

REFERENCE ONLY

**GEOCHEMISTRY OF INTERSTITIAL WATERS AND
SEDIMENTS OF VEMBANAD ESTUARY,
KERALA, INDIA**

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CERTIFICATE

This is to certify that this thesis is an authentic record of research work carried out by Sri. K. Abdulla Bava, M.Sc., under my supervision and guidance in the Department of Marine Geology and Geophysics, School of Marine Sciences, in partial fulfillment of the requirements for the Ph. D degree of the Cochin University of Science and Technology and no part of this has previously formed the basis for the award of any other degree in any university.

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PREFACE

Estuaries are the important pathways through which river-borne sediments as bed load as well as dissolved and particulate forms reach the sea. On entering the estuarine waters, most of the suspended particulate forms settle down whereas the more soluble species are flushed to the oceans. In the estuary, the bottom sediments undergo tremendous changes due not only to the peculiar physico-chemical factors such as tides, waves, currents, salinity, O_2 , Eh, pH, organic matter but also by human interferences.

The sediments not only act as a sink but also as a source for the dissolved species depending upon the reactions that take place between pore fluids and sediments. In due course, therefore, the bottom sediments have immense influence on the chemistry of estuarine waters and aquatic species. The transfer of chemical constituents between the sediments and overlying water at the sediment-water interface and between sediment column and interstitial water is a common phenomenon. Interstitial waters play a major role in transferring chemical ions from sediments of deeper layer to the overlying waters and vice versa. The composition of interstitial water is governed not only by that of the water entrained during sedimentation but also through microbially mediated breakdown of organic materials and by the accompanying changes in the redox conditions. Hence, investigations on interstitial waters are of particular interest with regard to post-depositional reactions and diagenesis.

However, studies on interstitial waters are rather very meagre in India and, therefore, the geochemistry of interstitial waters and sediments of Vembanad estuary has been studied and the results are presented in this thesis. The thesis is presented in six chapters.

The first chapter gives the general introduction about the topic chosen and the study area, as well as of the location, climate, river discharge, rainfall, estuarine hydrography and the geology

of drainage basin of rivers joining Vembanad estuary/backwaters. The main objectives of the study are listed at the end of the chapter. The methods of sample collection, processing, preservation and analytical procedures are presented in the second chapter.

The third chapter deals with textural characteristics of the core sediments as well as the physico-chemical parameters such as Eh, pH, salinity, alkalinity of interstitial waters and overlying waters. The distribution of organic matter in the core sediments has been discussed. Nutrients such as NO_2^- , PO_4^{3-} , SO_4^{2-} , and NH_4^+ have been studied in sediments and interstitial waters. Selected samples of overlying water have also been subjected to nutrient analysis so as to understand the changes taking place at the sediment-water interface.

In chapter IV, the variation of major elements like Si, Al, Fe, Mn, Na, K, Ca and Mg and heavy metals such as Cu, Cr, Ni, Pb, Zn, Cd, Co and Sr have been studied in sediments and interstitial waters. The distribution of these elements in the overlying waters has also been examined. The concentration of Hg has been estimated in selected sediment samples. Sequential extraction technique has been employed to determine the content of trace metals in the sediment associated chemical phases in a few cores. Grouping of elements have been studied using cluster analysis.

The fifth chapter is mainly concerned with the diagenetic changes in the sediment column and the transfer of metals and nutrients across sediment-water interface. Scanning electron microphotographs of quartz grains are used to decipher the post depositional changes that have occurred on the surface of the grains.

The sixth chapter abridges the results of the study and the conclusions arrived at therefrom.

The references cited are alphabetized at the end of the thesis.

CHAPTER 1

GENERAL INTRODUCTION


Introduction

An estuary is a semi-enclosed coastal body of water which has a free connection with the open sea and within which the sea water is measurably diluted with freshwater derived from land drainage (Pritchard, 1967). Estuaries constitute a very small part of the Earth's surface area and an even smaller part of the volume of the total marine hydrosphere. Because of mixing of salt and fresh waters, the distribution of salinity in an estuary varies in space and time (Perrels and Karelse, 1978). The hydrodynamics of the estuarine water bodies are complex as they are influenced by river flow, tide, wind, water density factors and the estuarine geometry.

The estuaries are complex systems where huge amount of chemical constituents reach from different sources. Rivers contribute dissolved species derived from chemical weathering of rocks in the watershed, suspended material from mechanical weathering of terrigenous matter and dissolved and particulate organic materials of biogenic origin. The influx of sea water through tides provides a strong electrolyte solution of nearly constant relative composition with respect to major ions Na, K, Ca, Mg, Cl, and SO₄, dissolved and particulate organic materials, and suspended sediments. In addition to the above some portions are added by the human activities.

Apart from river contribution other sources of sediments include the continental shelf, the atmosphere, erosion of the estuarine margins and bottom, and biological activity within the system. Sediments supplied to an estuary enter a remarkably complicated environment. They may undergo back - and - forth transport by ebb and flood tidal currents and would be resuspended many times prior to deposition. Some sediments meet sharp boundaries of fresh and salt water while some portion of sediments are consumed by animals that transform their physical and chemical form. Part of the river-borne sediments are

filtered within the estuaries while the remainder is flushed into the sea after considerable changes within the estuary. Consequently, the amount and kind of sediment discharged from an estuary to the sea may differ markedly from the original sediment supplied. The sedimentary processes in estuaries are determined by the dissipation of energy from river inflow, density gradients, the tide, waves, and other meteorological factors.

In estuaries the inputs are more or less balanced by outputs in the form of flow through the system and sinks within the system. Some of the more soluble elements escape to the ocean without much changes in the estuarine system whereas others combine to each other and precipitate as solid phases or settle to the bottom as particulate matter to be stored in the estuary, some times permanently. The biogeochemical characteristics of each element determine the type of behavior exhibited in its passage through the estuarine system. The balance between the inputs and outputs of elements together with the physical flow regime determines the overall chemistry of the estuarine sediments.

The influence of the sediment substratum on the chemistry of estuarine waters is least understood. The sediments and the trapped fluids may act either as a source or as a sink for the dissolved species depending upon the reactions that take place between pore fluids and sediments and the direction of transfer of materials across the sediment-water interface.

A clear understanding of the mechanisms and rates of processes that transport dissolved species through interstitial waters and across the sediment-water interface is required for two reasons: first, the exchange across this interface is of major importance in controlling the water column concentration and speciation of several elements, including nitrogen, silicon, and phosphorus; consequently, benthic exchange will be of major importance in controlling transport of these elements to the

ocean; second, in a steady state system, the flux of dissolved species through any horizon in the sediment is a measure of the depth-integrated reactions occurring below this horizon; thus fluxes can be used to identify and constrain diagenetic reactions occurring in sediments.

Interstitial waters: Interstitial waters - also known as interstitial solution or pore solution or pore waters or pore fluids or interstitial fluids - are aqueous solutions that occupy the pore spaces between particles in rocks and sediments. In recent sediments they are formed by the processes of entrainment and eventual trapping of waters during sedimentation, isolating it from the overlying waters, so that it may be considered to be in equilibrium with the sediments of which it is a part. Their composition reflects the nature of the original fluids buried with the sediments, particle fluid reactions, and migration of fluids and dissolved compounds by convection and diffusion (Manheim, 1976). The interstitial water-sediment complex is a site of intense chemical, physical and biological reactions, which can lead both to the formations of new and altered mineral phases as well as changes in the composition of the waters themselves. These changes are grouped together under the term **diagenesis**, which has been defined by Berner (1980) as "the sum total of processes that bring about changes in a sediment or sedimentary rock subsequent to its deposition in water". Many of the chemical changes that takes place during early diagenesis are redox-mediated, ie., they depend on the redox environment in the sediment-interstitial water-sea water system (Roy Chester, 1990).

Relative to sea water, the interstitial waters of oceanic sediments are generally enriched in Ca, Na and HCO_3^- and are depleted in K and Mg. The transport of dissolved material in interstitial waters takes place by convection and diffusion. The elemental composition of the interstitial waters is, therefore, controlled by a number of interrelated factors which include:

- a) the nature of the original trapped fluid;

- b) the nature of the transport processes ie., convection or diffusion;
- c) reactions in the underlying basement, including both high and low temperature basalt- sea water interactions;
- d) reactions in the sediment column; and
- e) reactions across the sediment-water interface.

Together, the reactions taking place in the sea water-sediment sandwich- basalt complex can involve both the release and the uptake of dissolved components. As a result major changes are produced in the composition of the interstitial waters relative to the present sea water and diffusion gradients would be set up under which the components would migrate from higher to lower concentration regions. Under these constraints the interstitial waters could act as either a sink or a source for dissolved components (Roy Chester, 1990).

Sediment-water exchange

A number of factors determine the nature of sediments-interstitial waters environments. During sedimentation in an (estuarine) environment a small amount of water is trapped between the interstices of sediment particles. Initially, the interstitial waters would be having the same composition as that of the bottom waters at that location. However, as sedimentation continues the sediments and the associated interstitial waters become increasingly buried deeper and deeper beneath the sediment- water interface. This hinder the free exchange of chemical constituents with the overlying waters and consequently the chemical and biological processes begin to exert an influence on the composition of both the sediment and the contained interstitial waters. In estuaries the organic carbon content of the sediments is high and so bacterial activity establishes strong reducing conditions within a short depth below the sediment-water interface. Therefore, river borne hydrous iron and manganese oxide coatings on mineral grains become unstable and get dissolved. Sulfates may be reduced to sulfides during bacterial oxidation of organic materials with a component production of bicarbonates and the release of

phosphate. Dissolved iron may react with sulfides, phosphates, or carbonates to form new stable minerals in the sediment-interstitial water systems.

As a result of these chain of reactions the chemical environment of the interstitial waters would be very much different from that of the overlying waters, even at shallow depths beneath the sediment-water interface. If the sediment-interstitial water systems are completely isolated from exchange with the overlying water column, the bulk composition of the systems remain constant and changes would be limited to the recombination of the species present in the solid and aqueous phases. However, in the highly porous and loose sediments of the upper layers, say one to one and half meters, diffusion of dissolved species would readily occur both within the sediment column and across the sediment-water interface. Additionally various other factors such as the activities of burrowing benthic organisms, movements of sediments by storm-generated waves and currents and disturbances of the sediment by the movements of internally generated gas bubbles by the decay of organic matter may all contribute to the transfer of materials across the sediment-water interface. The net result of these processes is that gradients in the concentrations of dissolved species are established in the interstitial water of the sediment column. Hence, in order to understand the chemistry of estuarine system it is necessary to have a knowledge of (a) the reactions occurring within the sediment reservoir which either take up materials from or release materials to the interstitial waters, and (b) the mechanisms and rates of transfer of materials across the sediment-water interface.

This investigation on the geochemistry of the interstitial waters-sediments system of the Vembanad estuary is an attempt to decipher the reactions which occur in this system so as to evaluate their diagenetic significance and to assess their effect on the overlying waters in response to transfer of material across the sediment-water interface.

Review of literature:

The first investigation on marine interstitial waters was published in 1895 by Sir John Murray, the pioneer British oceanographer, and R. Irvine. In the late 1930's several notable investigations have been published by the erstwhile Soviet workers (Bruevich et al. (1938), and Bruevich and Vinogradova (1940a and b). However, major Russian advances in pore fluid studies have taken place after world War II.

Development of piston corer by Kullenberg in the mid 1940's greatly expanded the scope of interstitial water studies. The Pore fluid - carbonate interactions have been studied by, among others, Berner (1966, 1971), Presley and Kaplan (1968), Thorstenson (1970), Berner et al., (1970), and Thorstenson and MacKenzie (1971). Equilibria between interstitial waters and silicate rock systems have been worked out by MacKenzie and Garrels (1966) and DeSegonzac (1970). Presley and coworkers have done a detailed investigation on interstitial waters (Presley et al., 1967; Presley and Kaplan, 1968 & 1970; Presley et al., 1972; Presley and Trefry, 1980). Diagenetic models incorporating carbonates, sulphate reduction and silicates reactions have been carried out by Berner (1971); Manheim and Sayles (1974). The role of pore fluids in the formation of authigenic phases such as polymetallic nodules (Lynn and Bonatti, 1965; Manheim, 1965; Calvert and Price 1972; Bender, 1971) and the iron - rich deposits on and around the East Pacific Rise which are formed possibly by hydrothermal origin (Bischoff and Sayles, 1972; Dymond et al., 1973).

Fabrications of in situ samplers (Sayles et al., 1976) and developments of instruments for recovery of interstitial waters (Manheim, 1965) have accelerated the momentum of the interstitial waters studies. A detailed account on the instruments for recovery of interstitial waters extraction techniques has been given in chapter 2 of this thesis. The concentration of phosphate and several elements have been determined in the interstitial waters of four piston cores from

the continental shelf area off the coast of southern California by Brookes et al., (1968). The diagenetic changes in interstitial waters of lake Constance of Holocene age by Muller (1969); in a reducing fjord by Nissenbaum et al., (1972); by Presley et al., (1972). Diffusion and accumulation of chloride and sodium in the lake Ontario sediments was deduced by Lerman and Weiler (1970). Siever et al., (1965) have found that under ideal conditions the composition of interstitial fluid may be a function of mineralogy and physical characteristics of mineral phases with which it is in contact. Studies on interstitial waters from recent sediments of the Black sea (Shishkina and Poznaniya, 1959) and in Atlantic Ocean (Siever et al., 1961; Friedman et al., 1968) indicate that the buried waters are geochemically different from the overlying sea water. Sharma (1970) has given a detailed account on the evolution of interstitial waters in Recent Alaskan marine sediments. Friedman and Gavish (1972) further investigated the chemical changes in interstitial waters from sediments of different environments.

Bischoff and Sayles (1972) have studied the chemistry of pore fluid and mineralogy of recent marine sediments. A comparative studies of interstitial water composition between nearshore basin and slope sediments have been carried out by Sholkovitz (1973); Sayles et al., (1973) have studied the chemistry of interstitial waters from the long core sediments obtained from Deep Sea Drilling Project. Studies on Kinetic models for the early diagenesis of N, S, P and Si from an anoxic marine sediments by Berner (1974) have received much attention. The time variability of pore water chemistry has been studied by Thorstenson and MacKenzie (1974). A general one dimensional equation for interstitial transport in accumulating and compacting sediments under non-steady state conditions is derived by Imboden (1975). Vertical concentration profiles of NO_2^- and NO_3^- in interstitial waters and sediments have been investigated by Vanderborcht and Billen (1975). Emerson (1976) has studied the early diagenesis and chemical equilibria in interstitial waters of an anaerobic lake sediments. A detailed

account on the migrational processes and chemical reactions in interstitial waters has been given by Lerman (1977). Jorgensen's (1977) study is concerned about the sulfur cycle of coastal marine sediments. Grundmanis and Murray (1977) have investigated the chemistry of interstitial waters to understand the processes of nitrification and denitrification in the sediments of Puget Sound. Interstitial nitrate profiles and oxidation of sedimentary organic matter in the Eastern Equatorial Atlantic has been investigated by Bender et al., (1977). Contreras et al., (1978) has probed the Mo concentration in the interstitial waters of an anoxic marine sediments by electron paramagnetic resonance spectroscopy. Sayles (1979) has calculated the flux rate of elements across the sea water-sediment interface of the Atlantic Ocean.

A remarkable advancement in the study of interstitial waters have been noticed in the 1980's. Works pertaining to diagenetic processes near the sediment-water interface and flux rate of elements/nutrients (Aller, 1980 a&b), the processes of CH_4 exchange at sediment-water interface (Martens and Klump, 1980), the trace metal geochemistry of interstitial waters (Lyons et al., 1980), and amino acids of interstitial waters from varied sedimentary environments (Henrich and Farrington, 1980) are of noteworthy. Diagenetic behavior by Sakata et al., (1981) flux and diagenesis of the sediment-water interface by Sayles (1981), nutrient sediment-water exchange processes by Klump and Martens (1981), interstitial water chemistry by Duff (1981) and geochemistry of coexisting Mn nodules, micro nodules; sediments and pore waters by Stoffers et al. (1981) are the major works reported in the beginning of 1980's.

Further investigations concerning the several aspects of interstitial waters such as the interaction between interstitial waters and sediments (Nembrini et al., 1982), the availability of dissolved oxygen in interstitial waters (Whitman and Clark, 1982), the pore water profiles as an indication of the upwelling of hydrothermal solutions (Maris and Bender, 1982), spatial and

temporal variations of the chemistry of interstitial waters (Watson et al., 1985a) of the Tamar estuary and later the nutrients distribution in the interstitial waters of reducing and oxic sediments (Watson, 1985b), the nutrient chemistry and hydrology of interstitial waters (Jordan and Correl, 1985), chemistry of interstitial water (Kawahata et al., 1985) are of special importance. Malcolm (1985) has demonstrated the importance of interstitial waters study to understand early diagenesis of Mo in estuarine sediments. Gaillard et al., (1986) have investigated the interstitial waters chemistry of Willerfranche bay sediments to understand the trace metal diagenesis. Malcolm et al., (1986) have investigated the organic degradation, SO_4 reduction and NH_4 production in the sediments of Loch Eil, Scotland. de Lange (1986) has illustrated the chemical composition of interstitial waters in cores from the Nares abyssal plain. Hosomi and Sudo (1987) have given the nutrient concentration in the interstitial waters of the sediments in Lake Kasumigaura. Gaillard et al., (1987) have studied the chemistries of interstitial waters and sediments chemistries of Lake Aiguebelette (Savos, France). Matsukawa et al., (1987) have calculated the benthic flux of nutrients on an intertidal flat. Camacho-ibar and Alvarez-Borrego (1988) have found the patchiness and temporal variations of nutrient concentrations in pore waters of intertidal sediments in a coastal lagoon. Duffy et al., (1988) have put forward a method for determining metal species in soil pore water. Klump and Martens (1989) have investigated the seasonality of nutrient regeneration in an organic rich coastal sediments. They have also derived a kinetic modeling of changing pore water nutrient and sulphate distribution.

In the 1990's, the important works are the effect of mangrove detrital outwelling (nutrient regeneration and oxygen fluxes) on coastal sediments (Alongi, 1990); hydrochemistry of mangrove tidal creek (Ovalle et al., 1990); chemical processes at the sediment-water interface (Santschi et al., 1990); sediment-water interaction and early diagenesis (Silverberg and

Sundby, 1990) and early diagenesis in differing depositional environment (Shaw et al., 1990). Further studies are also made on the dissolved organic manganese in interstitial water (Yagi, 1990), benthic organic carbon degradation and biogenic silica dissolution (Martin et al., 1991), and pore water Cd geochemistry (McCorkle and Klinkhammer, 1990).

de Lange (1992a) has explained the distribution and post depositional changes of various fractions of N_2 . Later he has also reviewed the problems and possible artifacts in extraction of pore water (de Lange, 1992b) in detail. Other recent works include that of the diagenetic metal profiles in recent sediments (Williams, 1992), content of pore water nutrients (Morell and Corredor, 1993) and fluorescence of dissolved organic matter (Chen and Bada, 1994). Recently Bertolin et al., (1995) have designed a new device for in situ pore water sampling.

In India, investigation on interstitial waters is the most neglected field although significant works have been done on the geochemistry of modern sediments. This negligence is mainly due to the lack of technique of extraction of interstitial waters and also due to the cumbersome procedures involved in collection of sediment samples, interstitial waters storage methods and necessity of rapid analysis of many parameters of interstitial waters. The only published literature on interstitial waters is that of Nath and Madholkar (1989) and Padmalal and Seralathan (1991).

As far as India is concerned, a number of workers have carried out geochemical studies on sediments from various environments which are as follows: cores of north eastern Arabian sea by Rao and Setty (1976); Bombay harbour sediments by Gogate et al., (1976) ; Murty et al., (1978), geochemical studies of Cauvery river basin by Subramanian et al., (1985), Cauvery delta sediments by Seralathan (1987), Seralathan and Seetharamaswamy (1987), Cambay basin sediments by Dalal and

Agarwal (1988), Gulf of Kutch sediment by Paropkari et al., (1980, 1990) and Matkar et al., (1981), heavy metal distribution in the sediments of southern east coast of India by Subramanian and Mohanachandran (1990), Mahanadi river basin by Chakrapani and Subramanian (1990), geochemistry of shelf sediments of south west coast of India by Paropkari (1990).

As far as the study area is concerned, nutrient distribution by Sankaranarayanan and Qasim (1969), Sankaranarayanan and Panampunnayil (1979), Sarala Devi et al., (1983), distribution of organic matter, phosphorus and trace metals by Murthy and Veerayya (1972a,b, 1981), various fractions of phosphorus by Ansari and Rajagopal (1974), trace metals by Paul and Pillai (1983a,b), sedimentological aspects of Vembanad estuary by Mallik and Suchindan (1984). Recent works have been taken into account in the text of this thesis.

Study area and location:

The main study area is the Vembanad estuary which is a part of the Cochin backwater system (Fig. 1). The Cochin backwater system is an extensive brackish/saline water body wherein seven rivers join. The backwaters are bound by barrier islands and have numerous interconnecting canals. This is the largest water body in Kerala and the third largest in the country. It is ecologically complex and exceptionally productive and therefore sensitive and stress vulnerable.

This backwater system is extending parallel to the coast from Alleppey in the south to Munambam in the north (Lat. $9^{\circ}28'$ - $10^{\circ}10'$ N and Long. $76^{\circ}13'$ - $76^{\circ}25'$ E). It has a length of about 113 km and the breadth varies from a few hundred meters to about 14.5 km, covering an area of about 235 sq.km. This backwater system has two openings with the Lakshadweep sea; one at Fort Cochin and the other at Munambam. Seven major rivers (Table 1) debouch in to this backwater system. On the southern side of this estuary, a barrage has been constructed near Thannirmukkam to prevent salt water intrusion especially during pre-monsoon

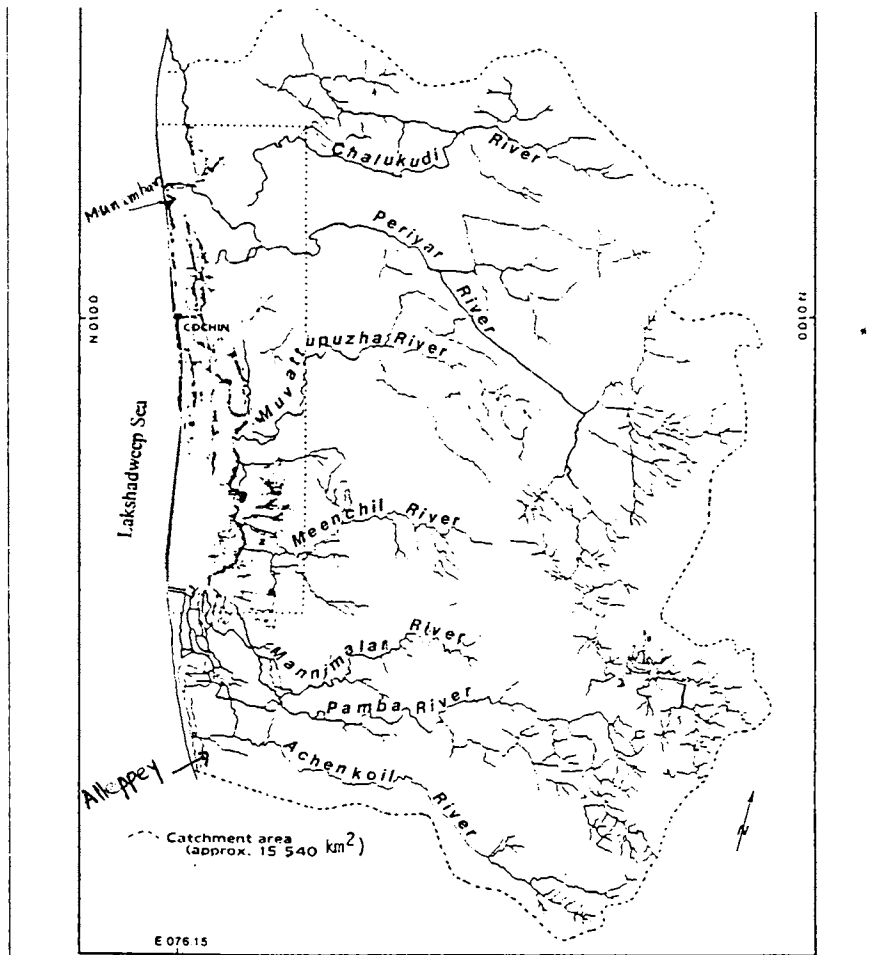


Fig.1 Vembanad Backwaters and river system

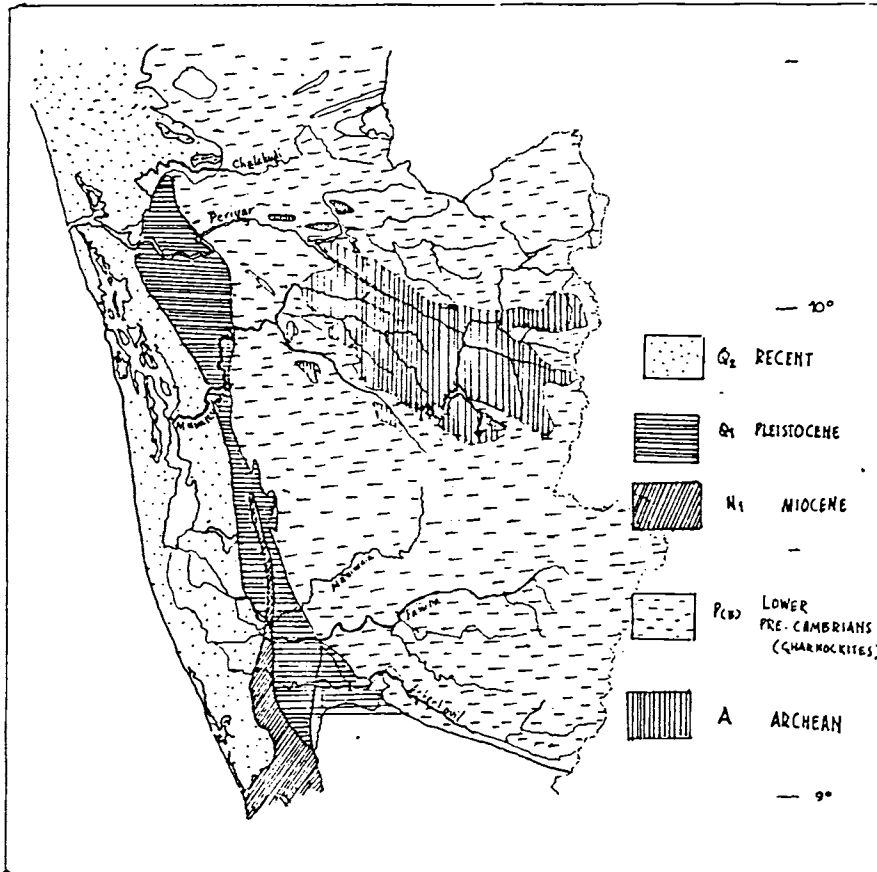


Fig.2 Geology of the study area

season.

