) - particulate exchangeable metal (PEM%).

I. iv. Elemental Budget

The budget calculations for this estuary (condensed from previous chapters) show that annually 1.77 x 10^3kg of copper, 2.27 x 10^3kg of cadmium and 25.36 x 10^3kg of lead are removed in excess of inputs from this estuary. It implies that this part of the Cochin estuary acts as a source for the above mentioned metals. On the other hand, the mass balance of zinc showed 79.57 x 10^3kg $yr^{-1}$to be deposited in the estuary. This estuary, hence acts as a sink for the metal zinc.

II. Anthropogenic Inputs

This investigation has proved beyond doubt the existence of anthropogenic inputs between Stations 5 and 6. Hence it became imperative to calculate the time average annual value for the extent of such inputs within the river reach. The 3D overlap figure (Fig.7.1) for the four metals (CLM + OBM + PTM) at

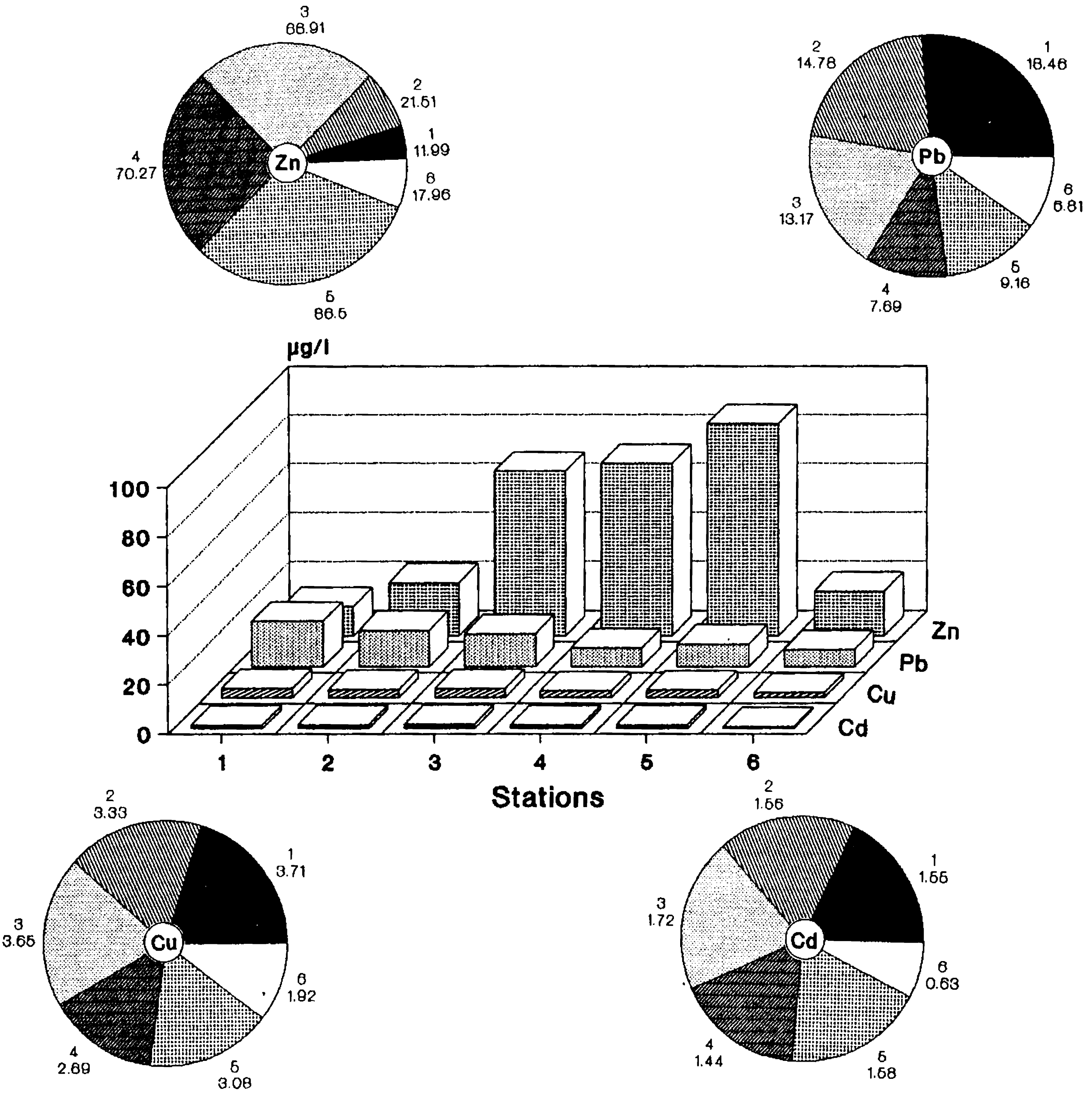


Fig. 7.1 Annual mean concentration (CLM + OBM + PTM) of metals Cu, Cd, Pb & Zn at Stations 1 to 6