Estuarine hydrography:

Hydrography plays an important role in sedimentation and geochemical processes of an estuarine environment. The quantum and duration of transport and settlement of particulate sediments depend directly on estuarine hydrography. The hydrography of the Vembanad estuary has been investigated by several researchers (Qasim and Reddy, 1967; Qasim et al., 1968; Josanto, 1971a; Lakshmanan et al., 1982; Sankaranarayanan et al., 1986; Anirudhan, 1988 and Joseph, 1989). In Vembanad estuary, the tides are of mixed, predominantly semi-diurnal character. The highest and lowest water levels occur at spring tides in all months (Joseph, 1989). The distribution of temperature in the estuary is a function of the input of fresh water from rivers as well as the intrusion of salt water from Lakshadweep sea. Processes like exchange of heat with atmosphere and other localized phenomena are also likely to influence the hydrographic conditions of the system. The temperature of water varies between 25 and 31°C. Seasonal variations are well reflected in water temperature in Vembanad estuary, where its temperature reaches its maximum during the dry pre-monsoon period with very weak thermal gradients indicating strong vertical mixing. The distribution of salinity depends mainly on the combined action of water movements induced by freshets and tidal actions. Variations in salinity occur vertically, horizontally and with time. Low salinity values ranging between 0 to 10 X 10⁻³ at the surface and 0 to 12 X 10⁻³ at the bottom have been observed during monsoon. These are brought about by the combined effect of land drainage from the prevailing monsoonal rains causing high fresh water discharge from the rivers and intrusion of salt water from the sea. As the season advances to post and pre-monsoon, higher salinity values ranging between 10 to 22 X 10⁻³ at the surface and from 12 to 24 X 10⁻³ at the bottom have been observed (Anirudhan, 1988). The circulation of water within an estuary is governed mainly by strong tidal oscillations on which residual water circulations

are superimposed. These residual circulations may be generated by non-linear interactions between the tidal flow and estuarine topography, density gradients, wind stress and mass input due to freshwater discharge into the estuary.

In the Vembanad estuary, the flow pattern during pre monsoon period, depends mainly on the tidal conditions as a result of reduced river discharge whereas during monsoon the flow is mainly the resultant of both the tidal influence and freshets. Thus the Vembanad estuarine hydrographical features vary annually, during July and August the estuary is that of almost salt-wedge type whereas during most of the months in post monsoon period it shows appreciable stratification while during pre monsoon the estuary shows almost well mixed nature (Joseph, 1989).

Regional Geology - General

Kerala State forms a part of the Peninsular Shield bounded by the western ghats on the east and the Lakshadweep sea on the west. The state is mainly covered by four major rock units namely (1) the Precambrian crystallines, (2) the Tertiary sedimentaries, (3) the Laterites (developed over the Pre-Cambrian crystallines and the Tertiary sedimentary rocks) and (4) the Recent to Sub-Recent sediments (Fig. 2).

1) **Pre-Cambrian crystallines:** The Pre-Cambrian crystalline rocks which include charnockites, garnet-biotite gneisses, hornblende gneisses, khondalites, leptinites, cordierite-bearing gneisses and other unclassified gneisses occupy a considerable area of Kerala. A large part of these crystalline rocks has undergone polymetamorphic and polydeformational activities. High-grade schists and gneisses of Wynad Surgurs cover some regions of the northern Kerala. The Pre-Cambrian crystallines are also traversed by several felsic (granite and pegmatite) and mafic (gabbro and dolerite) intrusions. The salient features of the major rock types of this terrain are given below with special reference to the hinterland of the Vembanad estuary.

a) **Charnockites:** Charnockites constitute the major part of the hinterland geology. They show wide variations in composition from mafic to felsic and mineralogically are characterized by the presence of hypersthene, feldspars, quartz, hornblende and garnets. Though charnockites are massive in appearance close examinations show well developed foliation or deformational banding. Apart from this patchy type of charnockite is also reported (Ravindrakumar et al., 1985).

b) **Khondalites:** A major part of Periyar and Thodupuzha river basins are occupied by Khondalite group of rocks. The group includes quartzite, calcgranulite, garnet gneiss and patchy charnockite. Age determination of these rock types indicates a range of 670 to 2200 Ma (Santhosh, 1987 and Chacko et al., 1988).

c) **Felsic intrusives:** Granites, pegmatites and quartz veins are the common felsic intrusives observed in Kerala. The granite bodies generally occur as fault/ lineament controlled plutons emplaced between 500 to 700 Ma ago (Santhosh and Drury, 1988). At several places the Pre-Cambrian crystallines are traversed by simple and complex pegmatites and quartz veins. In addition patches of syenitic intrusions are also reported from the State.

d) **Mafic intrusives:** Gabbros and dolerites constitute the most common mafic intrusives emplaced within the Pre-Cambrian crystallines. Two distinctive systems of basic dykes are recognized. They are: (1) the NNW - SSE trending leuco gabbros which are exposed intermittently for over a length of 100 Km and (2) the NW - SE trending doleritic dykes. K-Ar isotope dating has yielded an age of 81 ± 3 Ma for the former and 65-70 Ma for the latter (Radhakrishna et al., 1989).

2) **Tertiary sedimentaries:** The Tertiary sedimentary formations of Kerala unconformably overly the Pre-Cambrians (Poulose and Narayanaswamy, 1968). They extend as a narrow belt along the major part of Kerala coast and comprise of two facies of

sediments: (1) the continental facies - the Warkali beds - comprised of carbonaceous clays with lignified tissues/coal seams, china clays and friable sand stones and (2) the marine facies - the Quilon beds - composed of sandstones and carbonaceous clays with thin bands of fossiliferous limestones. These two facies depict the transgressive episodes occurred during Burdigalian (Upper part of Lower Miocene) time.

3) **Laterites:** Laterites are of Recent to Sub-Recent age and form the third major litho-unit of Kerala covering nearly 60% of the surface area of Kerala. They cap over both Pre-Cambrian crystallines and Tertiary sedimentaries. They are mainly composed of hydrated oxides of Fe and Al with minor amounts of Mn, Ti, V, and Zr. These sedimentary rocks are considered to be the primary source of black minerals in the beach sands of Kerala (Gilson, 1959).

4) **Recent to Sub-Recent sediments:** These deposits extend from Kasaragod in the north to Cape Comorin in the south. They include fringes of coast parallel sand bars, sandy flats, alluvial sands and lacustrine deposits. These geomorphic units are separated from the Tertiary sedimentaries by a polymict pebble bed. From the economic point of view this zone is the most important one due to its abundant occurrence of valuable placer mineral deposits.

Physiographic features of Kerala

Kerala is an elongated coastal state lies between the sun-drenched coast line of the Arabian sea and the mountain-rimmed craggy Western Ghats. The width of the state varies from 35 to 120 Km; with an average of about 65 Km. Even within this small width the topographical and physiographical characteristic features change distinctly.

From the low-lands adjoining the western sea-board the landscape ascends steadily towards the east to the mid-lands and further

in to the high-lands. The mountain ranges, which form a natural wall separating Kerala from neighbouring states, have an average elevation of about 1000 m from MSL with peaks rising to over 2000 m. The highest of these peaks is the Anai Mudi (2695 m) at the crest of Anamalai in Devikulam area of Idukki District.

Climate

Kerala receives moderate to very heavy rainfall for nearly nine months in a year in the form of monsoon rains and thunder showers. The hills and mountains of the Western Ghats provide an orographic lifting for the south-west monsoon winds resulting in heavy precipitation over the western slopes to good rain over mid- and low lands. The north east monsoon also contributes significantly to the annual rainfall, especially to the southern parts of the state.

The diversity of physiographical features of the State has resulted in the diversity of climate. In the mountainous regions pinching cold is experienced; lower down at elevations between 900 and 1500 m bracing cold is felt while in the coastal belt the climate is generally hot with a high degree of atmospheric humidity. The temperature in the plains ranges from 70° to 80° F. In the mountains the temperature goes to freezing point by winter nights. In the high ranges, the temperature varies from 45° to 60° F in March and April, and 30° to 60° F between November and January. The coastal area has a high percentage of humidity in the air reaching upto 90% while it progressively diminishes towards Ghats. The humidity is not, anyway, less than 70% even in the driest area.

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

- i) Winter (January - February)
- ii) Hot weather period (March - May)
- iii) Southwest monsoon (June - September)
- iv) Northeast monsoon (October - December)

The winter season is characterized by minimum cloudiness and rainfall whereas the hot weather period is uncomfortable due to high temperature and humidity. Thunderstorm activities are quite high during March to May. The southwest monsoon months constitute the principal rainy season while the northeast monsoon, which as a matter of fact the retreating phase of the southwest monsoon, becomes the secondary rainfall season. In general the weather is pleasant from September to February.

Rainfall

The total annual rainfall of the State varies widely i.e. from about 4500 mm in the northern part of Kerala to about 2000 mm in the south. The southwest monsoon, the principal rainy season of Kerala, accounts for about 73% of the total annual rainfall. Further the rainfall during southwest monsoon decreases from the northern districts (85%) to the southern districts (54%). The northeast monsoon (7 - 25%) and the hot weather pre-monsoon thunder showers during March-May (10 - 20%) respectively accounts for the rest of the rainfall.

Rivers

The Kerala State is blessed with 41 west flowing and 3 east flowing rivers, of which 7 west flowing rivers join the Vembanad lake (Fig. 1).

Table 1: List of rivers joining the Vembanad backwater system

Name	Length (km)	Catchment area (Sq.Km)	Annual yield (Mm ³)
Chalakkudi	138	1704	3,121
Periyar	244	5398	11,607
Muvattupuzha	121	1554	3814
Meenachil	78	1272	2349
Manimala	90	847	1829
Pamba	176	2235	4641
Achencoil	128	1484	2873

A brief description of the rivers are given below.

1) The Chalakudi River: The Chalakudi river is formed by the confluence of five streams, the Parambikulam, the Kuriarkutty, the Sholayar, the Karappara and the Anakkayam. All of them originate from the Anamalai Hills of the Western Ghats. The length of the river is 130 km. The total drainage area of the river is 1704 sq.km.

2) The Periyar River: The Periyar, the longest of all the rivers in Kerala and the largest in terms of flow potential, is formed by several tributary streams and having their origin in the Sivagiri group of hills at an elevation of about 1830 m above M.S.L. The length of the river from its origin to its confluence is 244 km. The drainage area of the river is 5398 sq.km.

3) The Muvattupuzha River: The Muvattupuzha river has three major tributaries called the Thodupuzha, the Kaliyar and the Kothamangalam. The length and the drainage area of the river are 121 km. and 1554 sq.km. respectively.

4) The Meenachil River: This river is formed by joining of several streams originating from the western ghats. Although the length of the river is only 78 km. the drainage area is considerably larger (1272 sq.km.).

5) The Manimala River: Rising at an altitude of 1156 m. above M.S.L. in Tatamala, the river gains shape only from Elamkadu estate. It drains an area of 847 sq.km. and the length of the river is just 90 km.

6) The Pamba River: The Pamba river is the third longest river (176 km) in Kerala. It is formed by the confluence of the Pamba Aar, the Kakki Aar, the Arudai Aar, the Kakkad Aar and Kall Aar. The drainage area of the river is 2235 sq.km.

7) The Achancoil River: Several small streams originating from the Pasikida Mettu, Ramakkul Teri and Rishi Malai at altitudes ranging between +700 m and +160 m above MSL join together to form Achencoil river. The length of the river is 128 km. The total drainage area is 1484 sq.km. .

OBJECTIVES: The objectives of this investigation are:

- i) to study the various physical parameters such as colour, water content and nomenclature of the sediments,
- ii) to study the nutrient variation in the core sediments and interstitial waters and causative forces,
- iii) to investigate the concentrations of certain major and trace elements in core sediments and interstitial waters and their mobility and
- iv) to study the diagenetic processes occurring within the sediment column and sediment water interface

CHAPTER 2

MATERIALS AND METHODS

Introduction

Although tremendous impetus have been made in the field of sediment geochemistry not much has been made in interstitial waters chemistry. Lack of scientists' attraction towards the field is due to the strenuous procedures adopted in the field and laboratory. One of the most important problems in the study of interstitial waters chemistry is the validity of sampling procedures as the sediment-interstitial waters system is a complex combination of an ion exchange matrix, the solid materials would mostly be in equilibrium condition with the interstitial fluids. If this system is indeed an equilibrium one or even if it is partly so, recovery of interstitial fluids other than in situ temperature and pressure conditions would give different results from the real situation. This was recognized by Mangelsdorf et al., (1969), Bischoff et al., (1970) and Fanning & Pilson (1971). Existence of such problems was later confirmed by Sayles et al., (1973a), Gieskes (1973,1974) and Hammond (1973).

Extraction of interstitial waters: A review

Since the early days of interstitial waters extraction by Murray and Irvine (1895), many types of extraction systems have been developed to separate interstitial waters from sediments. However, only in the last two decades has it become evident that conditions during collection, handling, and extraction of interstitial waters from the sediments should be closely controlled in order to generate accurate interstitial waters results (Mangelsdorf et al.,1969; Bischoff et al.,1970; Fanning and Pilson,1971; Bray et al.,1973; Sayles et al.,1973a,b; Gieskes,1973; Troup et al.,1974; Robbins and Gustinis,1976; Holdren et al.,1975; Loder et al.,1978; Fanning and Maynard-Hensley,1980; Masuzawa et al.,1980; De Lange,1984a; De Lange et al.,1992).

Although a number of laboratory oriented extraction methods namely leaching (Emery and Rittenberg,1952; Swarzenski,1959),

centrifugation (Powers,1957; Rittenberg et al.,1963; Edmunds and Bath,1976), squeezing (Siever, 1962; Hartmann, 1965), dilution (Murthy and Ferrel,1972), liquid displacement (Scholl,1963; Batley and Giles,1979) and vacuum filtration (Johnson,1967) have been developed in the past, squeezing techniques have been and still widely used as they are not only relatively simple and inexpensive but also they could produce reliable interstitial waters samples. In course of time several types of squeezers have been developed, some are gas operated (de Lange, 1984a, 1992), others are of hydraulic (Siever,1962; Hartmann,1965; Manheim,1966; Reeburgh,1967; Presley et al.,1967; Kalil and Goldhaber,1973; Horowitz et al.,1973; Manheim,1974; Robbins and Gustinis,1976; Shishkina and Tsvetkov,1978; Rozanov et al.,1978; Masuzawa et al.,1980; Ridout, 1981; De Lange,1984a, de Lange et al., 1992).

Compared to the above methods of interstitial waters extraction, the in-situ extraction method i.e. at site is considered to be the best possible way of recovering interstitial waters (Barnes, 1974; Sayles et al., 1976; Sayles, 1985; Masuzawa et al., 1991). Through this technique the decompressional effects which occur during raising of the sediment core from abyssal depth to the sea surface can be avoided, although they do cause a small pressure gradient during sub-sampling. However, in situ methods require long sampling times and could provide only a few samples from sub-bottom sediments upto 3 m depth of sediment. The main drawbacks of this technique are that 1) the associated solid phases can not be recovered and 2) the equipments are generally expensive and temperamental. Considering various options and constraints hydraulic squeezer (Kalil and Goldhaber,1973) have been used in the present study.

A number of factors have been reported to have an influence on the reliability of interstitial waters data. They are:

- 1) decompressional effect,
- 2) storage period and conditions prior to extraction of

- interstitial waters,
- 3) pressure exerted during squeezing,
 - 4) temperature elevation during interstitial waters extraction through squeezing and
 - 5) oxygen contamination during extraction of interstitial waters.

A brief description of the above is given below.

Decompressional effect: Large changes in pressure occur when the core is raised to the surface from the sea floor. Especially the carbonate equilibrium, which is highly sensitive to such changes, may lead to the precipitation of CaCO_3 and consequently resulting in lowering of alkalinity and Ca concentration in the remaining interstitial solution. This precipitation has been reported to depend on the presence of CaCO_3 crystallization nuclei. It is, therefore, natural to conceive that the effect of decompression is to occur mainly in carbonate-rich sediments but not in carbonate-poor sediments (Murray et al., 1980; Emerson et al., 1980, 1982; Jahnke et al., 1982; de Lange, 1986)

Storage time and conditions prior to interstitial waters extraction: Upon recovery, it is necessary to store rapidly the tightly sealed core sections at in situ temperature condition so as to prevent any changes in the interstitial waters composition due to oxygen or temperature artifacts. It is possible to store sediments at in situ temperature condition for a day without any detectable change in the concentration of dissolved elements with the possible exception of alkalinity (Masuzawa et al., 1980). However, when a core is stored for a week or more significant deviation from the original in-situ concentration of elements may occur.

Squeezing pressure: It is considered that a squeezing pressure of the order of 1 Kbar may exert a small or undetectable changes in the chemical composition of interstitial waters (Manheim and Sayles, 1974; Manheim, 1976; Gieskes et al., 1990). The normal squeezing pressure estimated for the gas based squeezer was

around 15 bar while the pressure occurred for the hydraulic squeezer and centrifugation was 100 bar. As these pressures are far below 1 Kbar no significant effect on the chemical composition of the interstitial waters are expected to occur in our samples.

Temperature of sediments during interstitial waters extraction:

If the temperature of the sediments during squeezing deviates too much from the in situ temperature condition the solid-liquid equilibrium conditions may change; causing a large differences between the extracted and the in situ concentrations for some ions. For a raise of 20° C during squeezing than the in situ temperature, the concentration variation is -20% for Sr and +60% for Si and B (Mangelsdorf et al.,1969; Bischoff et al.,1970; Fanning and Pilson,1971; Bray et al.,1973; Sayles et al.,1973a,b; Gieskes,1973;Troup et al.,1974; Robbins and Gustinis,1976; Holdren et al.,1975; Loder et al.,1978; Masuzawa et al.,1980; de Lange, 1984b).

Oxygen contamination: Oxygen artifacts during sub-sampling in laboratories have been reported to affect severely the concentration of Fe and PO_4^{3-} , especially in the interstitial waters which are rich in dissolved Fe_2 (Bray et al.,1973; Horowitz et al.,1973; Troup et al.,1974).

Realizing these problems recent workers have made efforts to obtain the interstitial waters samples at temperature as close as to that of the in situ temperature condition as possible. Pressure effects are usually ignored as they appear to be small for the major cations but they could be an important factor for alkalinity if carbonate solubility equilibria are involved. Under any circumstances the extraction of interstitial fluids should be accomplished as soon as possible after retrieval of the sediments, preferably at the in situ temperature condition. In the case of Vembanad estuarine sediments, the temperature ranges from 29° C to 31° C, this is very close to room temperature. The water depth is also less

than 15 m.

Another serious problem in the study of interstitial waters chemistry is the preservation of extracted interstitial waters. Especially some components from cores retrieved from reducing conditions are very labile. For instance, values of dissolved NH_4^+ have been found to decrease if not stored properly either at low pH or in a deep frozen state (Gieskes, 1974). Similarly, dissolved SiO_2 may be affected to some degree by biological activities upon improper storage (best storage is -20°C in polyethylene containers). Samples intended for trace metal analysis, storage at low pH is appropriate because under that condition the reduced valence states are stabilized. Storage of samples having high alkalinity is not a recommended practice as in such cases the CaCO_3 may get precipitated (Berner et al., 1970, Gieskes, 1973). Nutrient data can best be obtained from frozen samples (-20°C) and for storing purposes glass containers are preferred if the analysis is of an inorganic constituents (PO_4^{3-} and NH_4^+) and polyethylene bottles if analysed for SiO_2 .

In the case of Vembanad estuarine sediments none of the above problems have any affect on the result as 1) the depth is very shallow so decompressional effect is insignificant, 2) from all the cores interstitial waters were extracted within hours immediately after collection to avoid the artifacts due to the storage prior to the extraction, 3) the pressure used in the hydraulic squeezer is around 100 bar, 4) in situ temperature is close to the room temperature so temperature effect is negligible and 5) extraction of interstitial waters were done in nitrogen atmosphere to avert the oxygen contamination.

Field and laboratory methods

For this investigation 18 stations were fixed from the study area (Fig. 3) and samples were collected in March/April 1991. A total of 18 cores of length 75 cm each were collected. Further for a proper understanding of sediment-water exchange across the sediment-water interface, overlying water samples

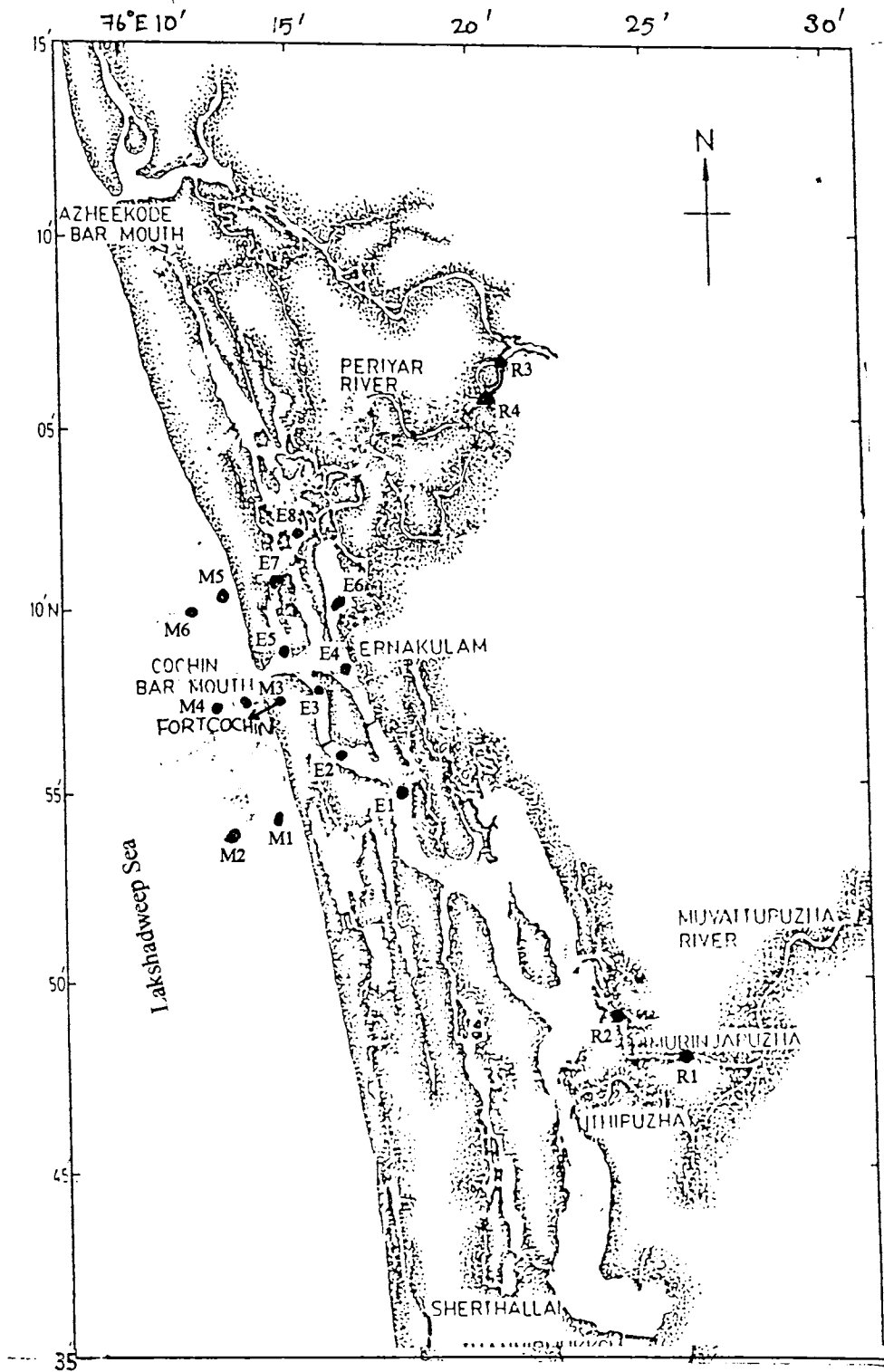


Fig.3 Sampling locations in the study area

were also collected just above the sediment water interface in all stations. Out of the 18 cores, 4 are from riverine environments, 8 from estuary and 6 from marine area. The cores were collected using a gravity Phleger corer from onboard. The PVC pipes containing the sediments were immediately sealed on either sides. The cores were kept in ice box (4° C) during transit to laboratory and extruded gently from PVC core liner in the N₂ chamber. The Eh, pH and temperature measurements of the sediments at various depths were made by gently pushing the corresponding probe in to the core. The cores were then sectioned from surface to 2 cm, 2 cm to 5 cm, 5 to 25 cm with every 5 cm interval and thereon at 10 cm interval. These sectioned sub-samples were transferred to sample retainer of the squeezer in the chamber itself. These sub samples were squeezed as rapidly as possible in a hydraulic squeezer (Kalil & Goldhaber, 1973) and the interstitial waters were collected in plastic syringes. The waters were immediately filtered through GF/C millipore filters. Interstitial water samples were then withdrawn for analyses and immediately preserved. Great care was taken in handling cores during transport, removal of supernatant water and sectioning not to disturb the near surface layers. Rapid and minimal handling of sediments during extraction could avoid detectable oxidation artifacts (Bray et al., 1973).

Analytical procedures

Overlying and interstitial waters analyses

In the laboratory salinity was determined by argentometric Mohr titration and alkalinity by titration nutrients such as NO₂, NO₃, NH₄⁺, PO₄³⁻, SO₄²⁻ and SiO₂ were measured spectrophotometrically following the techniques of Grasshoff et al., (1983) and Strickland and Parson (1977), major elements like Na and K by flame photometry, Ca and Mg by EDTA titration and Si, Al, Fe, Mn, as well as trace metals Cu, Co, Ni, Cd, Pb, Zn, Cr and Sr by atomic absorption spectrophotometry. All the analysis except the AAS analysis were made immediately after squeezing. A few drops of conc. HNO₃ were added to the interstitial water samples meant

for the trace metal analysis so as to keep them under reducing conditions until analysis. All the analyses were accomplished within few weeks.

Sediment analysis

Colour, temperature, Eh and pH of the sediment samples were measured. Water content of the sediments was determined. Organic elements (C, N, P), major elements (Si, Al, Fe, Mn, Na, K, Ca and Mg) and trace metals (Cu, Co, Ni, Cd, Pb, Zn, Cr and Sr) of the sediment samples were analyzed. For the analysis of Al and Si 'Solution A' was prepared by fusion method (Maxwell, 1968) using NaOH and for the remaining elemental analysis 'Solution B' was prepared by taking exactly 1 g of the powdered bulk sediment sample and digested with HF-HNO₃-HClO₄ acid mixture and was made to 100 ml. In addition to the above Hg content was analysed in a few cores. The analytical methods followed are outlined in Table 2. A brief description of the methods is given below.

Sediment organic carbon: The sediment organic carbon was determined by wet oxidation method of Elwakeel and Riley (1957). Organic matter was oxidized by a known quantity of chromic acid and the amount of chromic acid used was then determined by back titration with standard ferrous ammonium sulphate solution. Diphenylamine was used as an indicator. The average of triplicate measurements not differing more than 0.2% of the analyses was used for this study.

Nitrogen: The nitrogen was determined by Kjeldahl method (Barnes, 1959). The nitrogen content of sample was converted to acid ammonium sulphate by digestion with H₂SO₄ in presence of a catalyst. On making the reaction mixture alkaline, NH₄⁺ was liberated, which was removed by steam distillation and absorbed in boric acid solution containing methyle-red-methylene-blue indicator and titrated with standard HCl (0.01N HCl). Percentage of N₂ is calculated from the titre value assuming that 0.01N HCl is equivalent to 0.14 mg NH₃N.

Phosphorus: Phosphorus as phosphate ($\text{PO}_4\text{-P}$) form was determined based on the reaction of the ions with an acidified molybdate reagent to yield a phosphomolybdate complex (Murphy and Riley, 1962). It was then reduced to a highly blue coloured compound. The intensity of the colour developed is proportional to the concentration of the $\text{PO}_4\text{-P}$ in the solution. This blue coloured solution exhibits maximum absorption at 880 nm. The amount of $\text{PO}_4\text{-P}$ was determined by comparison with a set of standard samples.

Sodium and potassium: Na and K were determined using a flame photometer based on the procedure as described in APHA (1981). In order to avoid the inter elemental and anionic effects, Al and Fe were removed from solution by precipitating them with ammonia solution. The solution was then aspirated for the estimation of Na and K. Calibration curve for Na and K were drawn separately and concentrations of the metals were estimated.

Calcium and Magnesium: Ca and Mg in the sediment sample solution were determined titrimetrically with standard EDTA solution at a pH of 12 (APHA, 1981). Murexide was used as an indicator. Colour changes from pink to purple at the end point.

Si, Al, Fe, Mn and Trace metals: These elements were analyzed using an Atomic Absorption Spectrophotometer (Perkin Elmer Model 2380) following the method suggested by Rantala and Loring (1975).

Extraction technique: To investigate the distribution of elements (Fe, Mn, Cu, Co, Ni, Cd, Pb, Zn and Cr) among different constituent phases of sediments, selective chemical attacks were carried out on sediment sub-samples of a core (Core No. 5) using the leach technique (Jackson, 1958; Gupta and Chen, 1975, 1967; Tessier et al., 1979). The metal species determined were 1) Exchangeable phase, 2) carbonate bound, 3) easily reducible fraction (metals combined with Fe-Mn oxyhydroxides), 4) organic

bound including sulphides and 5) residual fraction.

Precision and accuracy: The precision and accuracy of the AAS analysis were checked against two USGS standard rock samples.

All the metal values were in agreement with the published values of Rantala and Loring (1975) and Flanagan (1976).

Mercury analysis: For Hg analysis all forms of the Hg present in the sediment should be converted first into divalent ionic form without any loss. For this purpose a Bethge's apparatus was used. The method consists of two steps viz. i) wet digestion and permanganate oxidation to convert all forms of Hg into ionic Hg, and ii) determination of Hg by cold vapour atomic absorption. Accordingly exactly 10 g of sediment sample was digested with conc. HNO_3 and H_2SO_4 in a 5:1 proportion and heated for about one and half hours in a Bethge's apparatus. Heating continued till the sample solution becomes pale yellow. Then 1.5 g of KMnO_4 and 3 ml of HCl were added boiled gently for 5 minutes, cooled, transferred into a 50 ml volumetric flask and made upto the volume. A blank was run as per the procedure. A suitable aliquot of the solution was pipetted out into the reaction vessel of the mercury analyzer and Hg content was determined.

Textural analysis: To understand the vertical grain size variations of sediment cores, textural analysis was carried out by sieving and pipette methods. A known quantity of sediments sample was dispersed overnight in 0.025 N solution of sodium hexametaphosphate. The coarse fraction was separated from the dispersed sediments by wet sieving using a 230 mesh ($63 \mu\text{m}$) ASTM sieve. The filtrate containing the silt and clay fractions was subjected to pipette analysis (Lewis, 1984) and the nomenclature of the sediments was found.

Scanning Electron Microscopic (SEM) Studies: Standard procedures as suggested by Goudie and Bull (1984) were used for SEM analysis. Subsamples containing coarse grains (from +80 mesh)

were treated successively with 10% HCl, SnCl₂ and Na₂(PO₄)₃ to remove carbonates, iron coatings, and clay particles respectively. Then the grains were washed, dried and mounted on stubs. The mounted grains were sputtercoated with gold and photomicrographs were taken using stereoscan 180° at standard magnifications ranging from 160X to 2400X. The interpretations of the photomicrographs thus obtained were made following Georgieva and Stoffers (1980) and Marshall (1987). The SEM photos and identification are carried at Physical Research Laboratory, Ahmedabad.

Table 2. List of Various analytical methods and instruments employed in the study

Parameters	Method	Instrument	Reference
1. Eh	Electrode	ISE Meter Orion No EA940	
2. pH	Electrode	pH Meter	
3. Carbon (Sediment)	Titrimetric		Elwakeel & Riley (1957)
4. Nitrogen	''	''	Barnes (1959)
5. Phosphorus	''	''	Murphy & Riley (1962)
4. Nutrients (NO ₂ , NO ₃ , NH ₄ , PO ₄ , SO ₄ , SiO ₂)	Colorimetric	Hitachi Model	Grasshoff (1983) and Strickland and Parson (1977)
5. Na & K	2000 Spectro- photometer Flame Photo-	Systronics FPM	APHA (1981)
6. Ca & Mg	Titrimetric	EDTA method	''
7. Elements (Si, Al, Fe, Mn, Cu, Co, Ni, Cd, Pb Zn, Cr and Sr)	AA Spectro- photometric	Perkin Elmer Model 2380	Rantala & Loring (1975)
8. Hg	Cold vapour AAS	Mercury Analyzer Anal. MA 5800A	Chim. Acta 84, 231 (1976)

CHAPTER 3

NUTRIENTS

Introduction

Interstitial waters play an important role in exchanging the dissolved species between sediments and water in aquatic ecosystems. Rapid exchange of dissolved species occurs across the sediment-water interface while within the sediment column, concentration gradients are established as a result of transport of dissolved species between the sediment and overlying water. Organic matter becomes the energy source for almost all transformations taking place in a sediment column though usually only a few percent of the organic matter produced in the water column is available to the microorganisms thriving in the sediments.

As a matter of fact about one-third of global primary production occurs in the oceans of which about 25% is produced in continental margins and estuaries which together constitute just less than 10% of the marine area. Together with the input of materials from the continents, the estuaries and continental margins will have a dominating influence on the biogeochemical cycling of nutrients and elements than the deep sea areas. The debouched materials from the continents first undergo severe changes during settling. The longer the residence time of an organic debris in the water mass, the more degraded it will be before reaching the bottom. Toth and Lerman (1977) have shown that the refractoriness of sediment organic matter and its rate of decomposition are a function of the sedimentation rate. After deposition, several chemical reactions (diagenesis) affect both the solid and fluid phases of sediments.

The process of ionic exchange at the sediment-water interface is governed by redox conditions which in turn are greatly influenced by microbial activities. As said earlier, the driving force for their activities is the organic matter. It should be stressed that the microbial activity is correlated

with the input of organic matter to the sediments rather than with the number of bacteria. The activities of heterotrophic organisms, which depend on the amount and refractoriness of organic matter as carbon source, are of great importance for the exchange of nutrients and metals between the overlying water and the sediment. These bacteria perform many transformations that cannot be brought about by even larger organisms or by inorganic reactions within a reasonable time-span. Denitrification and sulphate reduction are examples of such reactions. Most bacteria in sediments are anaerobic. They are affected adversely by oxygen and, therefore, try to create anoxic conditions. Significant number of viable bacteria ($>10^5$ /g sediment wet weight) can be found even at great water depths. Generally, their abundance in homogeneous sediments decreases with depth.

The organic material incorporated into a depositional environment is either degraded to soluble forms (remineralised) and released to overlying waters through the process of diffusion/sediment-water chemical exchange or it becomes a permanent component of the sedimentary deposit (Klump and Martens, 1987). In estuarine and coastal environments nutrients regeneration from benthic sediments can supply a significant fraction of the nutrient requirements of primary producers living in overlying waters (Billen, 1978; Nixon et al., 1980).

Results

In Table 3, colour and water content of sediments, nomenclature of sediment composition and percentage variations of sand, silt and clay are given. Values of salinity, Eh, ~~pH~~, alkalinity, nitrite, nitrate, ammonia, sulphate, phosphate and silicate of interstitial and overlying waters and organic carbon, total nitrogen and total phosphorus of sediments cores are given in Table 4 and plotted in Figs. 4 to 7. The relationships between different parameters are given in Figs. 8a to 8e.

Colour: The colour of sediments vary between moderate brown and

Table 3. Colour, percentages of water content, sand, silt and clay and nomenclature of core sediments

Core R1							Core R2					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	58.07	15.70	34.90	49.40	sandy clay	5YR3/4	57.32	35.40	10.60	54.00	sandy clay
2-5	5YR3/2	57.75	30.15	45.30	24.55	sandy mud	5YR3/2	57.28	27.63	22.18	50.19	sandy mud
5-10	5YR3/2	57.75	22.14	25.14	52.72	sandy clay	5YR3/2	56.11	15.50	24.70	59.80	sandy clay
10-15	5YR3/2	56.32	41.90	28.10	30.00	sandy mud	5YR3/2	56.32	30.72	22.28	47.00	sandy clay
15-20	5YR3/2	53.48	22.15	25.13	52.72	sandy clay	5YR3/2	53.48	30.15	45.30	24.55	sandy mud
20-25	5YR3/2	38.12	15.00	25.20	59.80	sandy clay	5YR3/2	44.23	28.05	24.35	47.60	sandy clay
25-35	5YR3/2	44.21	15.32	30.40	54.28	sandy mud	5YR3/2	41.61	22.14	25.14	52.72	sandy clay
35-45	5YR3/2	41.66	27.00	25.40	47.60	sandy clay	5YR3/2	38.74	30.50	36.65	32.85	sandy mud
45-55	5YR3/2	40.85	14.52	29.40	56.08	sandy mud	5YR3/2	35.99	30.00	22.30	47.70	sandy clay
55-65	5YR3/2	37.98	30.50	36.65	32.85	sandy mud	5YR3/2	34.98	20.14	27.24	52.62	sandy clay
65-75	5YR3/2	35.22	30.72	22.28	47.00	sandy clay	5YR3/2	33.68	16.00	26.20	57.80	sandy clay

Core R3							Core R4					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	59.12	34.30	26.00	39.70	sandy mud	5YR3/4	56.99	32.30	34.85	32.85	sandy mud
2-5	5YR3/2	58.33	32.30	23.20	44.50	sandy clay	5YR3/2	54.83	20.60	49.28	30.12	sandy mud
5-10	5YR3/2	58.12	27.00	25.40	47.60	sandy clay	5YR3/2	53.41	44.90	18.10	37.00	sandy mud
10-15	5YR3/2	57.66	14.32	29.40	56.28	sandy mud	5YR3/2	51.96	29.85	45.60	24.55	sandy mud
15-20	5YR3/2	55.22	29.52	23.48	47.00	sandy clay	5YR3/2	48.11	32.50	36.65	30.85	sandy mud
20-25	5YR3/2	48.91	44.30	18.60	37.10	sandy mud	5YR3/2	46.98	27.60	25.35	49.05	sandy clay
25-35	5YR3/2	42.85	50.70	21.10	28.20	muddy sand	5YR3/2	41.66	22.71	25.14	62.14	sandy clay
35-45	5YR3/2	41.87	50.20	20.30	29.50	muddy sand	5YR3/2	38.45	25.19	24.18	50.63	sandy mud
45-55	5YR3/2	39.88	8.00	30.30	61.70	mud	5YR3/2	35.45	15.80	28.90	54.30	sandy mud
55-65	5YR3/2	38.21	27.23	22.58	50.19	sandy mud	5YR3/2	33.69	15.80	25.70	58.50	sandy clay
65-75	5YR3/2	36.12	33.30	22.40	44.30	sandy clay	5YR3/2	32.85	27.19	24.18	48.63	sandy mud

Core E1							Core E2					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	60.94	7.50	29.70	62.80	Mud	5YR3/4	69.12	11.12	22.14	66.74	sandy clay
2-5	5Y3/2	57.76	7.75	28.85	63.40	Clay	5Y3/2	69.84	10.91	29.20	59.89	clay
5-10	5Y3/2	61.54	9.79	28.20	62.01	Clay	5Y3/2	68.22	4.97	22.77	72.26	clay
10-15	5Y3/2	60.79	11.23	18.52	70.25	sandy clay	5Y3/2	67.12	9.40	27.80	62.80	sandy clay
15-20	5Y3/2	59.23	8.20	29.91	61.89	Clay	5Y3/2	66.79	12.60	22.20	65.20	sandy clay
20-25	5Y3/2	57.11	7.20	28.97	63.83	Clay	5Y3/2	69.22	10.82	25.97	63.21	sandy clay
25-35	5Y3/2	56.88	6.50	30.70	62.80	Mud	5Y3/2	65.88	10.40	34.70	54.90	sandy mud
35-45	5Y3/2	58.12	6.97	20.77	72.26	Clay	5Y3/2	63.87	7.70	29.80	62.50	mud
45-55	5Y3/2	58.12	12.10	20.90	67.00	sandy clay	5Y3/2	62.45	9.40	28.91	61.68	clay
55-65	5Y3/2	56.31	8.50	28.80	62.70	Mud	5Y3/2	61.24	10.60	28.40	61.00	sandy clay
65-75	5Y3/2	56.31	7.75	28.30	63.95	Clay	5Y3/2	60.49	15.80	24.50	59.70	sandy clay

Core E3							Core E4					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	64.22	16.70	26.50	56.80	sandy clay	5YR3/4	63.12	10.45	28.55	61.00	sandy clay
2-5	5Y3/2	62.89	22.68	47.12	30.20	sandy mud	5Y3/2	60.55	9.29	28.70	62.01	clay
5-10	5Y3/2	62.34	27.18	22.19	50.63	sandy mud	5Y3/2	60.58	21.10	26.14	52.76	sandy clay
10-15	5Y3/2	60.79	13.40	30.32	56.28	sandy mud	5Y3/2	59.12	10.77	19.23	70.00	sandy clay
15-20	5Y3/2	59.23	30.50	45.55	23.95	sandy mud	5Y3/2	58.77	12.72	21.14	66.14	sandy clay
20-25	5Y3/2	59.78	30.28	22.72	47.00	sandy clay	5Y3/2	58.67	15.70	25.50	58.80	sandy clay
25-35	5Y3/2	59.33	22.71	25.14	52.15	sandy clay	5Y3/2	57.98	13.83	19.61	66.56	sandy clay
35-45	5Y3/2	58.69	16.10	24.10	59.80	sandy clay	5Y3/2	57.12	13.40	30.32	56.28	sandy mud
45-55	5Y3/2	58.44	12.00	20.90	67.10	sandy clay	5Y3/2	56.11	9.80	28.60	61.60	sandy clay
55-65	5Y3/2	58.46	15.70	24.80	59.50	sandy clay	5Y3/2	56.12	11.50	28.60	59.90	sandy clay
65-75	5Y3/2	57.11	22.71	25.10	52.19	sandy clay	5Y3/2	56.12	5.25	21.77	72.98	clay

Table 3 continue....

Core E5							Core E6					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	68.45	16.80	25.50	57.70	sandy clay	5YR3/4	71.55	10.99	21.98	67.03	sandy clay
2-5	5Y3/2	66.39	13.60	20.10	66.30	sandy clay	5Y3/2	71.22	11.01	30.00	59.99	clay
5-10	5Y3/2	64.87	10.20	26.90	62.90	sandy clay	5Y3/2	70.86	4.88	23.01	72.11	clay
10-15	5Y3/2	61.01	10.20	28.40	61.40	sandy clay	5Y3/2	70.22	9.51	28.13	62.36	sandy clay
15-20	5Y3/2	58.45	11.50	28.60	59.90	sandy clay	5Y3/2	69.44	12.12	21.90	65.98	sandy clay
20-25	5Y3/2	58.63	15.50	24.80	59.70	sandy clay	5Y3/2	68.77	11.01	28.10	62.89	sandy clay
25-35	5Y3/2	59.33	11.15	22.72	66.13	sandy clay	5Y3/2	68.46	10.88	35.00	54.12	sandy mud
35-45	5Y3/2	60.54	12.22	18.23	69.55	sandy clay	5Y3/2	67.21	8.31	29.80	61.89	mud
45-55	5Y3/2	60.89	22.68	47.20	30.12	sandy mud	5Y3/2	66.87	9.51	29.30	61.19	clay
55-65	5Y3/2	61.45	11.70	22.70	65.60	sandy clay	5Y3/2	65.33	11.22	27.89	60.89	sandy clay
65-75	5Y3/2	61.25	15.50	26.80	57.70	sandy clay	5Y3/2	64.42	16.23	24.51	59.26	sandy clay
Core E7							Core E8					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	61.43	7.89	30.12	61.99	Mud	5YR3/4	61.55	12.45	28.60	58.95	sandy clay
2-5	5Y3/2	58.46	8.12	29.31	62.57	Clay	5Y3/2	61.24	9.33	28.70	61.97	clay
5-10	5Y3/2	58.97	9.79	28.20	62.01	Clay	5Y3/2	59.22	22.45	47.12	30.43	sandy mud
10-15	5Y3/2	57.46	9.88	29.20	60.92	clay	5Y3/2	58.79	12.40	28.40	60.40	sandy clay
15-20	5Y3/2	57.22	8.20	29.91	61.89	Clay	5Y3/2	57.91	13.83	19.61	66.56	sandy clay
20-25	5Y3/2	56.82	7.20	28.97	63.83	Clay	5Y3/2	56.12	13.40	30.32	56.28	sandy mud
25-35	5Y3/2	55.86	6.50	29.70	63.80	Mud	5Y3/2	55.55	11.15	22.72	66.14	sandy clay
35-45	5Y3/2	54.73	7.21	22.45	70.34	Clay	5Y3/2	52.66	12.22	18.23	71.07	sandy clay
45-55	5Y3/2	54.69	9.40	29.00	61.60	clay	5Y3/2	51.22	23.41	47.20	30.12	sandy mud
55-65	5Y3/2	53.88	8.50	28.80	62.70	Mud	5Y3/2	49.87	12.87	29.87	57.26	sandy mud
65-75	5Y3/2	53.29	8.81	27.31	63.88	Clay	5Y3/2	49.32	11.89	29.11	59.00	sandy clay
Core M1							Core M2					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	68.45	10.30	34.70	55.00	sandy mud	5YR3/4	68.32	11.52	30.90	57.58	sandy mud
2-5	5Y3/2	68.45	9.40	26.80	63.80	clay	5Y3/2	65.87	2.40	23.40	74.20	clay
5-10	5Y3/2	67.29	6.20	30.40	63.40	clay	5Y3/2	64.30	8.50	25.25	66.25	clay
10-15	5Y3/2	68.83	5.60	28.90	65.50	clay	5Y3/2	62.85	10.60	9.40	80.00	sandy clay
15-20	5Y3/2	65.46	10.52	25.79	63.69	sandy clay	5Y3/2	61.35	6.80	28.60	64.60	clay
20-25	5Y3/2	63.45	8.50	30.10	61.40	Mud	5Y3/2	60.10	2.80	23.19	74.01	clay
25-35	5Y3/2	63.87	8.35	23.20	68.45	clay	5Y3/2	59.01	10.80	9.20	80.00	sandy clay
35-45	5Y3/2	62.73	2.40	23.20	74.40	clay	5Y3/2	58.34	2.41	18.59	79.00	clay
45-55	5Y3/2	62.57	5.90	28.80	65.30	clay	5Y3/2	57.89	7.84	26.26	65.90	clay
55-65	5Y3/2	61.89	4.10	30.30	65.60	clay	5Y3/2	57.45	8.25	25.55	66.20	clay
65-75	5Y3/2	61.55	8.90	25.30	65.80	clay	5Y3/2	56.42	3.20	17.21	79.59	clay
Core M3							Core M4					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	70.12	10.29	33.90	55.81	sandy mud	5YR3/4	70.98	12.01	29.31	58.68	sandy mud
2-5	5Y3/2	69.34	8.40	26.80	64.80	clay	5Y3/2	70.56	4.20	22.50	73.30	clay
5-10	5Y3/2	69.12	6.20	29.00	64.80	clay	5Y3/2	69.78	8.30	24.80	67.10	clay
10-15	5Y3/2	68.75	5.60	28.90	65.50	clay	5Y3/2	69.45	10.60	9.40	80.00	sandy clay
15-20	5Y3/2	67.86	11.12	25.79	63.09	sandy clay	5Y3/2	68.79	5.98	27.33	66.69	clay
20-25	5Y3/2	67.30	8.50	31.20	60.30	Mud	5Y3/2	68.50	4.21	23.19	72.60	clay
25-35	5Y3/2	66.89	8.33	23.20	68.47	clay	5Y3/2	67.89	10.80	9.20	80.00	sandy clay
35-45	5Y3/2	66.12	2.39	24.60	73.01	clay	5Y3/2	66.94	2.41	18.59	79.00	clay
45-55	5Y3/2	65.48	5.88	28.80	65.32	clay	5Y3/2	66.37	7.84	26.26	65.90	clay
55-65	5Y3/2	64.58	4.10	30.30	65.60	clay	5Y3/2	65.48	8.25	25.55	66.20	clay
65-75	5Y3/2	64.33	9.01	25.30	65.69	clay	5Y3/2	65.23	8.33	23.20	68.47	clay

Table 3 continue.....