Stations 1 to 6 is also presented as pie diagrams indicating the annual mean concentrations in the same figure. The calculations are presented on the basis that the mean concentration at Station 6 is used to calculate the fluvial contribution and the difference of the same from the calculations made at Station 5 will indicate the amount of anthropogenic input. The input values are calculated for each metals as below:

Discharge of Periyar river = 5.192×10^{12} l yr^{-1}

Copper:

Fluvial input at Station 6 = $1.92\ \mu g l^{-1} \times 5.192 \times 10^{12}$
= 9.969×10^{3} kg yr^{-1}
Amount at Station 5 = $3.08\ \mu g l^{-1} \times 5.192 \times 10^{12}$
= 15.992×10^{3} kg yr^{-1}
Anthropogenic input = $\underline{6.023 \times 10^{3}\ \mathrm{kg\ yr}^{-1}}$

Cadmium:

Fluvial input at Station 6 = $0.63\ \mu g l^{-1} \times 5.192 \times 10^{12}$
= 3.271×10^{3} kg yr^{-1}
Amount at Station 5 = $1.58\ \mu g l^{-1} \times 5.192 \times 10^{12}$
= 8.203×10^{3} kg yr^{-1}
Anthropogenic input = $\underline{4.932 \times 10^{3}\ \mathrm{kg\ yr}^{-1}}$

Lead:

Fluvial input at Station 6 = $6.81\ \mu g l^{-1} \times 5.192 \times 10^{12}$
= 35.358×10^{3} kg yr^{-1}
Amount at Station 5 = $9.16\ \mu g l^{-1} \times 5.192 \times 10^{12}$
= 47.559×10^{3} kg yr^{-1}
Anthropogenic input = $\underline{12.201 \times 10^{3}\ \mathrm{kg\ yr}^{-1}}$

Zinc:

Fluvial input at Station 6 = $17.96\ \mu g l^{-1} \times 5.192 \times 10^{12}$
= 93.248×10^{3} kg yr^{-1}
Amount at Station 5 = $86.50\ \mu g l^{-1} \times 5.192 \times 10^{12}$

$= 449.108 \times 10^3$ kg yr^{-1}

Anthropogenic input $= \underline{355.860 \times 10^3 \text{ kg yr}^{-1}}$

III. Enrichment Factors

The enrichment factors at Stations 1 to 6 were worked out on the basis of the background value at Station 6 (Table 7.3)and it is shown in Fig 7.3. This table shows that the factors of enrichment for copper and lead are comparatively higher in the estuarine Stations (Stations 1, 2 & 3) than at Stations 4 and 5. Zinc is considerably enriched at Stations 3, 4 & 5 and noticeably depleted at Station 1. On the other hand, cadmium is enriched to about 2.5 times throughout the estuary. Obviously, the anthropogenic inputs at the industrial site (upstream of Station 5) cause extensive enhancement in the content of zinc and cadmium.

Table 7.3

Station	Enrichment Factor			
	Cu	Cd	Pb	Zn
1	1.93	2.46	2.71	0.67
2	1.73	2.48	2.17	1.20
3	1.90	2.73	1.93	3.73
4	1.40	2.29	1.13	3.91
5	1.60	2.51	1.35	4.82

IV. Selective Processes in Metal Cyling in the Environment

To explain the processes in simple terms the environment is subdivided as water media, sandwiched between atmosphere and sediment. The four metal species, CLM, OBM, PEM and PTM form the nuclei of processes in the aquatic environment. External sources such as industrial and sewage effluents are also incorportated. The regulating processes of metal cyling in the environment, pertaining to Cochin estuary are given in Fig. 7.3. The CLM fraction is found to be transformed to PEM and