Core M5							Core M6					
Depth	Colour	Water%	Sand	Silt	Clay	Nomenclature	Colour	Water%	Sand	Silt	Clay	Nomenclature
0-2	5YR3/4	67.10	11.12	25.10	63.78	sandy clay	5YR3/4	69.45	11.87	29.31	58.82	sandy mud
2-5	5Y3/2	66.75	8.80	24.80	66.40	clay	5Y3/2	68.69	5.10	22.50	72.40	clay
5-10	5Y3/2	66.23	7.10	23.20	69.70	clay	5Y3/2	68.12	8.80	24.60	66.60	clay
10-15	5Y3/2	65.45	5.80	27.14	67.06	clay	5Y3/2	67.78	10.60	9.40	80.00	sandy clay
15-20	5Y3/2	64.89	10.80	11.70	77.50	sandy clay	5Y3/2	67.26	6.01	26.72	67.27	clay
20-25	5Y3/2	64.12	7.90	33.20	58.90	Mud	5Y3/2	66.58	5.43	23.19	71.38	clay
25-35	5Y3/2	63.48	9.10	24.60	66.30	clay	5Y3/2	66.23	10.80	12.87	76.33	sandy clay
35-45	5Y3/2	63.14	2.33	25.80	71.87	clay	5Y3/2	65.45	2.41	18.59	79.00	clay
45-55	5Y3/2	62.87	6.10	29.40	64.50	clay	5Y3/2	64.88	7.84	26.26	65.90	clay
55-65	5Y3/2	62.45	3.89	31.60	64.51	clay	5Y3/2	64.44	8.25	25.55	66.20	clay
65-75	5Y3/2	62.14	8.20	23.60	68.20	clay	5Y3/2	64.12	8.33	24.24	67.43	clay

Olive gray. According to Goddard et al., (1970) rock colour chart, the riverine core sediments are moderately brown (5 YR 3/4) at the top 2 cm level and grayish brown (5 YR 3/2) at the bottom. The estuarine and nearshore bottom core sediments show an Olive gray colour (5 Y 3/2) while the core top thin layer shows moderately brown colour. The brown colour in the upper 2 cm and gray colour in the lower parts of the cores are due to oxidation and reduction processes of iron complexes in the sediments respectively (Lynn and Bonatti, 1965). Since the reducing condition in the river sediments are moderate the sub-bottom sediments are grayish brown.

Water content: The water content of sediments steadily decline with depth. Water content as high as 69.12% is observed at the surface of the estuarine core sediments (Core E2). In general the water content is low in riverine sediments.

Nomenclature of sediments:

As far as the sediment composition is concerned, the riverine sediments are mainly composed of sandy clay followed by sandy mud. The maximum sand content of the river sediments is 50.7%. In estuarine area sandy clay predominates while in marine, clayey sediments are the chief constituent. The maximum sand contents in estuarine and marine sediments are 30.50% and 12.01% respectively.

Salinity: The salinity of the riverine area is negligible. However, the salinity of interstitial waters of marine sediments are more or less similar to that of the overlying waters. On the other hand the salinity of estuarine interstitial waters increase with depth. The salinity range of interstitial waters in estuarine and marine regions vary from 2 to 38 ppt and 29 to 38 ppt respectively.

Alkalinity: Table 4 shows the alkalinity values for the overlying and interstitial waters. In the overlying waters of the river the value is just 4 meq/l and that of estuarine and

Table 4. Analytical results for the overlying (OV) and interstitial waters (IV) and sediments of the cores (Salinity in ‰, Eh in mV, C in ‰, N and P in mg/g and others in µM; except pH)

RI	Depth (cm)	Sal.	Eh	pH	Alk	NO2	NO3	NH4	PO4	SO4	SiO2	Sediment		
												C	N	P
OV		0.65	228	6.50	4.0	0.0	7	3	4	3	12	--	--	--
IV	0-2	0.65	93	6.50	4.1	3.0	12	20	2	4	138	4.00	5.5	1.5
	2-5	0.65	-21	6.53	4.2	3.0	12	20	2.2	6	210	3.60	5.5	1.4
	5-10	0.65	-147	6.37	4.2	3.0	10	19	54	6	297	3.88	5.5	1.4
	10-15	0.65	-140	6.43	3.1	2.5	14	36	76	6	281	2.82	5.2	1.4
	15-20	0.65	-97	6.49	3.2	3.1	13	37	97	5	284	3.41	5.3	1.2
	20-25	0.65	-175	6.51	4.2	3.2	9	49	121	6	279	3.79	5.2	1.2
	25-35	0.65	-118	6.30	4.5	2.1	9	78	142	8	270	3.38	5.0	1.1
	35-45	0.65	-170	6.30	4.2	3.1	4	96	119	6	268	3.42	5.0	1.2
	45-55	0.65	-106	6.45	5.1	1.6	4	118	148	5	264	3.42	5.1	1.2
	55-65	0.65	-100	6.45	5.6	2.1	4	127	146	6	223	3.36	5.0	0.9
	65-75	0.65	-88	6.31	6.5	2.2	4	126	173	5	197	3.21	5.1	1.1
R2														
OV		0.65	190	6.58	4.1	0.1	5	3	5	3	15	--	--	--
IV	0-2	0.65	13	6.54	4.1	0.5	11	18	3	5	142	4.00	5.5	1.5
	2-5	0.65	-79	6.50	3.1	1.5	8	15	2.2	6	210	3.60	5.8	1.2
	5-10	0.85	-116	6.55	4.2	1.0	10	20	54	5	297	3.66	5.4	1.3
	10-15	0.65	-74	6.52	3.4	1.5	9	25	75	5	280	3.50	5.4	1.3
	15-20	0.85	-63	6.40	4.1	2.0	5	25	98	6	287	3.50	5.5	1.3
	20-25	0.65	-122	6.40	4.8	1.0	5	12	121	5	275	3.80	5.3	1.3
	25-35	0.65	-100	6.48	3.9	1.5	4	38	137	6	264	3.37	5.3	1.2
	35-45	0.65	-82	6.43	4.8	1.0	5	61	112	7	265	3.47	5.2	1.1
	45-55	0.65	-64	6.50	5.4	0.8	3	78	148	5	260	3.20	5.2	0.9
	55-65	0.85	-70	6.41	5.1	0.5	2	126	145	4	218	3.20	5.2	0.9
	65-75	0.65	-98	6.44	5.2	0.0	2	105	177	4	211	3.11	5.2	0.9
R3														
OV		0.65	116	6.58	4.1	0.1	4	2	4	1	19	--	--	--
IV	0-2	0.65	33	6.55	4.1	0.2	11	19	4	2	154	4.00	5.5	1.5
	2-5	0.65	-147	6.55	4.2	3.0	10	20	54	6	297	3.68	5.5	1.4
	5-10	0.65	-140	6.43	3.1	2.5	14	35	75	6	280	2.84	5.3	1.4
	10-15	0.65	-97	6.49	3.2	3.0	12	33	99	5	285	3.47	5.3	1.2
	15-20	0.65	-122	6.50	3.5	2.0	11	46	121	5	265	3.51	5.3	1.2
	20-25	0.65	-175	6.51	4.2	2.0	11	52	127	6	275	3.62	5.3	1.2
	25-35	0.65	-118	6.52	4.8	2.5	9	87	138	8	272	3.37	5.2	0.9
	35-45	0.65	-170	6.50	4.9	3.0	5	93	116	8	265	3.47	5.2	0.9
	45-55	0.65	-106	6.49	5.1	1.5	5	126	147	5	263	3.48	5.0	1.2
	55-65	0.65	-100	6.47	5.7	2.0	3	125	151	6	225	3.31	5.0	0.8
	65-75	0.65	-88	6.50	6.1	1.8	4	131	168	3	217	3.12	5.1	0.8
R4														
OV		0.65	98	6.55	4.1	0.2	5	2	4	2	22	--	--	--
IV	0-2	0.65	11	6.50	2.2	0.2	5	12	3.5	2	188	4.00	5.5	1.5
	2-5	0.85	-79	6.50	3.1	1.5	8	15	2.2	6	210	3.60	5.8	1.2
	5-10	0.65	-118	6.54	4.2	1.0	10	20	54	5	297	3.66	5.4	1.3
	10-15	0.65	-74	6.50	3.4	1.5	9	24	76	5	280	3.51	5.3	1.3
	15-20	0.65	-63	6.47	4.2	2.0	5	24	97	6	285	3.51	5.5	1.2
	20-25	0.65	-122	6.44	4.3	1.0	5	12	121	5	275	3.64	5.3	1.2
	25-35	0.65	-100	6.40	4.1	1.5	4	38	138	5	273	3.37	5.3	1.1
	35-45	0.65	-82	6.40	4.8	1.0	4	59	112	5	265	3.41	5.2	1.1
	45-55	0.65	-64	6.49	5.4	0.8	3	83	151	5	268	3.22	5.2	1.1
	55-65	0.65	-70	6.44	5.8	0.5	2	123	147	6	225	3.19	5.2	0.9
	65-75	0.65	-98	6.44	6.6	0.6	2	121	176	4	211	3.06	5.2	0.6

Table 4 continue....

E1	Depth Cm	Sal.	Eh	pH	Alk	NO2	NO3	NH4	PO4	SO4	SiO2	Sediment		
												C	N	P
OW	28	33	7.50	3.5	1.2	8	5	2	4	21	--	--	--	
IW	0-2	8	21	7.48	4.0	3.1	20	50	2.2	16	210	3.05	4.8	2.3
	2-5	8	-212	7.38	4.0	4.0	23	55	54	16	297	3.98	4.8	2.3
	5-10	12	-201	7.38	9.0	4.0	26	61	71	15	280	2.84	4.5	2.4
	10-15	15	-189	7.33	11.0	3.5	18	77	101	12	285	3.47	4.6	2.3
	15-20	15	-211	7.35	12.0	2.8	10	99	122	12	278	3.84	4.6	2.2
	20-25	19	-213	7.31	13.0	2.0	8	121	134	11	270	3.37	4.5	2.0
	25-35	25	-218	7.30	12.0	1.6	9	189	133	9	265	3.47	4.4	1.8
	35-45	26	-213	7.27	15.0	1.5	7	227	148	8	261	3.42	4.5	1.8
	45-55	24	-217	7.21	19.0	0.9	6	288	147	9	225	3.32	4.5	1.5
	55-65	36	-218	7.21	17.0	0.5	8	302	178	9	228	3.05	4.3	1.5
	65-75	38	-218	7.21	16.0	0.5	8	397	188	9	206	3.58	4.3	1.4
E2														
OW	21	33	7.50	4.0	1.2	9	4	1	5	52	--	--	--	
IW	0-2	14	23	7.50	5.0	2.6	22	60	2.2	17	210	3.60	4.2	2.5
	2-5	14	-131	7.48	8.0	3.0	20	60	54	17	297	3.50	4.2	2.5
	5-10	16	-170	7.41	10.0	3.0	23	64	73	17	280	2.84	4.1	2.2
	10-15	19	-191	7.32	10.0	2.5	15	88	96	14	285	3.50	3.8	2.2
	15-20	23	-187	7.35	13.0	2.0	13	97	121	14	275	3.50	3.8	2.1
	20-25	23	-165	7.31	19.0	2.1	11	112	138	13	270	3.40	3.4	2.1
	25-35	25	-163	7.33	24.0	2.0	10	111	124	13	266	3.47	3.4	2.2
	35-45	25	-59	7.28	24.0	1.8	9	124	148	11	260	3.42	3.4	2.1
	45-55	31	-33	7.35	31.0	1.9	8	187	149	11	224	3.40	3.4	2.0
	55-65	38	-185	7.28	36.0	0.8	9	241	176	12	188	3.20	3.3	2.0
	65-75	36	-172	7.29	36.0	0.2	5	322	196	11	210	3.40	3.3	2.0
E3														
OW	22	96	7.55	2.0	1.5	8	4	1	5	45	--	--	--	
IW	0-2	2	21	7.54	3.0	4.6	18	45	2.2	20	210	3.80	4.9	1.8
	2-5	15	-238	7.48	5.0	5.0	20	60	54	20	288	3.68	4.9	1.8
	5-10	15	-214	7.37	10.0	5.0	15	58	77	20	280	3.70	4.5	1.6
	10-15	18	-225	7.21	10.0	2.5	10	77	91	17	285	3.50	4.4	1.6
	15-20	21	-229	7.10	13.0	2.3	5	126	121	17	277	3.70	4.2	1.6
	20-25	21	-239	7.20	13.0	2.1	3	120	138	15	270	3.60	4.2	1.5
	25-35	29	-179	7.20	15.0	1.8	1	148	126	17	265	3.40	4.1	1.5
	35-45	32	-224	7.20	15.0	1.4	2	241	151	17	264	3.40	4.1	1.4
	45-55	35	-262	7.10	17.0	0.9	3	156	143	8	225	3.20	4.1	1.5
	55-65	24	-219	7.11	17.0	0.6	1	289	167	8	214	3.10	4.1	1.5
	65-75	26	-249	7.13	18.0	0.3	1	351	198	6	233	3.10	4.1	1.5
E4														
OW	28	112	7.49	2.5	1.5	8	5	1.5	5.5	87	--	--	--	
IW	0-2	37	15	7.44	5.0	2.6	10	25	2.2	23	210	3.90	5.1	2.2
	2-5	37	-198	7.38	10.0	3.0	10	31	54	29	297	3.90	5.1	2.2
	5-10	37	-211	7.33	10.5	2.0	5	55	73	25	280	3.80	5.1	2.2
	10-15	36	-197	7.31	12.6	2.0	6	68	97	22	285	3.80	4.4	2.1
	15-20	36	-231	7.30	13.1	1.0	5	97	121	22	275	3.70	4.2	1.8
	20-25	36	-241	7.28	14.8	2.1	4	112	139	14	264	3.80	4.1	1.8
	25-35	38	-213	7.30	15.6	1.5	1	127	117	14	265	3.40	4.1	1.8
	35-45	38	-209	7.30	16.9	1.0	2	222	146	15	261	3.20	4.2	1.8
	45-55	32	-231	7.31	17.1	1.1	1	264	149	12	225	3.20	4.1	1.7
	55-65	32	-203	7.31	17.7	0.9	1	289	174	12	198	3.20	4.0	1.8
	65-75	33	-203	7.35	18.9	0.5	1	297	198	12	203	3.40	4.0	1.8

Table 4 continue....

E5	Depth Cm	Sal.	Eh	pH	Alk	NO2	NO3	NH4	PO4	SO4	SiO2	Sediment		
												C	N	P
OW		22	115	7.58	2.0	1.5	8.5	4	2.1	5	31	--	--	--
IV	0-2	14	-25	7.51	7.0	1.3	9.5	10	2.2	21	247	4.10	4.4	2.2
	2-5	14	-253	7.50	8.0	2.8	10	52	54	22	297	3.68	4.4	2.2
	5-10	13	-249	7.48	12.0	2.5	4	69	75	21	238	3.80	4.4	2.3
	10-15	13	-297	7.48	17.0	2.0	3	12	96	15	285	3.47	4.2	2.1
	15-20	17	-285	7.51	17.0	2.0	2	136	118	14	264	3.60	4.1	2.0
	20-25	17	-321	7.40	23.0	2.0	2	131	139	12	270	3.37	4.1	2.0
	25-35	16	-326	7.51	23.0	1.0	1	189	112	12	291	3.20	4.1	2.0
	35-45	15	-259	7.39	27.0	0.5	1	213	146	11	312	3.42	4.1	2.1
	45-55	15	-260	7.38	27.0	0.5	1	288	145	8	225	3.20	4.1	1.9
	55-65	13	-266	7.33	31.0	0.0	0	297	188	8	210	3.05	4.1	1.9
	65-75	18	-266	7.30	31.0	0.0	0	312	203	5	195	3.20	4.2	1.9
E6														
OW		28	115	7.55	1.8	1.5	18	6	12	4	28	--	--	--
IV	0-2	5	-23	7.51	7.0	1.0	20	8	8	22	145	3.90	3.8	1.8
	2-5	13	-225	7.52	15.0	3.0	22	10	54	22	297	3.40	3.8	1.8
	5-10	13	-219	7.46	15.0	5.0	10	20	65	23	245	2.90	3.8	1.8
	10-15	8	-262	7.44	18.0	2.0	5	88	78	21	285	3.47	3.5	1.5
	15-20	8	-238	7.20	18.0	2.0	2	116	109	18	260	3.84	3.5	1.5
	20-25	11	-234	7.30	23.0	1.0	2	128	138	20	270	3.37	3.3	1.4
	25-35	13	-240	7.21	23.0	2.0	1	148	126	14	245	3.47	3.3	1.3
	35-45	11	-250	7.25	23.0	2.5	2	196	148	14	260	3.20	3.3	1.3
	45-55	12	-234	7.11	24.0	0.5	0	238	145	10	210	3.32	3.3	1.3
	55-65	12	280	7.12	24.0	0.0	0	366	176	11	200	3.05	3.3	1.3
	65-75	10	-215	7.03	29.0	0.0	1	281	211	11	212	3.10	3.3	1.3
E7														
OW		27	180	7.39	2.0	2.0	22	8	8	2.5	22	--	--	--
IV	0-2	22	21	7.33	6.0	2.0	18	55	14	20	156	4.50	2.2	1.8
	2-5	22	-217	7.30	8.0	2.5	19	55	12	22	247	4.28	2.2	1.8
	5-10	21	-213	7.29	15.0	3.0	17	64	15	20	232	4.24	2.1	1.5
	10-15	21	-223	7.20	15.0	2.0	15	76	20	18	181	3.47	1.8	1.5
	15-20	26	-227	7.20	14.0	2.5	8	88	15	16	216	4.84	1.8	1.5
	20-25	26	-230	7.21	19.0	2.0	8	85	21	15	215	3.37	1.8	1.5
	25-35	28	-280	7.21	21.0	2.0	2	121	26	12	215	3.47	1.8	1.2
	35-45	25	-280	7.20	25.0	0.0	2	148	35	11	234	3.42	1.8	1.2
	45-55	25	-280	7.10	26.0	0.0	4	176	48	12	234	3.32	1.8	1.2
	55-65	24	-289	7.11	29.0	0.0	2	198	58	11	227	3.05	1.8	1.2
	65-75	24	-287	7.11	22.0	0.0	2	176	62	12	212	3.58	1.8	1.3
E8														
OW		24	120	7.40	2.5	2.0	23	8	8	2.5	13	--	--	--
IV	0-2	21	-11	7.43	4.0	3.2	21	40	10	15	147	4.50	4.8	2.5
	2-5	21	-180	7.44	8.0	3.5	24	15	12	16	240	4.00	4.8	2.5
	5-10	28	-231	7.38	11.1	3.2	18	64	12	16	232	3.24	4.8	2.5
	10-15	28	-231	7.10	12.8	3.2	8	71	15	12	187	3.50	4.7	2.1
	15-20	31	-217	7.20	12.9	1.8	9	88	16	10	216	3.84	4.7	2.1
	20-25	31	-217	7.20	18.7	1.8	10	96	20	10	224	3.37	4.8	2.3
	25-35	32	-260	7.20	23.8	1.0	5	112	27	8	320	3.47	4.7	2.3
	35-45	31	-280	7.20	24.6	0.9	5	156	33	9	234	3.42	4.7	2.5
	45-55	36	-273	7.19	31.2	0.0	4	178	41	8	280	3.32	4.7	2.3
	55-65	36	-287	7.18	36.7	2.0	0	211	45	6	227	3.05	4.6	2.3
	65-75	35	-289	7.18	36.2	1.0	4	188	43	7	240	3.82	4.6	2.1

Table 4 continue....

M1	Depth cm	Sal.	Eh	pH	Alk	NO2	NO3	NH4	PO4	SO4	SiO2	Sediment		
												C	N	P
OW		35	180	7.60	4.5	1.2	18	4	4	1.5	12	--	--	--
IV	0-2	34	31	7.30	8.0	4.1	12	11	3.5	12	65	4.60	1.4	2.5
	2-5	35	-131	7.39	28.1	6.2	13	12	54	18	120	3.69	1.4	2.5
	5-10	35	-180	7.35	32.4	6.1	20	18	76	14	281	3.53	1.2	2.2
	10-15	35	-180	7.33	35.6	6.0	15	54	89	19	285	3.51	1.2	2.2
	15-20	38	-170	7.31	33.9	5.8	5	76	112	13	175	3.84	1.9	2.1
	20-25	34	-171	6.98	34.6	3.4	5	77	139	8	271	3.32	1.2	2.1
	25-35	36	-187	7.18	32.5	3.0	4	82	122	8	195	3.20	1.1	2.2
	35-45	36	-190	7.16	32.6	2.6	5	98	148	6	262	3.21	1.1	2.2
	45-55	33	-217	7.15	35.9	2.5	5	121	151	3	221	3.20	1.0	2.1
	55-65	37	-217	7.12	35.8	2.1	5	126	169	3	198	3.01	1.0	2.2
	65-75	32	-217	7.12	36.2	2.0	1	133	211	0	188	3.13	1.0	2.1
M2														
OW		34	165	7.60	4.5	1.2	12	4	2.5	1.5	8	--	--	--
IV	0-2	32	29	7.48	12.1	2.1	13	10	2.2	12	54	4.10	1.8	1.4
	2-5	35	-131	7.44	18.6	8.6	18	12	35	14	85	3.66	1.8	1.4
	5-10	34	-180	7.41	31.9	7.2	18	11	78	13	130	2.81	1.8	1.4
	10-15	35	-179	7.39	32.6	6.1	16	15	82	11	283	3.99	1.5	1.2
	15-20	34	-170	7.31	36.6	4.8	10	22	112	11	244	4.10	1.5	1.1
	20-25	34	-171	7.30	36.8	4.1	8	36	128	10	269	3.87	1.5	1.1
	25-35	36	-188	7.30	36.9	3.9	7	88	11	8	268	3.50	1.6	1.1
	35-45	33	-190	7.30	37.9	2.1	4	89	139	3	266	3.42	1.6	1.2
	45-55	33	-217	7.26	38.5	0.9	4	121	147	4	215	3.22	1.5	1.2
	55-65	37	-221	7.21	41.6	1.0	2	119	163	4	211	3.05	1.5	1.1
	65-75	29	-217	7.20	36.2	0.8	2	127	198	0	218	3.11	1.5	1.1
M3														
OW		34	88	7.40	4.5	0.8	8	8	3.1	2.1	13	--	--	--
IV	0-2	35	-21	7.33	29.1	10.2	19	21	2.2	19	210	4.50	4.5	2.5
	2-5	34	-131	7.33	31.6	9.1	20	12	54	19	297	4.21	4.4	2.5
	5-10	35	-180	7.29	32.3	9.1	20	38	75	20	280	4.21	4.4	2.2
	10-15	35	-180	7.30	33.1	6.8	12	34	96	17	285	3.47	4.1	2.1
	15-20	32	-170	7.31	34.2	5.9	10	88	121	20	275	3.84	4.1	1.8
	20-25	34	-171	7.29	38.2	2.1	5	92	143	11	270	3.37	4.1	1.8
	25-35	36	-187	7.25	33.2	2.1	5	112	112	10	265	3.28	4.1	1.8
	35-45	38	-190	7.19	36.1	1.5	5	123	148	3	263	3.21	4.1	2.1
	45-55	33	-217	7.22	36.0	1.1	2	128	145	3	227	3.20	4.1	2.1
	55-65	37	-217	7.21	38.1	0.0	5	137	168	3	203	3.19	4.1	1.8
	65-75	31	-217	7.19	34.9	0.0	2	148	198	2	201	3.14	4.1	1.6
M4														
OW		34	96	7.50	5.0	1.1	18	6.5	2.5	1.8	12	--	--	--
IV	0-2	35	-11	7.38	33.1	5.1	22	31	2.2	21	210	3.50	3.9	2.5
	2-5	33	-131	7.33	34.8	6.2	20	33	54	21	297	3.68	3.9	2.5
	5-10	35	-180	7.33	36.9	9.0	25	35	77	23	280	3.90	3.9	2.3
	10-15	33	-180	7.32	33.5	6.8	12	56	96	20	285	3.47	3.5	2.3
	15-20	32	-170	7.31	36.4	2.8	12	82	127	14	275	3.84	3.6	2.2
	20-25	34	-171	7.30	38.8	2.4	8	88	138	13	273	3.46	3.6	2.2
	25-35	35	-187	7.30	33.1	4.3	8	101	112	14	286	3.45	3.6	2.0
	35-45	35	-190	7.30	36.4	1.8	2	123	148	8	260	3.22	3.5	2.0
	45-55	32	-217	7.28	44.9	2.1	5	153	145	0	224	3.22	3.5	2.0
	55-65	37	-217	7.26	43.2	2.0	2	148	176	6	211	3.15	3.5	2.1
	65-75	33	-217	7.22	48.3	1.6	2	151	197	6	211	3.12	3.5	2.0

Table 4 continue....

H5	Depth cm	Sal.	Eh	pH	Alk	NO2	NO3	NH4	PO4	SO4	SiO2	Sediment		
												C	N	P
OV	34	88	7.40	4.5	0.8	8	8	3.1	2.1	18	--	--	--	
IV 0-2	33	-38	7.38	28.6	8.0	21	52	31	12	290	4.10	3.5	1.8	
2-5	35	-131	7.33	34.6	10.0	21	55	44	12	290	3.80	3.8	1.9	
5-10	35	-250	7.30	36.9	8.0	13	63	56	13	287	3.64	3.5	1.9	
10-15	33	-180	7.30	34.4	8.0	13	72	88	10	214	3.50	3.4	2.1	
15-20	35	-250	7.31	38.5	3.0	11	88	91	8	214	3.20	3.4	1.8	
20-25	34	-171	7.29	41.2	3.0	7	99	112	8	233	3.37	3.5	1.8	
25-35	37	-289	7.28	43.3	3.0	7	121	123	7	214	3.37	3.4	1.8	
35-45	35	-290	7.25	30.0	0.0	0	148	145	6	216	3.33	3.2	1.8	
45-55	37	-217	7.20	45.2	0.0	3	167	167	5	288	3.21	3.1	1.7	
55-65	37	-217	7.22	33.0	0.0	0	192	188	5	244	3.20	3.2	1.7	
65-75	36	-217	7.22	44.2	0.0	0	183	192	5	246	3.18	3.2	1.7	
H6														
OV	34	123	7.50	4.4	1.1	13	6	4	1.8	22	--	--	--	
IV 0-2	34	-25	7.31	28.1	12.6	23	41	22	10	287	3.90	3.5	2.1	
2-5	35	-131	7.31	33.6	12.1	23	55	46	11	287	3.90	3.5	2.1	
5-10	32	-251	7.30	36.8	9.1	23	63	88	11	115	3.64	3.5	2.1	
10-15	33	-180	7.30	34.6	6.3	16	74	97	10	216	3.50	3.3	1.8	
15-20	35	-258	7.31	39.8	6.3	13	88	112	10	215	3.44	3.3	1.8	
20-25	31	-171	7.29	42.2	6.0	12	89	143	8	228	3.37	3.4	1.8	
25-35	37	-298	7.22	33.8	6.1	13	121	143	5	220	3.30	3.4	1.9	
35-45	31	-290	7.21	34.5	6.2	6	156	168	6	197	3.30	3.5	1.7	
45-55	37	-217	7.20	45.0	6.1	6	171	169	5	212	3.32	3.5	1.7	
55-65	31	-230	7.20	44.2	2.0	5	189	188	4	214	3.05	3.1	1.6	
65-75	36	-217	7.18	46.1	0.0	0	188	191	5	217	3.30	2.8	1.5	

marine vary from 1.8 to 5 meq/l. Alkalinity values of interstitial waters increase with increasing depth. The values vary from 3 to 15 meq/l in the first 5 cm of the estuarine cores while in marine cores the variation is from 8 to 35 meq/l. In riverine sediments the interstitial waters alkalinity is uniformly low throughout the core (<6.5 meq/l).

Eh: The Eh values in the overlying waters of riverine are highly positive (+98 to +228 mV) while those of estuarine (+33 to +180 mV) and marine (+88 to +180 mV) are less positive. The Eh in sediment cores (Table 4) shows a general similarity at all stations, values increase with depth. In the riverine core only top layers (0-2 cm) show positive Eh values ranging from +11 to +93 mV. However, in estuarine and marine cores negative values are recorded even in the top layers. The range of values in the top 2 cm of these environments are +31 to -38 mV.

pH: The pH values of overlying waters of the river are uniformly about 6.5 at all stations whereas that of estuarine and marine waters range between 7.39 and 7.60. The pH values of sediment cores from estuarine and marine regions range consistently between 6.98 and 7.60 in accordance with the prediction of Ben-Yaakov (1973) for anoxic sediments. But in the riverine cores, the pH values show a narrow range around 6.5. In general the pH decreases with depth in all the cores of riverine, estuarine and marine environments.

Sediment organic carbon: The organic carbon content of the sediment cores shows a more or less similar pattern and range. The content in the top sediment cores ranges from 3.05% to 4.6% and the values decrease slightly with depth. The lowest organic carbon value of the sediment is 2.84% (river, estuary, marine region) and the highest is 4.84% (estuary).

Sediment nitrogen: The N₂ concentrations in the sediment cores are depicted in the Fig 7 a & b. The N₂ content of the sediment cores from the river ranges from 5 to 5.8 mg/g. A slightly lower

value has been recorded in estuarine (1.8 to 5.1 mg/g) and marine sediments (1 to 4.5 mg/g). Similar values have been reported by earlier workers from this area (Sankaranarayanan and Panampunnayil, 1979; Remani et al., 1981). The content of N_2 decreases with depth in all cores irrespective of the environment.

Sediment Phosphorus: Total P content in surficial sediments of the river is about 1.5 mg/g while in estuary it ranges from 1.8 to 2.5 mg/g and in marine sediments from 1.4 to 2.5 mg/g. The river sediments exhibit lowest concentration. In all the cores the P content decrease with depth. Setty and Rao (1972) have reported phosphorus decrease with depth in sediment cores from the shelf off Bombay.

NO_2^- , NO_3^- , NH_4^+ :

In the overlying waters the NO_2^- contents of the study area show a small range from 0 to 2 μM . Lowest NO_2^- is recorded in the river area. The NO_3^- content in overlying waters vary widely; from 4 to 7 μM in river, from 8 to 23 μM in estuary and in marine area from 8 to 18 μM . NH_4^+ in overlying waters ranges from 2 to 3 μM in river, 4 to 8 μM in estuary and 4 to 8 μM in marine area.

In the interstitial waters, high NO_2^- is observed in the upper 15/20 cm of the sediment column whereas NO_3^- concentration is restricted to the upper 10/15 cm only. In both the cases the concentrations decrease with increasing depth but steeply in the case of NO_3^- . In some cores both NO_2^- and NO_3^- first increase and then decrease. The maximum concentration of NO_2^- in river, estuary and marine area are 3.2, 9, 12.6 μM respectively. Generally NO_2^- levels are very low below 20 cm depth. Similarly the NO_3^- levels in the interstitial waters are also uniformly low below 25 cm. The NH_4^+ profiles show that low concentrations are observed only at upper 10 - 20 cm of the core but the concentrations increase rapidly with depth beyond 20/25 cm and attain a maximum of 131 μM in river, 394 in estuary and 192 μM in marine area

respectively.

SO_4^{2-} : In the overlying water SO_4^{2-} ^{of river} ranges from 1 - 3 μM while in estuary a higher range is observed (2.5 - 5.5 μM). The values in marine environment is almost similar to that of river (1.5 - 2.1 μM). The SO_4^{2-} concentrations in interstitial waters fluctuate in the upper 10 to 15 cm of the core. Below this level the concentrations systematically decrease with depth. In the river sediments the range of SO_4^{2-} is 2-8 μM , while a wider range is recorded in estuarine (5-29 μM) and marine region (0-23 μM) respectively.

PO_4^{3-} : The PO_4^{3-} concentration in the overlying waters ranges widely from 4 to 5 μM in river, 1 to 12 μM in estuary and 2.5 to 4 μM in marine environment respectively. Similar variation of PO_4^{3-} have been reported from the study area by earlier workers (Joseph, 1974; Manikoth and Salih, 1974; Anirudhan, 1988; Sarala Devi et al., 1991). The interstitial PO_4^{3-} concentrations within the top 5 cm of the cores range similarly from 2-54 μM in riverine, estuarine and marine area. It is also observed that the concentration steadily increases down the cores.

SiO_2 : The SiO_2 content in the overlying waters of river ranges between 12 and 22 μM while the values are between 13 and 87 μM in estuarine and from 8 - 22 μM in marine waters. Highest values are measured in the estuary. The SiO_2 content of the interstitial waters differs considerably from the overlying waters (Table 4). The interstitial SiO_2 contents rapidly increase from surface to 20 cm depth but further down the concentrations variation are small. The respective ranges of SiO_2 in sediments of river, estuary and marine area are from 138 to 297 μM , 145 to 320 μM and 54 to 297 μM . Increase of interstitial SiO_2 with depth have been recorded by earlier workers (Wakefield, 1982; Gieskes, 1983; Nath and Mudholkar, 1989).

DISCUSSION:

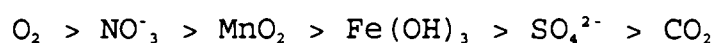
Sediment Characteristics: Textural study reveals that four size classes namely mud, sandy mud, muddy sand and sandy clay are the textural pattern observed in the riverine sediments (Table 3). Of these, sandy clay predominates whereas mud is sparingly noted. Most of the sediments are composed chiefly of silt and clay. Only a few samples show sand content as high as around 50%. On the other hand the estuarine sediments are chiefly composed of sandy clay. Sandy mud and sandy clay occur more or less equally. In the nearshore marine sediments clay dominates over the others. This clearly shows that fine sediments gradually increases from river to marine area. While studying the sediment and organic carbon distribution in the Cochin harbour area, Seralathan et al., (1993) have stated that within the last two decades the supply of coarse clastics in the estuarine region is considerably reduced after the commissioning of several bunds and dams. Further, because of increased organic input in association with fine clastics, reducing condition prevails. Therefore, the colour of the bottom sediment exhibits uniformly olive gray. The water content of the sediments gradually decrease with depth due to compaction. However, below 40 cm depth the gradation of water contents is less.

Salinity: A major variation is observed with regard to salinity between the three environments. The negligible salinity in the riverine cores clearly establishes the dominance of fresh water conditions. The marine interstitial waters are distinctly enriched in salinity. Also, the salinity of the estuarine interstitial waters at depth is almost equal to that of overlying waters (Table 3). The higher interstitial salinity at the bottom portion of estuarine cores may have resulted in part from salt wedging phenomenon and in part from the cyclic gravitational convection of more saline (denser) solution down the sediment column. On the other hand the lower salinity values at the top and middle of cores are due to the dilution effects caused by fresh water flow.

Eh: The importance of Eh for the chemical and biological processes in marine sediments has been discussed by Becking et al., 1960; Whitefield (1969) and others. The overlying waters of riverine area show highly positive Eh values than those of estuarine and marine areas which show less positive Eh (Table 4). This shows the consumption of the oxygen by biota and bacteria at and above the substratum in the latter environments. Rapid decaying and deposition of salvinia under the influence of salinity cause the rapid depletion of dissolved oxygen in the estuarine area (Gopalan et al., 1987). Ponnampetund (1972) has stated that oxygen content will disappear from the water/sediments at about +250 mV. As the observed highest Eh in water is only 228 mV (Table 4) prevalence of a slightly anoxic condition just above the sediment-water interface is possible. Further the observed oxygen content of the overlying waters (4 - 4.5 mg/l in surface and 3 - 4.2 mg/l in bottom) as well as earlier reports (Nair, 1992; Jayasree and Nair, 1995), confirms the existence of slightly anoxic condition just above sediment-water interface.

Many of the post depositional changes are determined by the redox potential of the sediment. In this study only the surface layers (2 cm) of the riverine and some estuarine and marine cores show positive Eh values. Cores E5, E6, E8, M3, M4, M5 and M6 exhibit negative Eh even at the surficial level (Table 4). But below 2 cm depth all cores show invariably high -ve Eh values. The estuarine and marine core sediments show Eh values consistently around -200 mV and reach a maximum of 326 mV. The decrease of Eh profiles is somewhat sharp in estuarine cores. The decrease of Eh indicates the prevalence of a moderate to strong reducing condition at or below the sediment-water interface. A reduction of Eh values in interstitial waters reflects bacterial removal of oxygen just below the sediment-water interface. Existence of reducing condition in bottom and interstitial waters is a common trend in brackish and marine environments (Friedman and Gavish, 1970). However, as observed earlier (Nissenbaum et al., 1972) the Eh of the interstitial

water is also controlled by dissolved sulphide. As SO_4^{2-} decreases, so does Eh in almost all cores. Berner (1963) has observed a direct relationship between Eh and concentration of dissolved sulphide. Therefore, the sharp decrease of the redox potential from the sediment - water interface to the bottom of the core is caused primarily by oxidation of organic matter (Bonatti et al., 1971) consuming oxygen first and then reduction of SO_4^{2-} and NO_3^- . According to Watson et al., (1985) biogenic decomposition of sedimentary organic matter proceeds by the reduction of available oxidants in an orderly sequence depending upon their relative energy yields as



The above sequence is accompanied by decrease in redox potential (Eh) which may be summarized by the following ranges of values

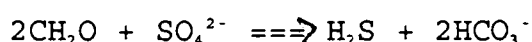
+300 - +500mV	aerobic oxidation; redox couple of oxygen, nitrate/nitrite and manganese;
+200 - +300mV	denitrification;
0 - 200mV	Fe (III) to Fe (II) reduction;
< +50mV	sulphate reduction

When sulphate reduction is completed methane is formed by reduction of CO_2 and fermentation reactions. Therefore, the very low Eh at the bottom sediment layers is a combined effect of oxygen consumption by microbes and reduction of oxihydroxides of Mn and Fe, NO_3^- and SO_4^{2-} .

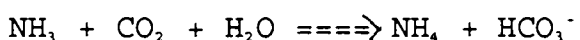
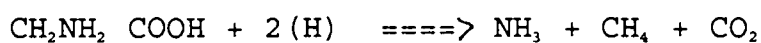
pH: The pH values of overlying waters of the river are around 6.5 whereas the estuarine and marine waters show a narrow range between 7.39 and 7.60 (Table 4). The pH values of sediment cores from estuarine and marine regions fall consistently within the range of 7 - 8 in accordance with the prediction of Ben-Yaakov (1973) for anoxic sediments. But in cores from the riverine area, the pH value is around 6.5. In this study the pH decreases with depth in all the cores of riverine, estuarine and marine environments. According to Presley (1969) the most important causes attributed for the lowering of pH with depth

are the sulphate reduction and other biological processes. Decrease of pH values with depth have also been noted by Brooks et al., (1968) off the coast of California. Siever et al., (1965) have attributed that the decrease in pH with depth is as a result of decrease in CO₂-pressure caused by the decay of organic matter.

Alkalinity: In general, interstitial waters will have high alkalinity values than overlying waters because of higher levels of carbonate. Further, where high rate of sedimentation occurs particularly in many nearshore environments not only large increase in interstitial waters have been observed (Berner et al., 1970; Sholkovitz, 1973; Goldhaber, 1974) but also in alkalinity (Manheim and Sayles, 1974; Gieskes, 1975). The increase is caused by the bacterial SO₄²⁻ reduction process. As SO₄²⁻ profiles show a steep decline with depth the alkalinity profiles increase (Table 4 and Figs. 8b). Presley and Trefry (1980) have stated that nearly 80 - 90% of interstitial water alkalinity is caused by a progressive depletion of SO₄²⁻ with depth; while remaining 10 - 20% is due to NH₃ build up at depth. A simplified carbonate production during SO₄²⁻ is given below (Berner et al., 1970).



The alkalinity increase caused by the liberation of NH₃ and its subsequent hydrolysis of basic nitrogen compounds can be expressed by the following reaction



The sharp increase of NH₄⁺ profiles below 10 cm and more particularly below 35 cm (Figs 5a-b) clearly shows that the high alkalinity values at the bottom layers of the core are a direct effect of NH₄⁺ build up. In accordance with high SO₄²⁻ and NH₄⁺ in estuarine and marine sediments the alkalinity values show a manifold increase in these environment. The strong correlation of alkalinity with NH₄⁺ and SO₄²⁻ is shown in Figs. 8a & b.

According to Sholkovitz (1973) in addition to SO₄²⁻ reduction

and NH_4^+ , interstitial water Ca and Mg contents would also play a significant roll in the concentration of alkalinity in interstitial waters. Presley and Trefry (1980) have not observed any depletion of Ca and Mg in interstitial waters and so their role in alkalinity variation is negligible. As in this study, both Ca and Mg content of interstitial waters decrease significantly (Table 5) the alkalinity increase at the bottom of the sediment layers could also be caused by the precipitation of CaCO_3 and Mg - Ca precipitation (Sholkovitz, 1973). However, he stressed that CaCO_3 precipitation is more important in affecting alkalinity values than Mg - Ca precipitation, because about 0.5 - 1% of sedimentary carbonates should be of authigenic. The alkalinity increase due to phosphate production (Sholkovitz, 1973) is shown in Fig. 8b. Further, the correlation between alkalinity and NO_3^- and alkalinity with SO_4^{2-} are given in Figs. 8a & b respectively.

Sediment organic carbon: The organic carbon content of the sediments show more or less high values and a decreasing trend with depth (Table 4). Recent studies on the chemistry of interstitial waters have shown that the extent of diagenetic processes and the related geochemistry are very much dependent on the organic carbon content of the sediments (de Lange, 1984a). Therefore, major differences can be expected in the composition of the interstitial water of the estuarine sediments as these sediments, in general, have a much higher organic content. .

In Vembanad estuary, as in the present case, high organic carbon content has been reported by earlier authors (Murty and Veerayya, 1972; Padmalal, 1992; Seralathan et al., 1993; Padmalal and Seralathan, 1995). Several earlier workers have further noted a characteristic decrease in organic carbon content with depth of the sediments (Setty and Rao, 1972). The high organic carbon content of this study area is due to the cumulative effects of fine grain sizes (Padmalal and Seralathan, 1995), waste disposal from urban sewage, terrestrial runoff,

coconut husk retting, and decayed Salvinia (a fresh water macrophyse). Similar observations have been made earlier by Seralathan et al., (1993). They have also stated that the organic carbon content of the estuary steadily increases over the past two decades due to increased deposition of fine sediments. Further, the high primary production contributes significantly to the enrichment of organic carbon in this region (Nair, et al., 1975).

In addition, phytoplanktons contribute significantly to the enrichment of organic matter of this area (Devassy and Bhattathiri, 1979). Qasim (1979) has estimated the gross primary production of the Cochin backwaters which ranges between 0.35 to 1.5 g C/M²/day. The hourly primary production reported was 245 mg C/M³/h (Pillai et al., 1975). Also a high chlorophyll value (2.4 mg/m³ to 21 mg/m³) has been observed by Joseph and Pillai (1975).

The low organic carbon content of the sediments at depth is caused by the degradation of organic matter by bacteria. In Vembanad estuarine sediments the maximum heterotrophic bacterial population has been estimated to be 79.19×10^5 (Rosamma Philip, 1987) which comprises of *Vibrio*, *Pseudomonas*, *Aeromonas*, *Acinetobacter*, *Moraxella*, *Flavobacterium*, *Micrococcus* and *Bacillus*. Like organic carbon, the total phosphorus and total nitrogen contents of the sediments also show a characteristic exponential decrease with depth in the sediment column (Figs. 7a & b). On the other hand all the byproducts of organic matter remineralisation such as NH_4^+ , PO_4^{3-} and titration alkalinity show an exponential increase in concentration with depth in interstitial waters (Figs. 4 - 6). This clearly indicates the degradation of organic carbon at depths causing an anoxic condition within the study region. Klump and Martens (1987) have observed that nearly 80% of mineralization of labile organic matter occurs within 8 months of deposition.

The microbiological transformation of organic matter in an

anoxic sediments can be represented by the following generalized formula:



This reaction gives rise to HCO_3^- and other byproducts which would affect the chemical interactions at the sediment-water interface. Moreover, it would also have an impact on the exchange and turnover processes of S, N and P.

When the bacterial oxidation of organic matter quickly consumes dissolved oxygen or the oxygen values fall to near zero, then nitrate is being used as the preferential terminal acceptor for oxidation of organic matter (Stumm and Morgan, 1970). As and when the interstitial NO_3^- has been completely utilized SO_4^{2-} reduction becomes the next dominant microbiological process. All the results are clearly in accordance with the above observation.

Sediment nitrogen: N concentrations in sediment cores are depicted in Figs. 7a & b. The total N content in sediments ranges narrowly between 5 and 5.8 mg/g from riverine area, from 1.8 to 5.1 mg/g in estuarine and from 1.0 to 4.5 in marine area. Concentration of N decreases with depth irrespective of environments. In some cores the N content maintain a steady level in the lower layers (Table 4)

The depth distribution of N in the cores illustrates some of the processes taking place in the sediments. The N, which is contained in the sediments in the form of amino acids ($RCH-NH_2-COOH$) and organic constituents, on decomposition mainly by bacterial action gives rise to NH_4^+ . This NH_4^+ then can be oxidized to NO_3^- particularly in the upper oxidized zone of sediments (Rittenberg et al., 1955); giving rise to high NO_3^- but low NH_4^+ (Table 4 and Figs. 5). The gradual progress of these reactions can explain the decrease of N, but increase of NH_4^+ with depth in all core sediments of this study area (Table 4). In course of the reactions N is transferred from the sediment to the interstitial solution. The NO_3^- formed in the upper layer

Depth (cm)

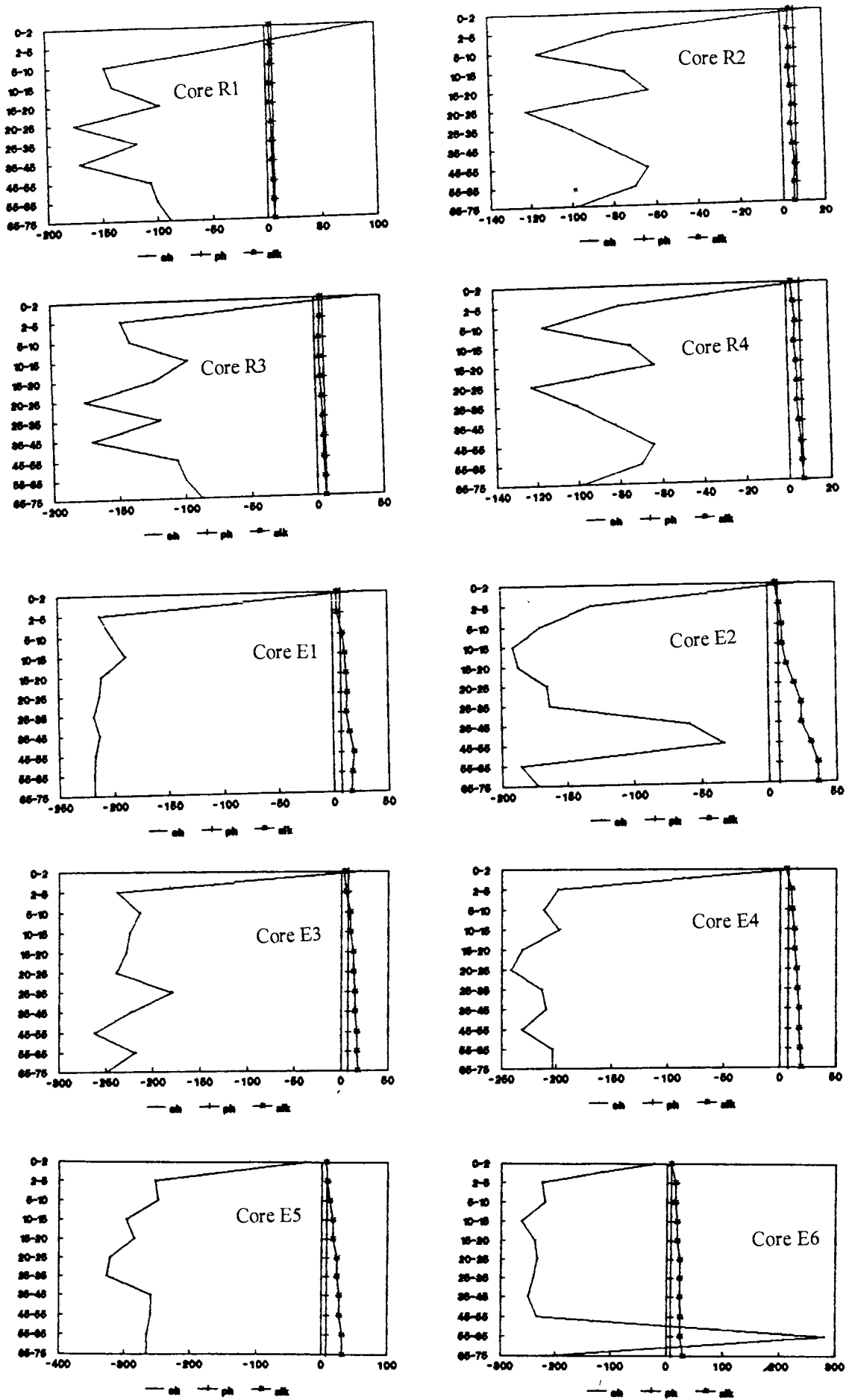


Fig.4(a) Vertical variations of Eh, pH and alkalinity in interstitial waters (Eh in mV, alkalinity in meq/l)

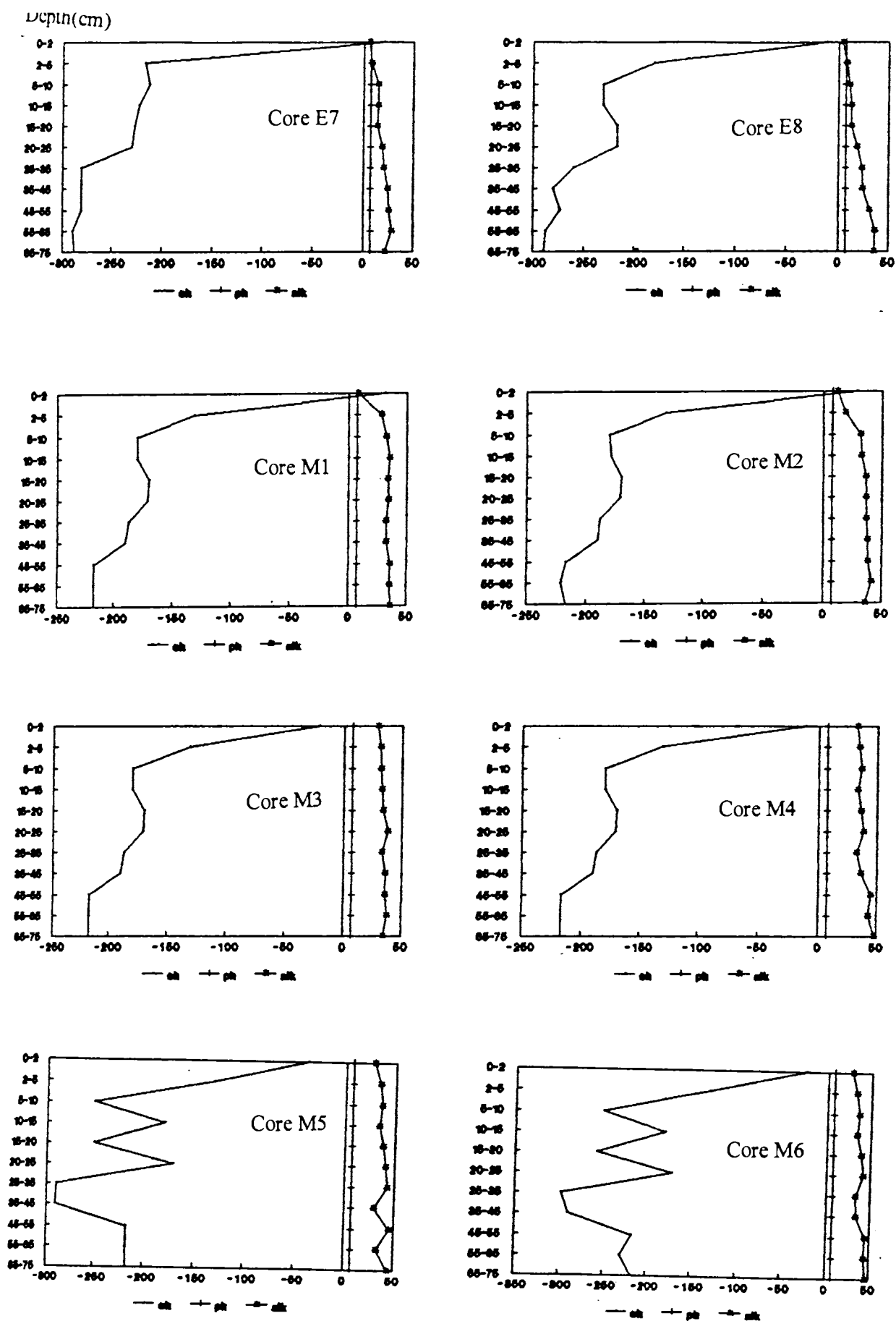
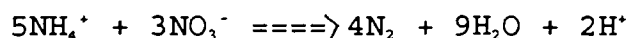
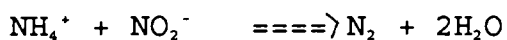
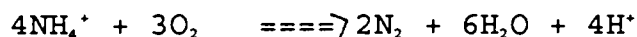


Fig.4(b) Vertical variations of Eh, pH and alkalinity in interstitial waters
(Eh in mV, alkalinity in meq/l)

could be converted to molecular N_2 in the lower part of highly reduced zone of the core, according to process described by Rittenberg et al., (1955); loss of N_2 from the sediment to the overlying water may result from such process (Bonatti et al., 1971). Denitrification is the only identified biochemical process which releases free N_2 . From a thermodynamic point view, the following reactions could occur (Bender et al., 1977).