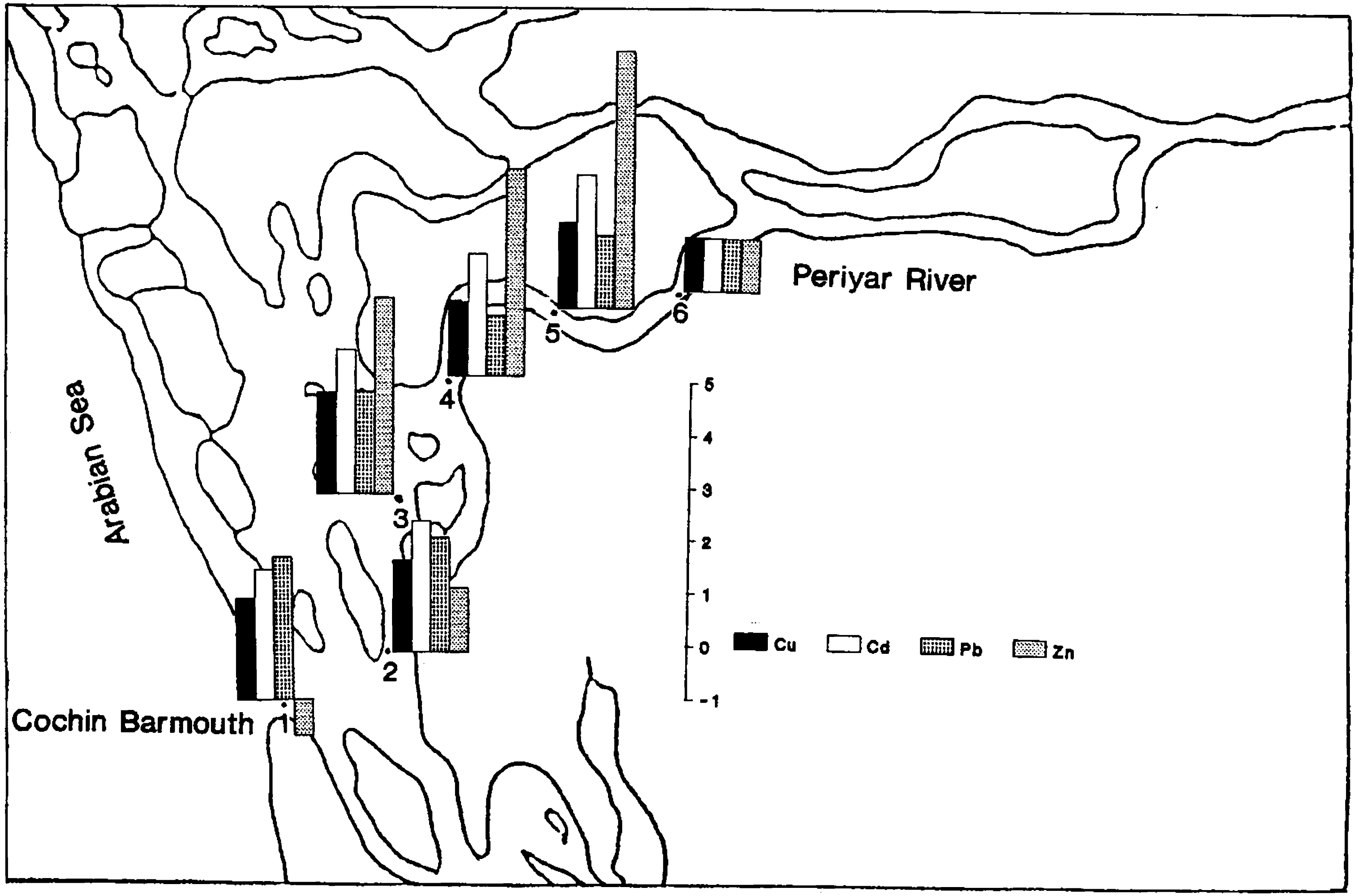


Fig. 7.2 Enrichment factors at Stations 1 to 6

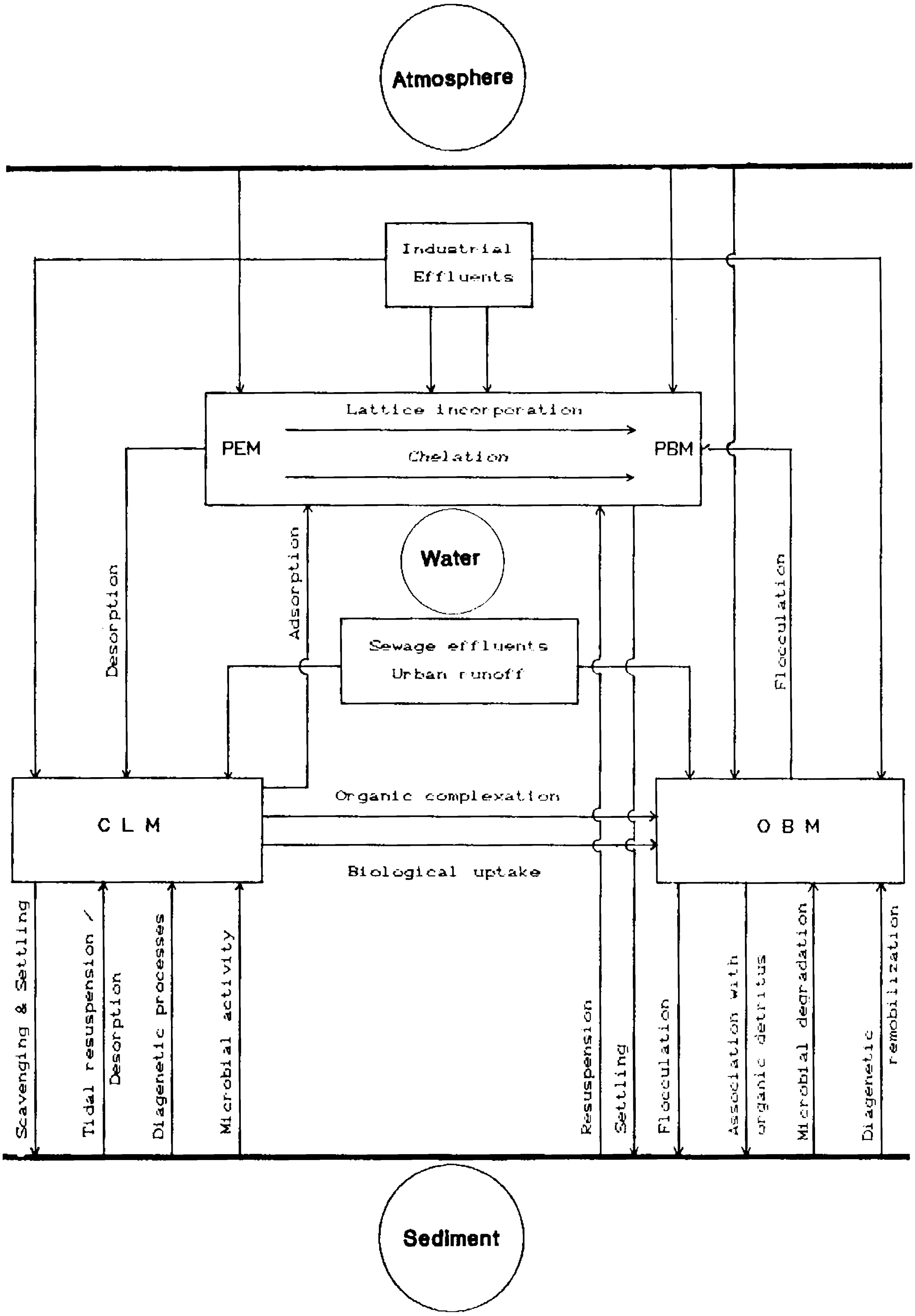


Fig. 7.3 Selective processes in metal cycling in the environment

vice-versa by processes as shown. In estuaries, modifications in the distributions of river-born components in dissolved and particulate phases may occur in response to sharp gradients of parameters like salinity , pH, concentrations of dissolved organic and suspended matter. Thus particles play an important role in the formation and distribution of metal species. The most important processes which control metal concentrations are the sorption processes which include:
i) non-specific adsorption of species on particle surface which is a physical process originating from electrostatic forces
ii) chemisorption of species, which takes place as hydrolytic adsortpion or condensation reactions, including co-precipitations with Fe and Mn hydroxides and
iii) ion-exchange, aslo a chemical process.
The above processes are better understood in terms of competition for surface sites with protons and cations (Bourg, 1983). This concept leads to the determination of surface complex formation constants, corresponding to interface reactions such as:

$$\mathrm{SOH} + \mathrm{M}^{z+} \rightleftharpoons \mathrm{SOM}^{(z-1)} + \mathrm{H}^{+}$$

(where SOH: surface and M: metal).In solution chemistry, activity coefficients do affect the value of the surface constant. The adsorption of Cu is not affected by a greater number of Na^+ or NO_3^- ions; Cd, however is not as competitive with Na^+ with respect to adsorption. The Ca^{2+} and Mg^{2+} ions present in solution are capable of replacing the metal ions thus leading to desorption. For the sorption of trace metals in aquatic systems, the more important sites generally are comprised of thermodynamically metastable phases, which exhibit extensive isomorphic substitution. This is mainly true for Fe and Mn oxyhydrates.

The CLM fraction also would be transformed to OBM either by organic complexation or biological uptake. The major processes by which the sediment associated metal is converted to the CLM form include tidal resuspension followed by desorption, diagenetic processes and microbial activity. The major process in the reverse direction is the scavenging by Fe and

Mn oxyhydrates and subsequent settling.

The variations in OBM content are well reflected in sediment metal levels. This may be explanied as the relationship between the amount of primary productivity in the overlying waters and the extent to which the organically associated metal would be preserved in the bottom sediments; the greater the magnitude of primary productivity the greater the extent of preservation of the metal in the sediment media as also repoted earlier (Chester *et al.*, 1988). The other possible mechanism by which the OBM gets transferred to sediments is the flocculation process and the opposite is mainly by microbial degradation and diagenetic remobilization.

The processes by which the exchangeable particulate metal is converted to strongly bound form are lattice incorporation and chelation. The major processes by which the particulate metals and sediment metals equilibrated are thought to be purely physical (settling and resuspension).

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