However, no organisms capable of catalyzing these reactions have ever been reported. Yoshida and Alexander (1970) have found that nitrifying bacteria are capable of producing N_2O from NH_3 .

According to Barnes et al., (1975) excess N_2 estimated from the N_2/Ar ratio in interstitial waters of Santa Barbara basin sediments exceeded what was expected from denitrification of interstitial NO_3^- . They suggested that N_2 is formed from NH_3 via intermediates or as products of nitrification.

NO_2^- , NO_3^- and NH_4^+ : The distributions of NO_2^- and NO_3^- in interstitial waters are controlled by several factors such as their concentrations in the overlying waters, their diffusivities in the sediments and lastly by bacterial nitrification and denitrification activities in the sediments. Model calculations by Vanderborght and Billen, (1975) Vanderborght et al., (1977) and Billen (1978) postulate that the process of nitrification and denitrification take place in two separate layers respectively, an upper oxic and a lower anoxic layer.

The NO_3^- source in these sediments must be biochemical in nature since NO_3^- is not present in any mineral phases. According to Painter (1970), autotrophic nitrification is the major biochemical source of NO_3^- , involving oxidation of NH_4^+ to NO_2^- by Nitrosomonas and further oxidation to NO_3^- by Nitrobacter. Other

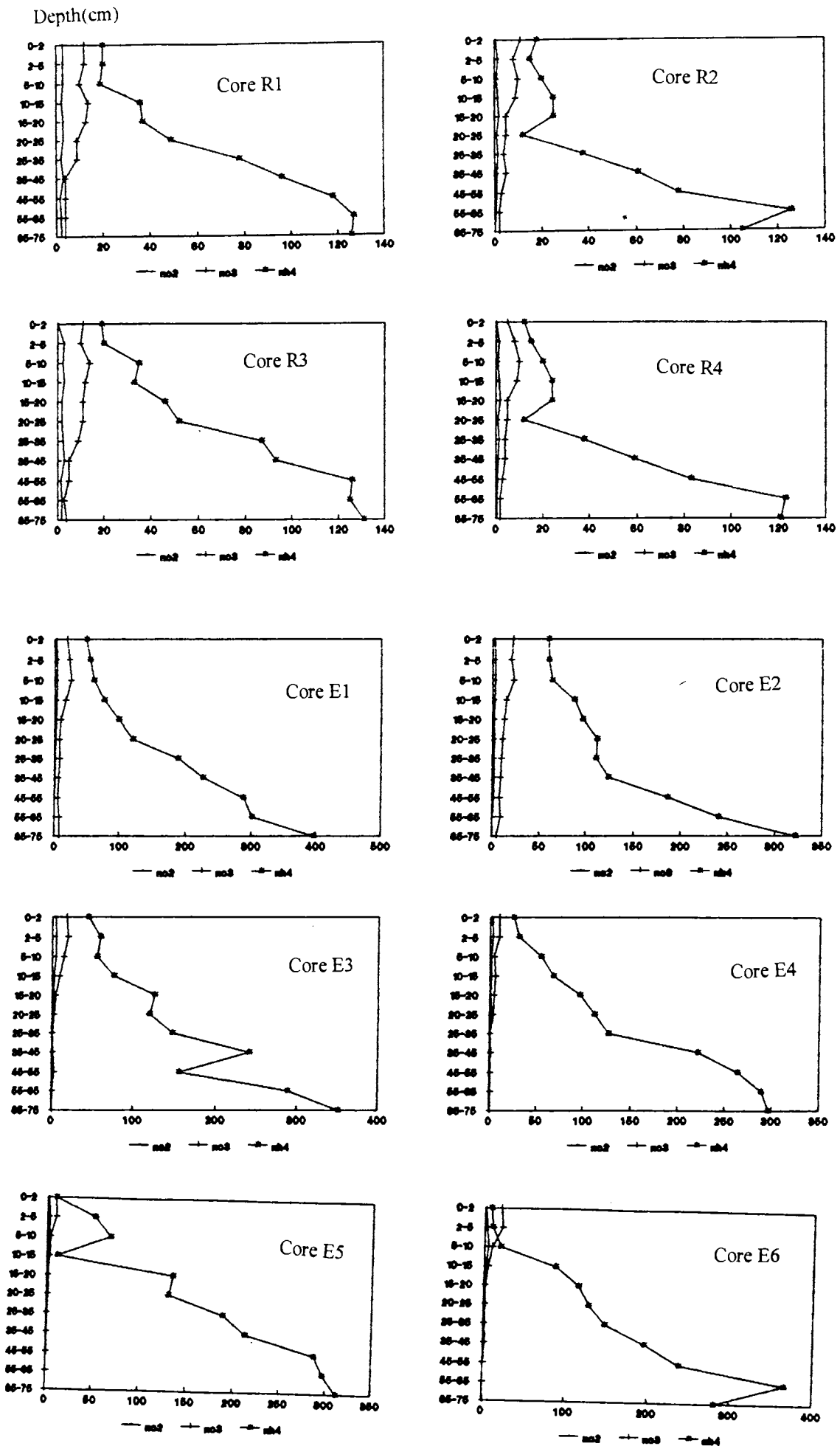


Fig.5(a) Vertical variations of NO_2^- , NO_3^- and NH_4^+ in interstitial waters (μM)

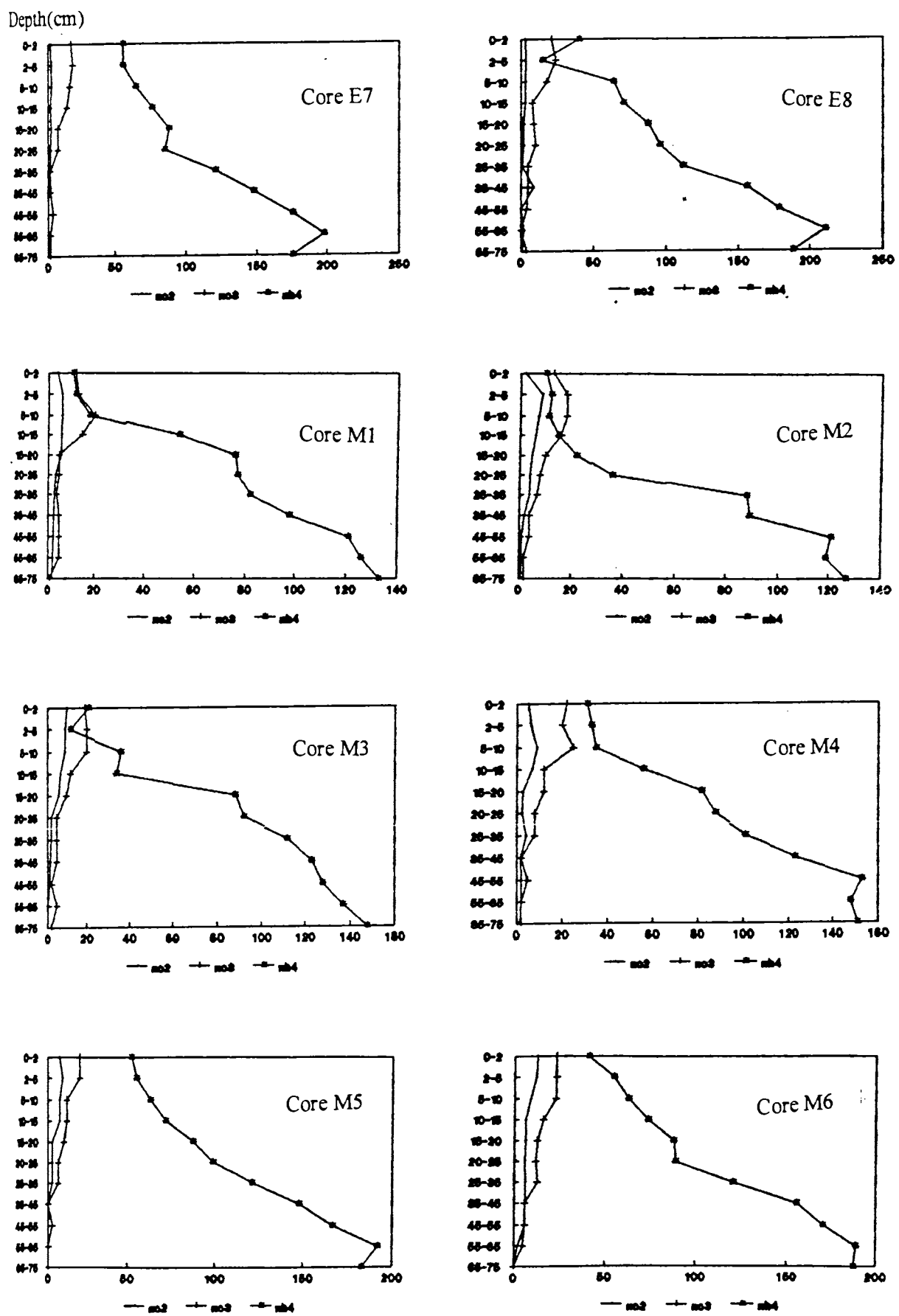
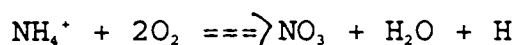


Fig.5(b) Vertical variations of NO_2^- , NO_3^- and NH_4^+ in interstitial waters (μM)

genera of nitrifying bacteria have also been reported but the above two are quantitatively the most important.

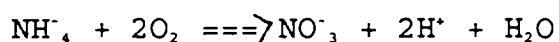
The results (Figs. 5a & b) show that significant enrichment of NO_2^- in interstitial waters is recorded only at the top 10 cm level and this indicates the oxidation of NH_4^+ and or reduction of NO_3^- (Suess et al., 1980; Jahnke et al., 1982). The sharp decline of NO_3^- values and the uniformly very low NH_4^+ profiles at surficial levels attest the occurrence of the above processes. On the other hand the uniformly low interstitial NO_2^- and NO_3^- at least below 20 cm level and the steady decline of NO_2^- , and NO_3^- with depth are due to biochemical consumption of N. This clearly indicates that in this anoxic/reducing subsurface layers NO_3^- has been used for the degradation of organic matter as an alternative to O_2 (Stumm and Morgan, 1970). Denitrification in low O_2 areas has been identified as a major sink for fixed N_2 (Cline and Richards, 1972).

The initial increase in interstitial NO_3^- just below the top layers of the sediment cores (Nos. R3, R4, E1, E2, E3, E6, E8, M1, M2, M3 and M4) clearly suggests oxygen respiration accompanied by nitrification. But in none of the cores the nitrification process goes beyond 10 - 15 cm from surface. Further, from the data (Table 4) it is clear that within the top 10 -15 cm layer both nitrification and denitrification processes simultaneously occur (eg. Core No. R1, R2, R3, E2 and M4). Grundmanis and Murray (1977) have observed a similar profile in Puget Sound. van der Bourght and Billen's (1975) work indicates that nitrification occurs in sandy sediments. Bioturbation and irrigation can supply the required oxygen to the sediments which can oxidize NH_4^+ (Goldhaber et al., 1977). Koike & Hattori (1978) have demonstrated the co-occurrence of nitrification and nitrate reduction in a coastal sandy sediment using ^{15}N isotope dilution technique. A possible occurrence of denitrification in oxic sediments of the eastern Atlantic has also been discussed by Wilson (1978). Thus, the increased NO_3^- at the surface level might also be due to the oxidation of NH_4^+ to NO_3^- as expressed below:



Therefore, NH_4^+ concentration at that level is uniformly very low where nitrification occurs (Grundmanis and Murray, 1977). The antipathetic relationship between NO_3^- and NH_4^+ is shown in Fig. 8c. In some cores (eg. E4, E5, M5 and M6) the interstitial NO_3^- concentration decreases right from the surface layers to depth which indicates denitrification due to anoxic condition. Therefore, in this area denitrification must be the dominant microbial process at the upper subsurface levels or at least below 15 cm level. Under normal steady state diagenetic conditions, denitrification should produce an exponentially decreasing NO_3^- profile (Vanderborght and Billen, 1975).

As discussed above the consistent NH_4^+ minimum in the upper sedimentary layer is mainly caused by the chemical removal of NH_4^+ by oxidation to NO_2^- and NO_3^- . The reaction can be written as follows



For the above reaction, molecular oxygen is required for nitrification however, below a oxygen concentration level of $5\mu\text{g-atoms/l}$ nitrifying bacteria apparently cannot oxidize NH_4^+ (Painter, 1970). Therefore, the oxygen concentration must be much greater than the above level in the interstitial water. On the other hand the required oxygen concentration for denitrification is just $<2\mu\text{g atom/l}$ (Cline and Richards, 1972). Since the available oxygen content in this area is very low only the reduction of NH_4^+ to NO_2^- and NO_3^- are possible.

SO_4^- : The concentration of SO_4^- decreases with depth at all stations. In some cores (eg. M1, M2 and M4) the SO_4^- values approach zero at depth. This suggests that SO_4^- reduction may be in terminal stage of organic matter decomposition in this zone. The higher SO_4^- in interstitial waters in all cores and in particular the esturine area attests the intensity of sulphate reduction. The higher SO_4^- concentration in interstitial waters

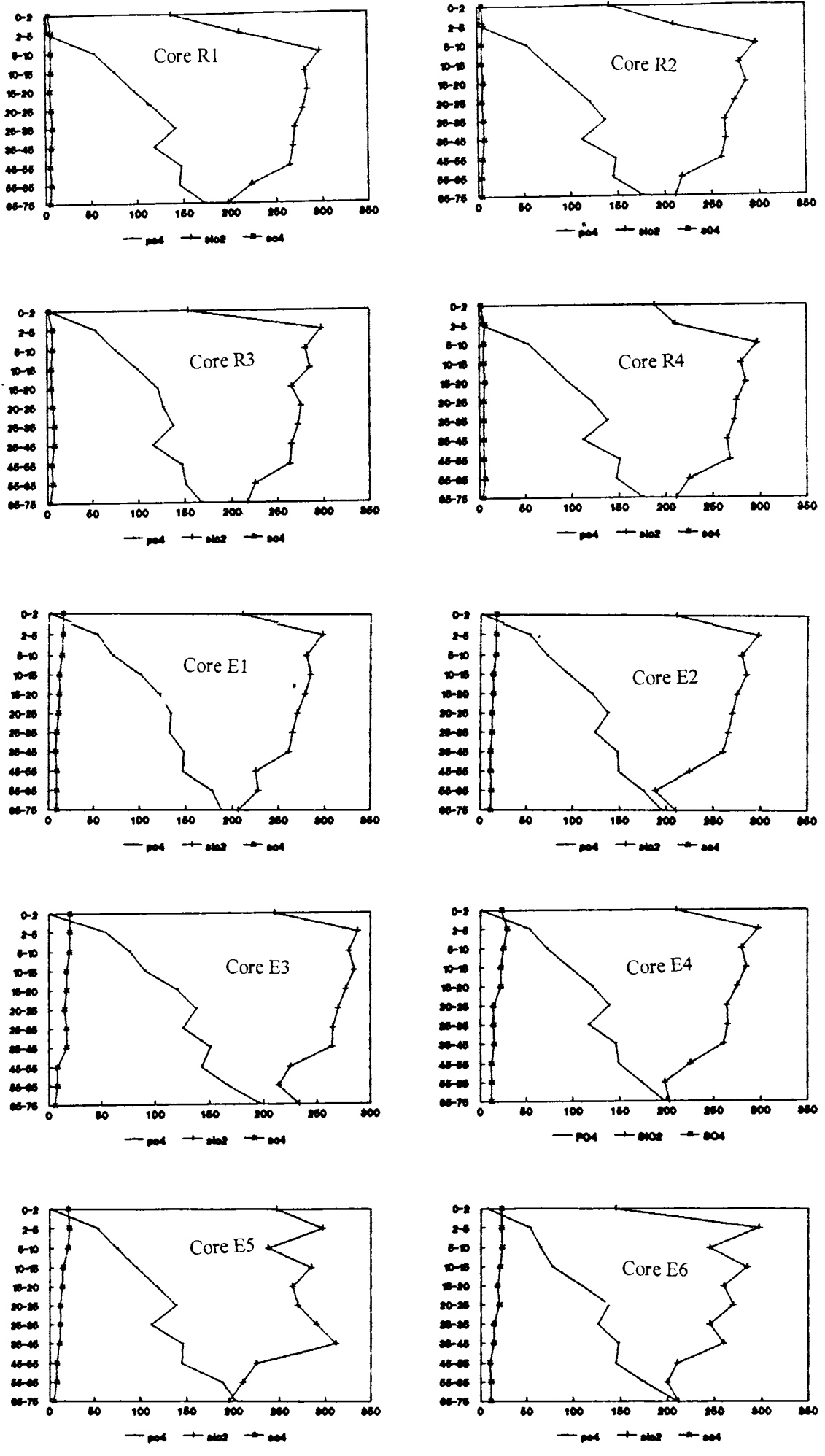


Fig.6(a) Vertical variations of SO_4^{2-} , PO_4^{3-} and SiO_2 in interstitial waters (μM)

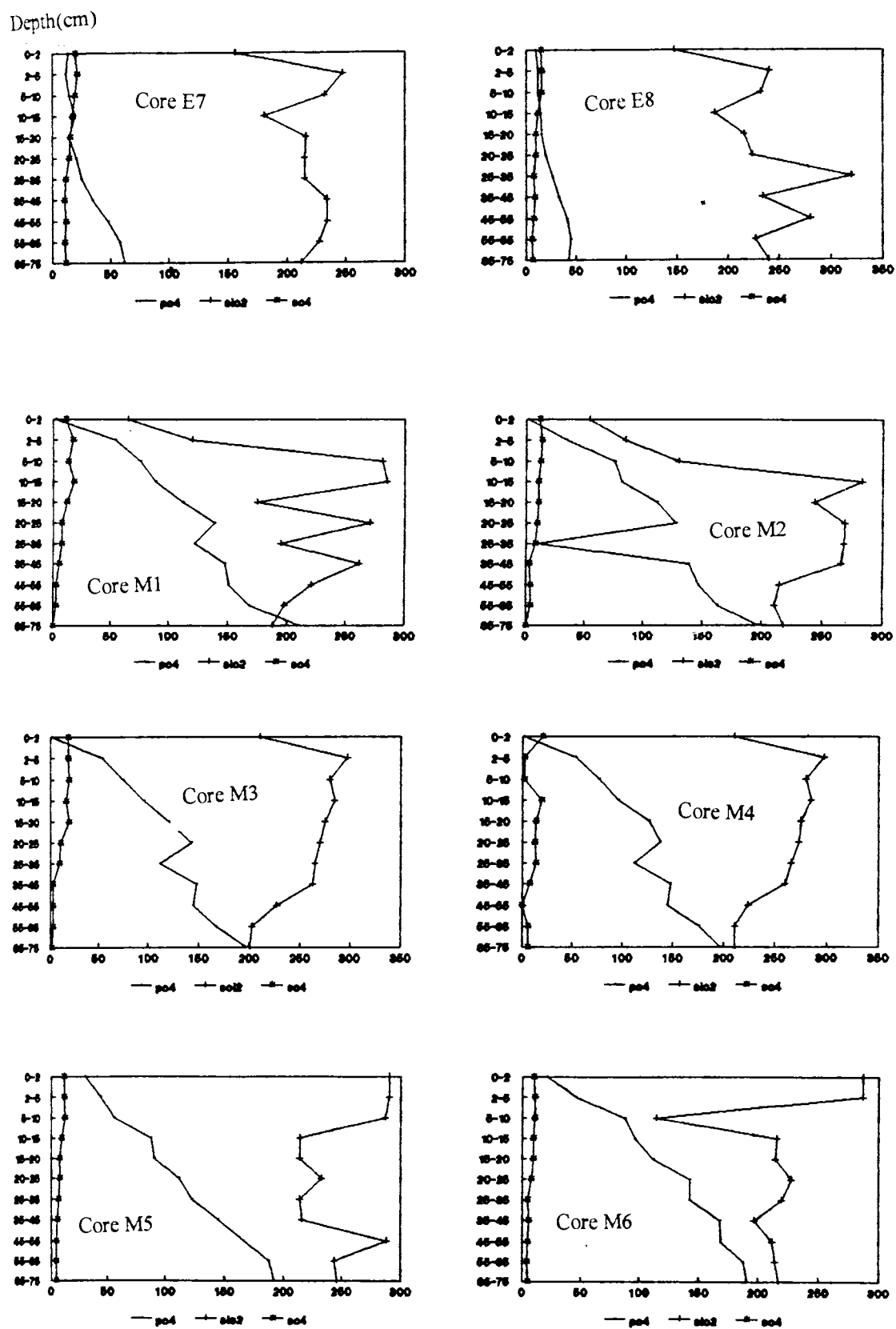


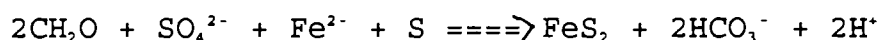
Fig.6(b) Vertical variations of SO_4^{2-} , PO_4^{3-} and SiO_2 in interstitial waters (μM)

just below the sediment surface (core No. R3, R4, E7, M1 and M2) indicates that the reduced SO_4^{2-} is again oxidized and or that sulphate is being diffused into the sediment column at least to a depths of about 15 cm. Bioturbation and bioirrigation by the small polychaetes present in the upper 15 cm of the sediment column is the most likely mechanisms which could account for this transport (Malcolm, 1986).

Titration alkalinity, a measure of the intensity of the major mineralization product, increases with depth at all stations consistent with the overall mineralization of organic matter by the sulphate reduction process.

The depletion of SO_4^{2-} in the interstitial waters is the result of bacterial reduction of sulphide during oxidation of organic matter. This type of reaction was first noted in a pore waters study by Murray and Irvine (1895). The SO_4^{2-} depletion with depth has been reported and discussed by a number of authors (Shishkina, 1966; Berner et al., 1970; Bischoff and Ku, 1971; Nissenbaum et al., 1972 and Hartmann et al., 1973; Geiskes, 1975; Jorgenson, 1977). Jorgenson (1977) has stated that SO_4^{2-} reduction accounted for 53% of the total mineralization of organic matter in the sediments.

Further, the formation of iron sulphides by reduction of pore water SO_4^{2-} has long been recognized as the major by-product of decomposition of sediment organic matter by sulfate - reducing bacteria of genus Desulfovibrio in fine grained near shore sediments (Berner, 1964 and 1980; Goldhaber and Kaplan, 1974). As the bacteria responsible for sulfate reduction requires anoxic condition, the above reduction process can readily occur in the study area. The bacterial sulfate reduction can be expressed as



where the CH_2O represents the composition of organic matter.

Where high sedimentation occur, as in the case of Vembanad

estuary, oxygen renewal by advection is greatly restricted and therefore, decomposition of organic matter will be retarded. In such environment of large deposition and anoxic conditions sulphate reducing bacteria will begin to multiply (Presley and Trefry, 1980) and thereby large depletions in interstitial SO_4^{2-} .

Sediment P: Total P content in the core sediments from river ranges from 0.8 to 1.5 mg/g, that of estuarine from 1.2 to 2.5 mg/g and that of marine from 1.1 to 2.5 mg/g (Table 4). Similar concentrations have been reported by various workers from the study area (Qasim and Sankaranarayanan, 1972; Murty and Veerayya, 1972 and Sankaranarayanan and Panampunnayil, 1979). Padmalal and Seralathan (1991) have observed a slight lower values during monsoon season; however, P is mainly associated with silt and clay fractions (Padmalal and Seralathan, 1995). In all the cores the P content decreases with depth.

The sediment P in the study area are mainly associated with organic matter (Padmalal and Seralathan, 1991). Here, both sediment organic carbon and P decrease with depth thus showing a good relationship. While working on Vembanad lake sediments Murty and Veerayya (1972, 1981) have also stated that organic matter is the prime source of sediment P. Padmalal and Seralathan (1991) have stated that river supply, urban sewage pollution and precipitation of ferric phosphate complexes are the main reasons for an enhanced P concentration in the surficial sediments of Vembanad lake. In addition, increased productivity (Nair et al., 1975) and upwelling (Purushan and Rao, 1974) enhance the P content in marine sediments. Phosphate may also have been concentrated through the complexes of iron and calcium.

The decreasing sediment P content with depth is attributed to mineralization, dissolution and diffusion of P in anoxic condition as discussed in interstitial PO_4^{3-} section.

PO_4^{3-} : The PO_4^{3-} concentration in the overlying waters of the

river ranges between 4 and 5 μM while in estuarine and marine waters the respective ranges are from 1 and 12 μM and from 2.5 to 4 μM . Similar concentration of PO_4^{3-} have been reported from the study area by earlier workers (Joseph, 1974; Manikoth and salih, 1974; Anirudhan, 1988; Sarala Devi, 1991). The interstitial PO_4^{3-} concentration in the top 10 to 15 cm of the cores from riverine, estuarine and marine environments ranges similarly and steadily increases downwards except a few values at 10 cm level. The observed high sediment PO_4^{3-} content in the study area may be due to the entrapment of the river derived phosphorus through assimilation and subsequent deposition by the profuse growth of organic life particularly phytoplankton.

In the published diagenetic models for marine interstitial PO_4^{3-} (eg. Froelich et al., 1979), a regular increase of the PO_4^{3-} concentration with depth is assumed. Similar increasing trends in interstitial PO_4^{3-} with depths have been observed earlier by Setty and Rao (1972); Sholkovitz (1973); Presley and Trefry (1980); Jahnke et al., (1982); de Lange (1984) and Nagender Nath and Mudholkar (1989).

The sharp increasing PO_4^{3-} concentration in interstitial waters with the depth (Fig.6a-b) can be explained due to the release of PO_4^{3-} during mineralization of organic matter and dissolution of phosphorus bearing solid phases in the existing reducing condition. The scatter plot PO_4^{3-} versus SO_4^{2-} (Fig. 8e) clearly shows the above process. Sholkovitz (1973) has stated that under reducing conditions iron oxide coatings absorbed on clay minerals and/or iron hydroxy interlayers are removed to form iron sulfides. Froelich et al., (1979) have observed large increase in pore water phosphate; attributing it to the release of phosphate during mobilization of iron bearing oxyhydroxide coatings. Release of PO_4^{3-} adsorbed onto $\text{Fe}(\text{OH})_2$ following reduction by H_2S (Krom and Berner, 1988) is also possible. The PO_4^{3-} is also involved in the cycle of Fe transformations (Belzile, 1988; Bouchard, 1983) when high level of ferrous iron are present PO_4^{3-} solubility may be controlled by the formation

of authigenic minerals such as vivianite: $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Berner, 1980).

Therefore, the major geochemical control effecting regeneration of phosphorus in the Vembanad estuarine bottom sediments are dissolution of P from fine grained amorphous iron oxyhydrates and degradation of sedimented organic matter. At the surficial level the low interstitial PO_4^{3-} content is due to the large adsorption potential of ferric hydroxides for phosphate and precipitation mechanisms. Therefore, phosphate concentrations of interstitial water in contact with these suboxic sediment layer tend to be low. Precipitation of ammonium phosphate and ammonium sulphate (Fig. 8d) are other possible control phosphate in reducing conditions (Sholkovitz, 1973).

SiO_2 : SiO_2 levels, like those of NO_3^- and PO_4^{3-} do not correlate well with those in the water column. In the overlying waters the SiO_2 is generally low. The SiO_2 in the interstitial waters is principally derived from the dissolution of diatoms, however, the final concentration dependent on complex adsorption and exchange reactions with clay minerals (Willey, 1978). It, therefore, seems that interstitial SiO_2 levels are mainly controlled by the supply of biogenic SiO_2 , which is highest in the estuary.

The concentration of dissolved SiO_2 is significantly high even in the top few cm of the core sediments (54 to 290 μM) however, a general increase with depth is observed. The concentration of SiO_2 in the overlying bottom water is only about 21-87 μM , so that diffusion into the overlying water is possible. Deeper in the sediments the concentrations appear to approach constancy.

Therefore, it is evident that the action of benthic organisms and microbial degradation affect organic matter and other unstable mineral complexes of the sediments and interstitial waters in the immediate vicinity.

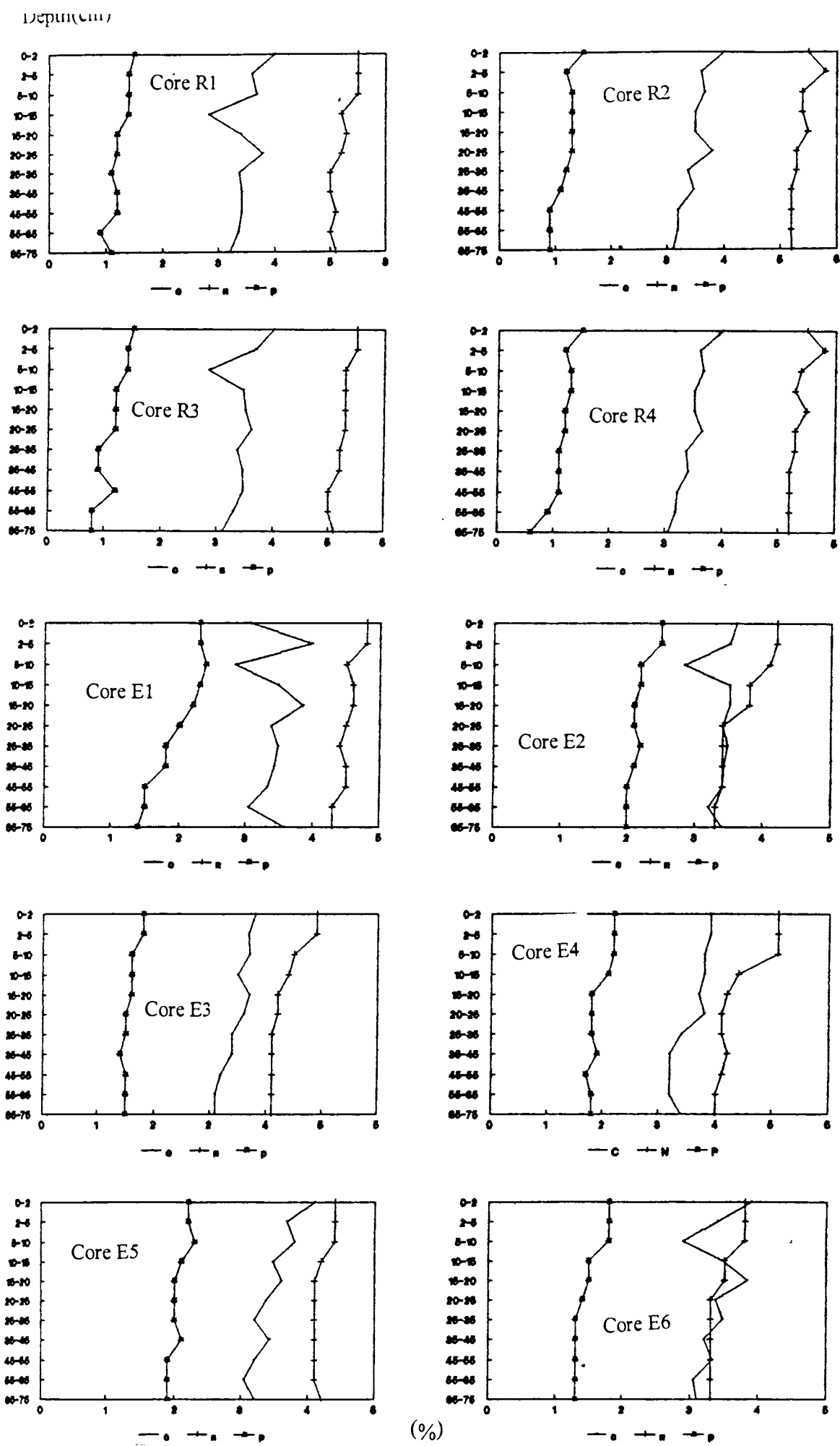


Fig. 7(a) Vertical variations of C, N and P in sediments
(C in % and N & P in mg/g)

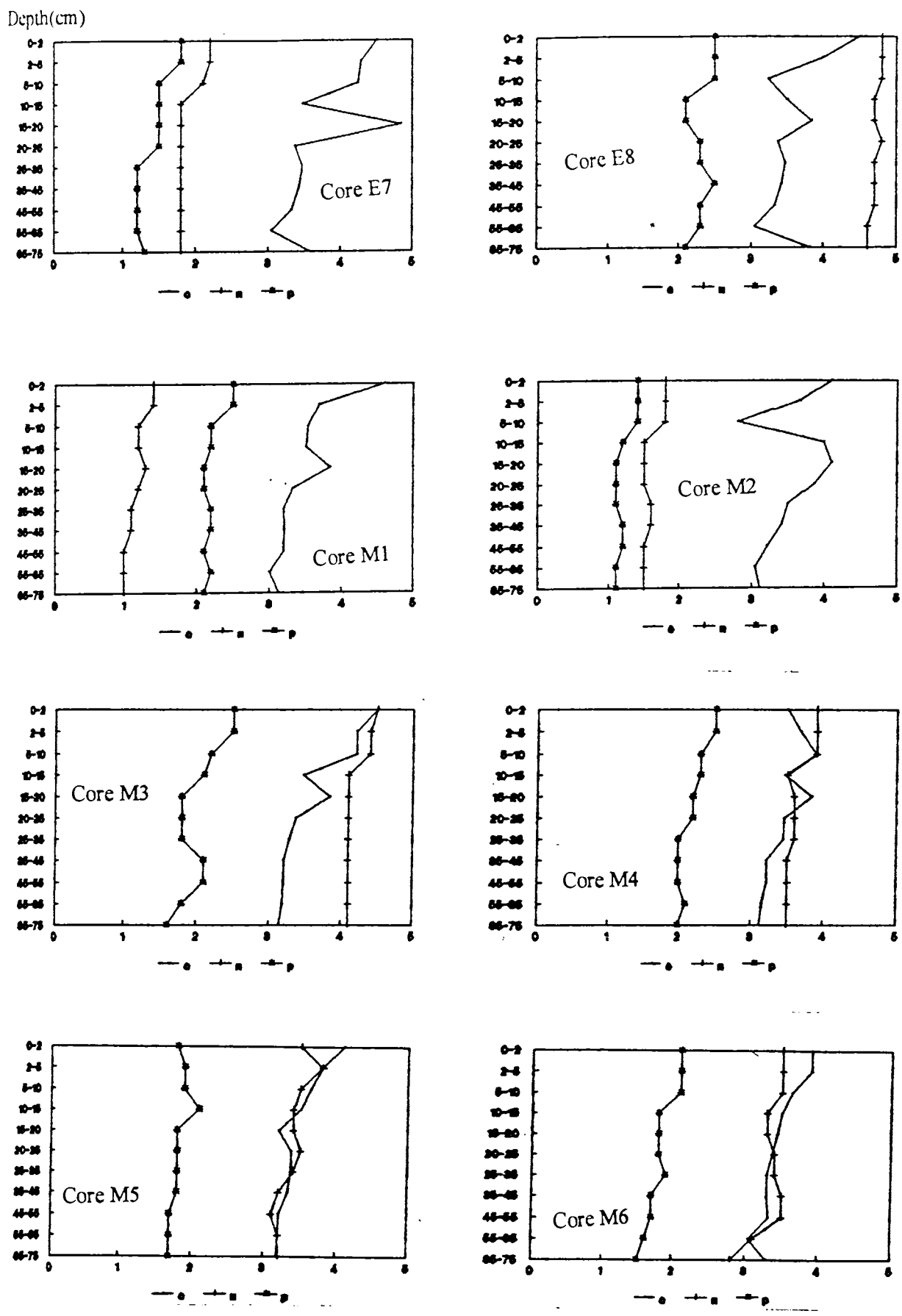


Fig. 7(b) Vertical variations of C, N and P in sediments
(C in % and N & P in mg/g)

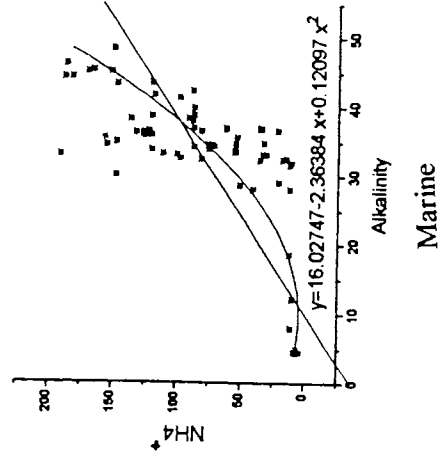
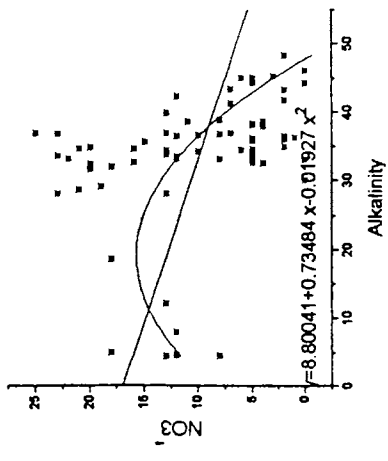
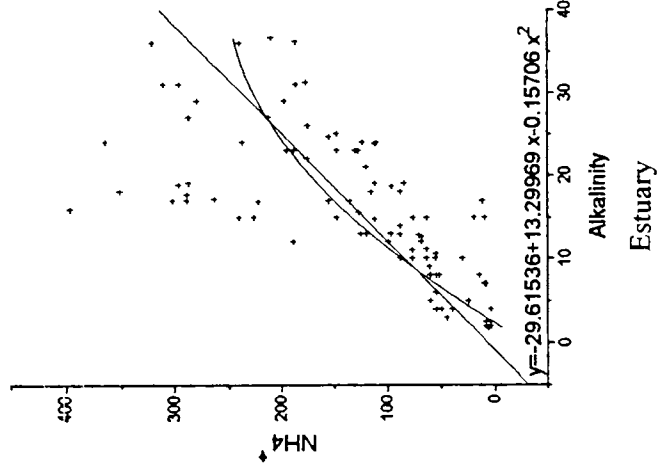
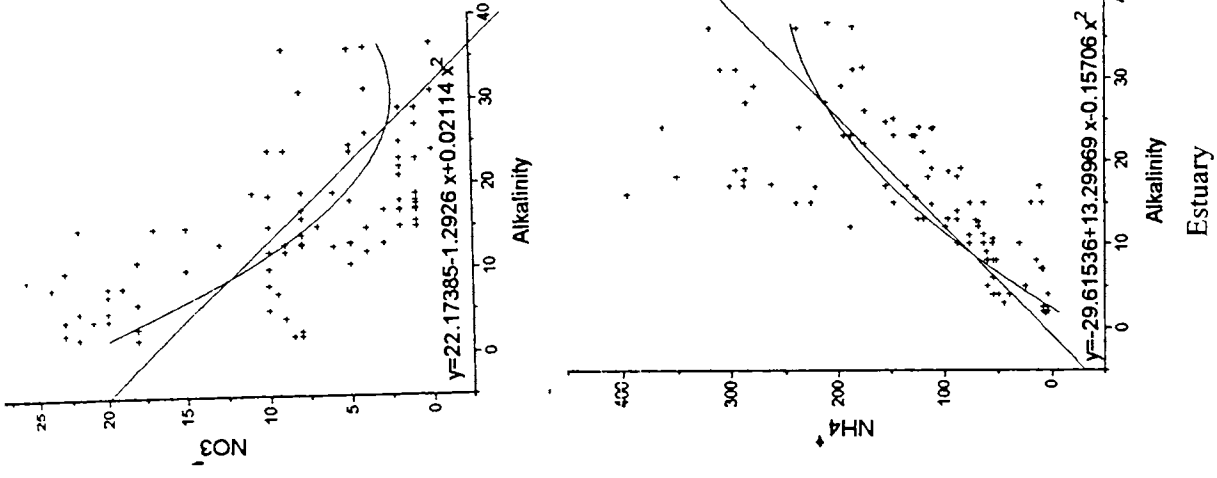
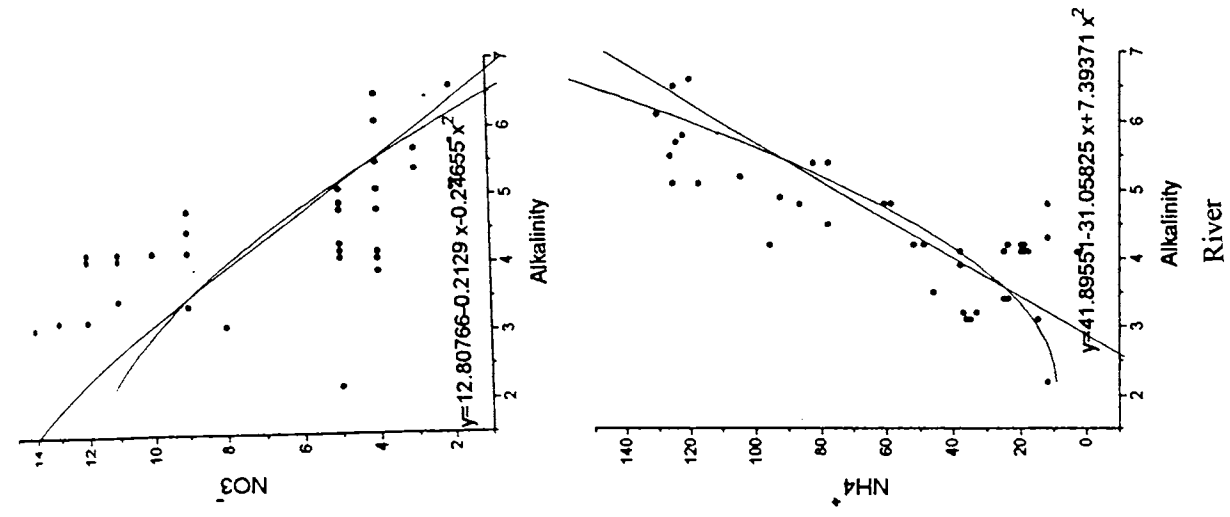
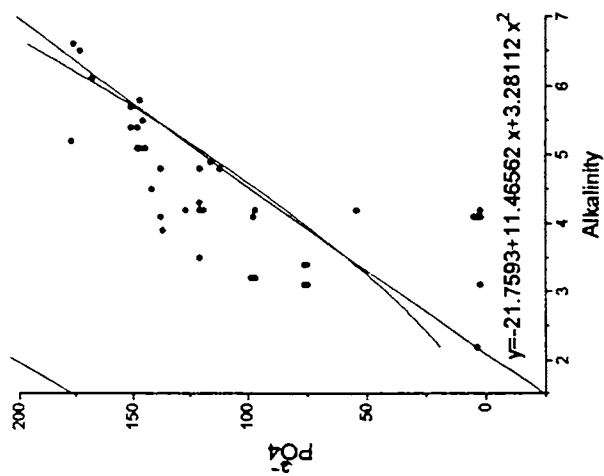
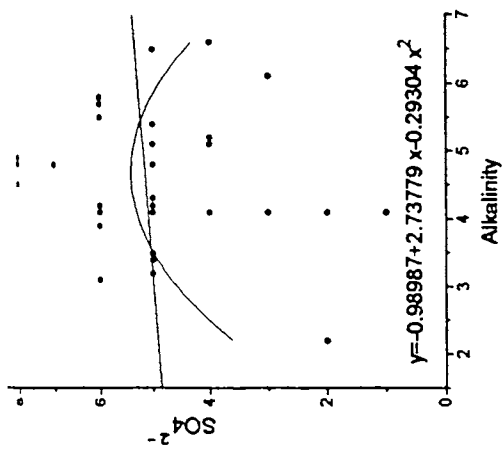
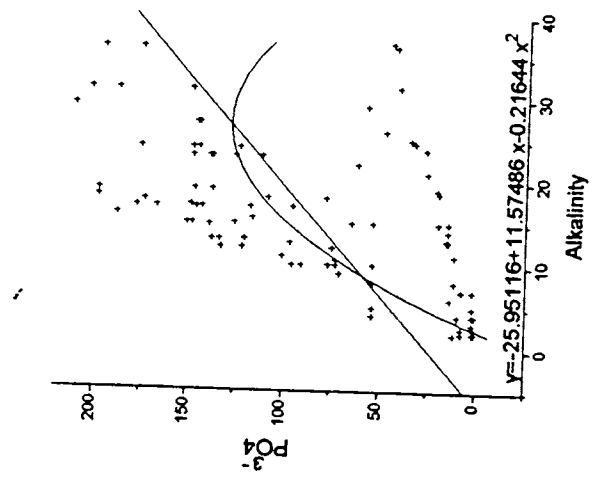
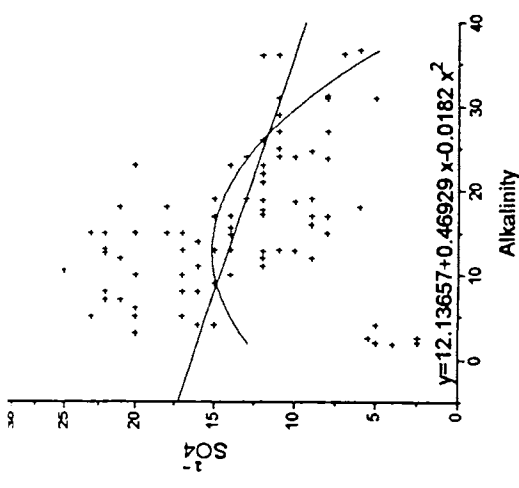


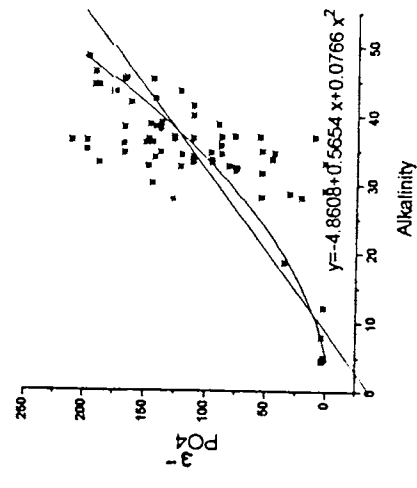
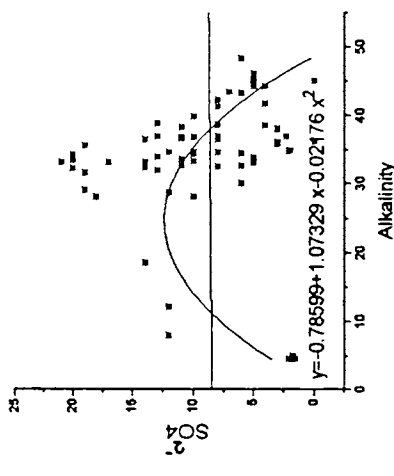
Fig.8(a) Correlation of alkalinity with NO_3^- and NH_4^+ in different cores



River



Estuary



Marine

Fig.8(b) Correlation of alkalinity with SO_4^{2-} and PO_4^{3-} in different cores

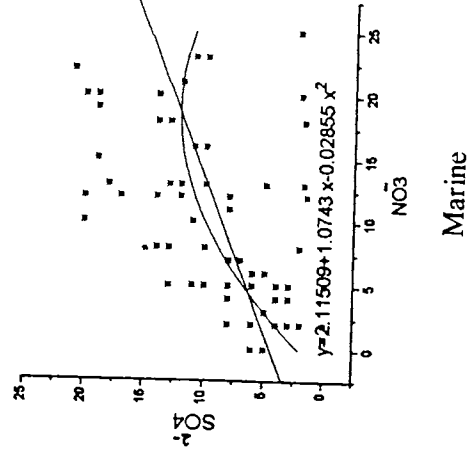
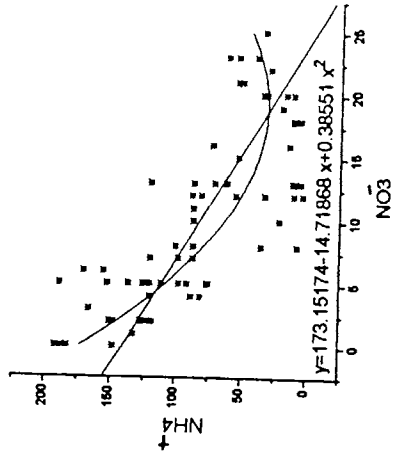
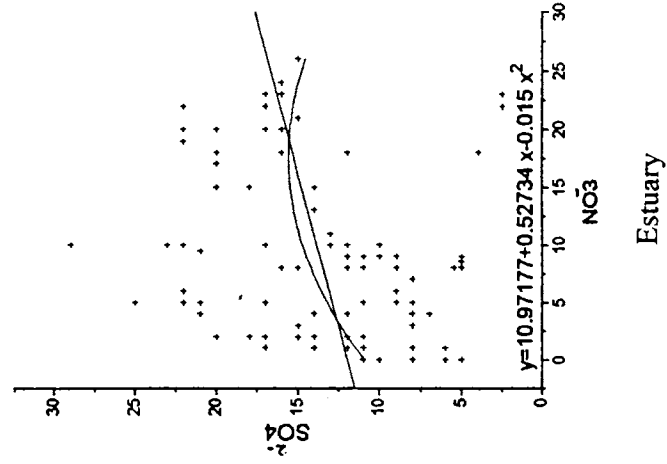
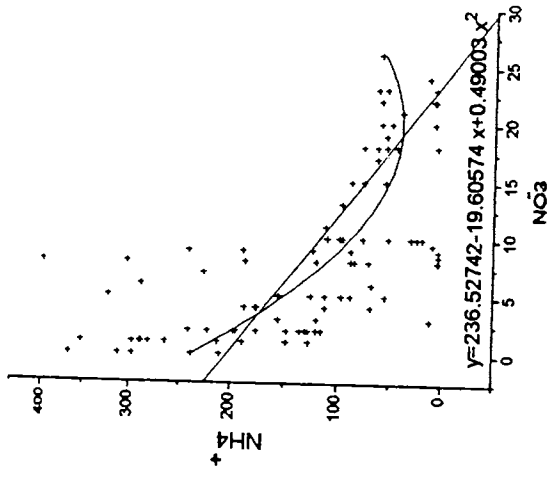
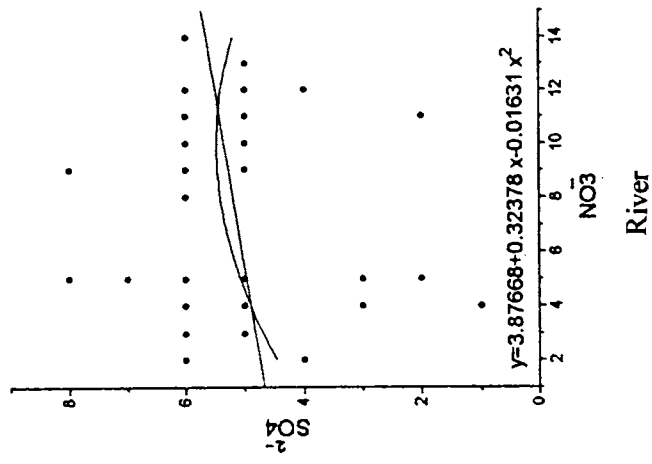
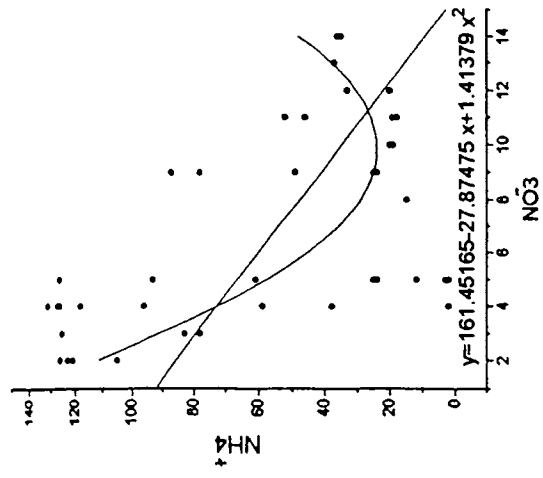
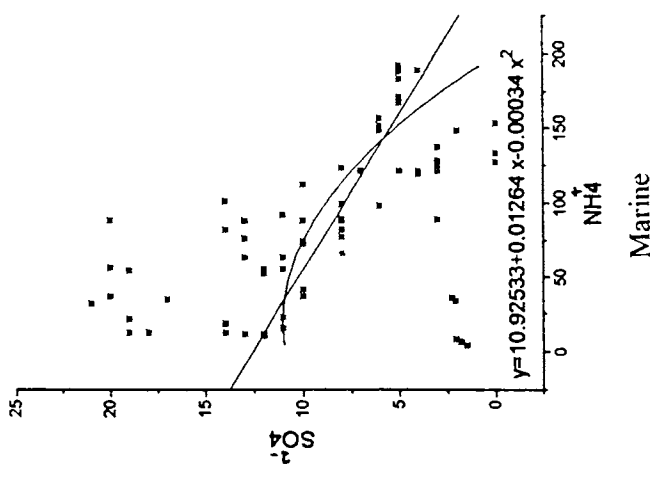
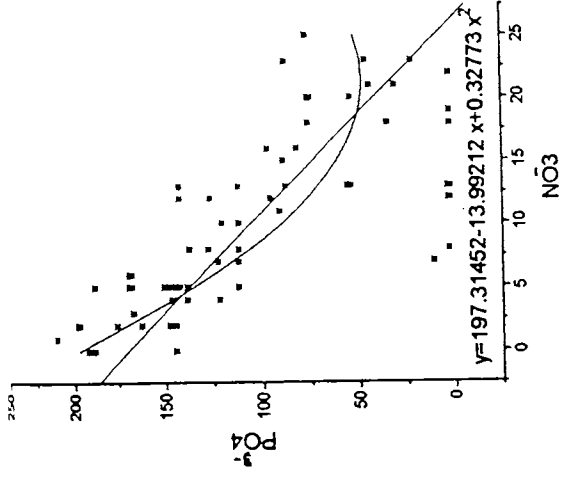
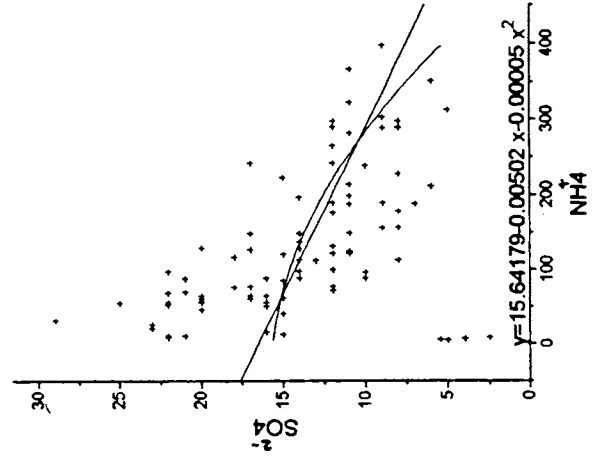
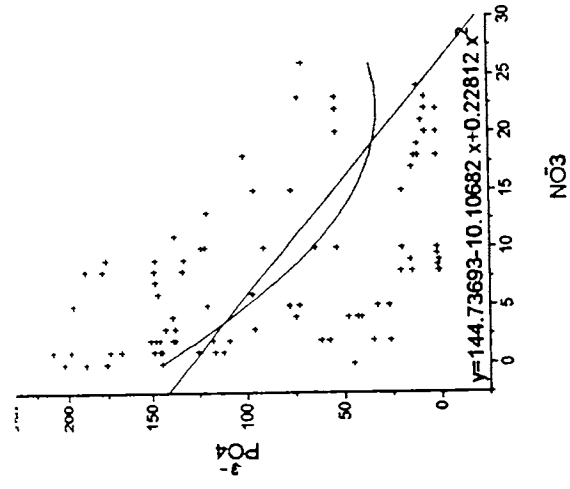


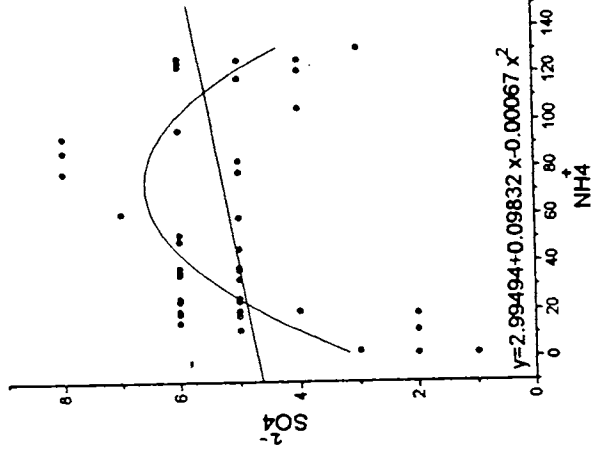
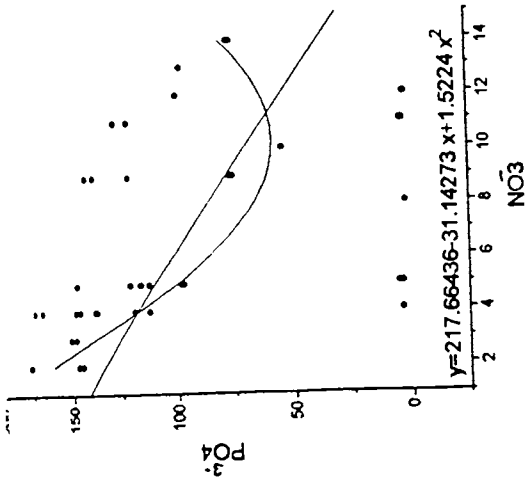
Fig. 8(c) Correlation of NO_3^- with NH_4^+ and SO_4^{2-} in different cores



Marine

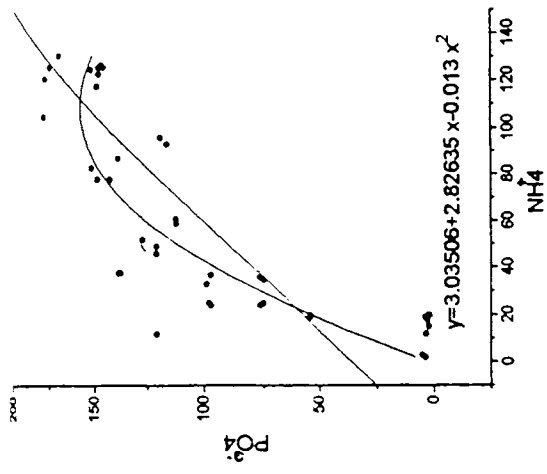


Estuary

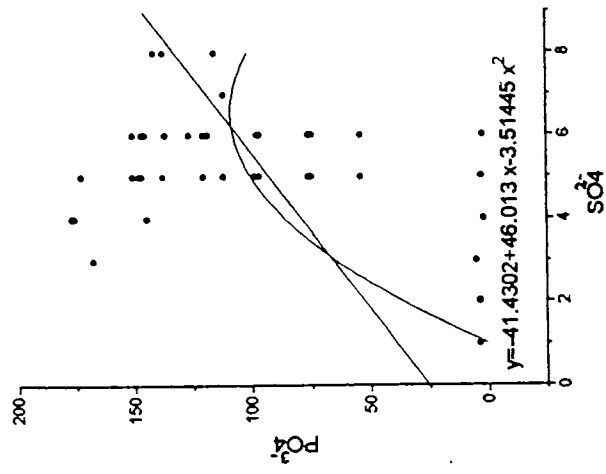


River

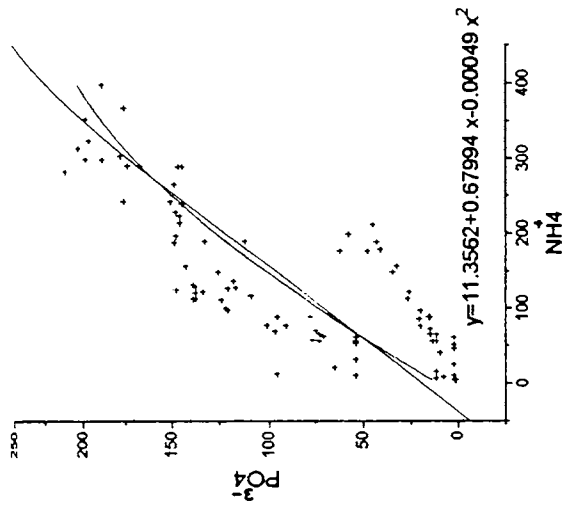
Fig.8(d) Correlation between NO_3^- and PO_4^{3-} ; and NH_4^+ with SO_4^{2-} in different cores



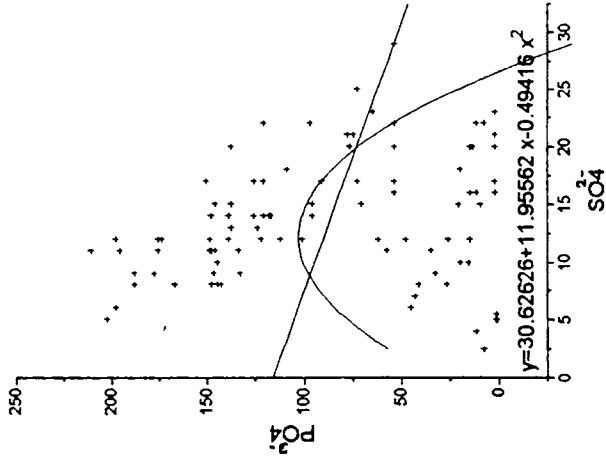
River



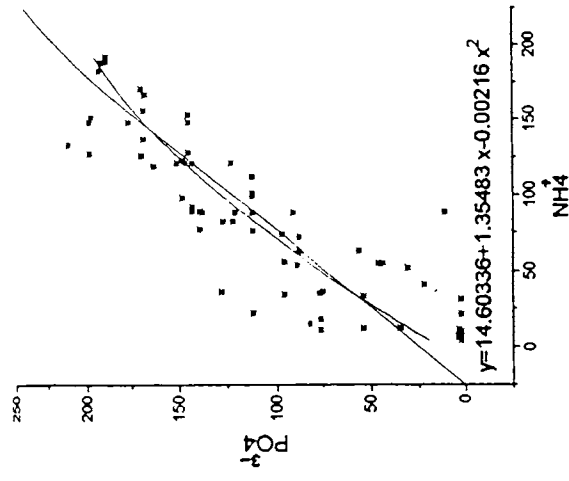
River



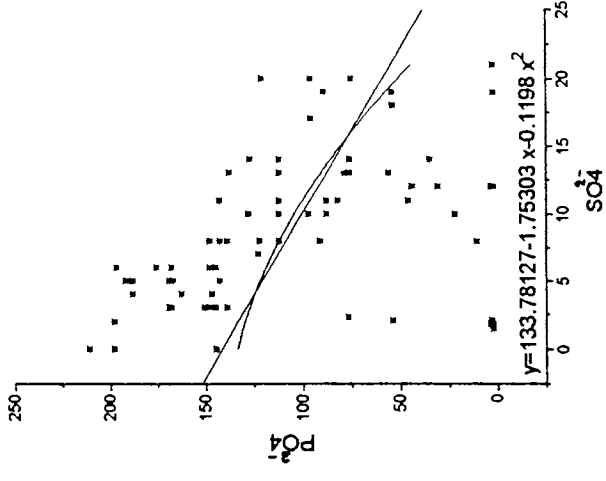
Estuary



Estuary



Marine



Marine

Fig.8(e) Correlation between NH_4^+ and PO_4^{3-} ; and SO_4^{2-} with PO_4^{3-} in different cores

CHAPTER 4

MAJOR AND TRACE ELEMENTS

Introduction

In recent years attention has been paid to estuarine and shelf sediments by geochemists because the physical, chemical and biological conditions are more variable in these marginal environment than on the continents or in the deep seas. The behavior of the major and minor elements in sediments and elucidation of different factors controlling their distribution have been the objectives of a number of geochemists. The interstitial water study helps to understand clearly the various processes operating within the sediments. The estuarine and nearshore sediments are considered as an important removal site for several elements from the overlying water because the accumulation rates are very much higher and the environmental factors are very much different from the open ocean. Further, the modern industrialization and civilization have aggravated the geochemical mass balance in these transitional environment.

The concentration and distribution of many metals in sea water and sediments are influenced by adsorption or coprecipitation with Fe and Mn oxides (Goldberg, 1954; Krauskopf, 1956; Jenne, 1968; Murray and Brever, 1977). The general geochemistries of Fe and Mn are well known as both metals are relatively mobile under reducing conditions, but are rapidly precipitated under oxic condition. Further the ranges of major and trace metal composition are influenced by different proportions by major minerals present in the sediments such as quartz, feldspar and other alumino silicates; clay mineral like montmorillonite, kaolinite, illite and chlorite and those of minor elements in heavy minerals. Influence of organic matter and other biogenic material over certain major and many trace elements are well known. Hence an attempt has been made in this chapter to understand the variation of major and trace elements

in sediments as well as interstitial waters.

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Si and Al: Detrital quartz, aluminosilicates and siliceous skeletons invariably comprises SiO_2 . In marine sediments Al_2O_3 , which is derived principally from the aluminosilicate minerals is detrital in origin though some of them could also be derived from authigenic process (Cronan, 1980).

Results:

Concentration of Si and Al in sediments and interstitial waters are given in Table 5 and plotted in Figs. 9 a-b and 10 a-b respectively. In riverine cores sediment Si content ranges between 26% and 54% whereas the range in estuarine and marine cores (28 to 37%) is considerably less (Table 5). Earlier, Ramachandran (1992) has observed an average of 46.9% of SiO_2 in the innershelf surficial sediments off Cochin, with maximum samples showing a range of 30-40%. A slight decrease of Si with depth is noticed in all core sediments of this study. The Si content in interstitial waters does not show any specific trend with depth; showing a high range from 211 ppm to 488 ppm. Al content in riverine sediment cores ranges between 7% and 9% and the range in estuarine and marine cores is also more or less same (Table 5). Al profiles fluctuates throughout the cores without any remarkable variation with depth. The average Al_2O_3 content in the surficial sediments off Cochin is reported to be 12.34% (Ramachandran, 1992). In interstitial waters Al ranges between 14 and 196 ppm and no specific trend is observed in many cores. However, the surficial interstitial waters values are uniformly very low.

Discussion:

Si is the dominant constituent of the sediments. The Si in the sediments is derived mainly from detrital quartz, aluminosilicates and siliceous skeletons. The relatively high concentration of Si in riverine sediments is mainly attributed to high sand content (Table.3). On the other hand since the sand

Table 5. Major element distribution in sediments (ppm) and interstitial waters (µg/l) in different cores, but Si & Al in %. (S=Solid; IW=Interstitial water)

	Si		Al		Na		K		Ca		Mg	
	S	IW	S	IW	S	IW	S	IW	S	IW	S	IW
R1												
Depth (cm)												
0-2	39	320	8	36	7986	10	11945	25	8143	149	5124	18
2-5	36	333	8	41	7830	10	11987	24	8241	148	5122	15
5-10	33	451	7	38	7988	11	11915	21	8436	158	5163	15
10-15	38	463	8	46	7965	11	11898	17	8948	156	5221	15
15-20	38	454	9	88	7998	12	11862	15	9131	132	5312	16
20-25	42	337	9	31	7541	14	11812	12	9145	130	5488	14
25-35	48	357	7	49	7285	14	11852	12	9252	130	5626	14
35-45	39	341	8	36	7140	17	11611	10	9856	128	5884	12
45-55	41	448	7	45	7280	17	11621	11	9632	126	5602	12
55-65	33	316	9	38	7190	17	11601	10	9612	125	5911	11
65-75	34	211	8	31	7012	20	10120	10	9967	125	5989	11
R2												
Depth												
0-2	33	312	9	41	7888	11	11987	24	8012	147	5112	17
2-5	38	311	8	38	7938	10	11961	24	8136	150	5098	15
5-10	38	487	8	36	7619	12	11987	23	8144	149	5163	17
10-15	26	424	7	43	7894	11	11654	23	8465	148	5246	14
15-20	34	412	8	49	7716	12	11856	19	9514	141	5248	13
20-25	43	389	9	37	7542	15	11345	18	8897	139	5347	14
25-35	41	355	6	48	7314	15	11546	12	9252	130	5556	13
35-45	43	341	7	39	7217	16	11456	16	9465	128	5724	12
45-55	41	487	7	41	7280	16	11458	11	9632	127	5814	12
55-65	33	348	8	39	7210	17	11214	15	9713	121	5814	11
65-75	39	244	9	51	7096	19	11211	11	9899	121	5997	10
R3												
Depth												
0-2	33	312	9	38	7925	11	11845	24	8000	150	5124	18
2-5	38	312	8	44	7999	11	11899	23	8241	148	5198	15
5-10	31	445	7	39	7865	12	11789	21	8436	158	5167	15
10-15	33	417	6	43	7654	12	11648	19	8948	156	5248	15
15-20	29	428	6	39	7514	12	11541	17	9131	132	5312	16
20-25	41	331	6	36	7423	16	11379	12	9145	130	5514	14
25-35	41	341	8	44	7214	16	11289	11	9252	130	5721	14
35-45	39	341	8	32	7140	17	11245	11	9856	128	5721	12
45-55	41	311	7	43	7124	18	11354	11	9632	126	5589	12
55-65	41	297	7	39	7215	19	11112	11	9612	125	5914	11
65-75	38	211	8	48	7012	19	10237	12	9987	124	5888	11
R4												
Depth												
0-2	39	415	9	33	7989	11	11978	24	8015	144	5142	19
2-5	36	338	9	41	7955	12	11654	24	8116	148	5169	20
5-10	38	398	7	32	7932	12	11687	23	8198	149	5248	18
10-15	31	412	8	43	7945	11	11489	17	8279	139	5242	16
15-20	35	466	8	38	7998	12	11654	15	8246	132	5445	16
20-25	41	389	7	39	7415	15	11745	19	9465	130	5488	14
25-35	43	354	7	41	7365	14	11245	12	9521	131	5568	15
35-45	54	341	9	37	7215	19	11654	15	9856	129	6878	12
45-55	44	487	7	42	7280	17	11452	11	9712	124	5876	11
55-65	31	346	9	39	7145	19	11214	12	9745	112	5897	11
65-75	36	342	7	62	7014	18	11456	11	9987	121	5899	11

File 5 continue.....

	Si		Al		Na		K		Ca		Mg		
	S	IW	S	IW	S	IW	S	IW	S	IW	S	IW	
E1													
Depth													
0-2	29	355	8	18	1000	118		987	70	10214	249	6011	29
2-5	32	355	8	74	9840	121		993	58	10217	249	6148	29
5-10	32	381	7	78	9880	121		988	65	10238	246	6156	28
10-15	28	388	8	81	9860	128		991	62	10412	241	6098	28
15-20	31	412	8	78	9880	131		968	61	10627	238	6117	26
20-25	32	412	7	81	9646	126		966	48	11124	230	6208	22
25-35	28	488	6	62	9640	136		962	41	11137	225	6217	21
35-45	28	222	7	51	9732	135		954	36	11181	226	6228	18
45-55	28	288	7	68	9791	136		958	32	11514	218	6287	18
55-65	27	314	7	72	9846	147		948	31	10927	212	6189	14
65-75	27	388	8	81	9638	150		941	30	11814	211	6311	14
E2													
0-2	33	349	9	21	9889	123		1124	121	10147	257	5987	31
2-5	32	349	8	69	9673	129		1038	86	10768	248	6214	30
5-10	32	376	7	69	9764	127		974	91	10258	246	6125	30
10-15	28	386	8	79	9860	132		985	72	10369	239	6245	27
15-20	31	422	8	81	9880	139		973	66	10874	238	6128	26
20-25	32	417	7	81	9716	136		986	54	11245	231	6278	22
25-35	29	467	8	67	9640	137		957	49	11264	222	6249	22
35-45	29	231	7	46	9687	138		953	41	11398	226	6288	18
45-55	28	274	7	66	9664	141		947	38	11587	220	6293	14
55-65	28	311	7	68	9489	148		948	38	10987	218	6247	14
65-75	29	296	6	79	9267	146		921	39	11946	218	6215	15
E3													
0-2	34	315	9	24	9945	131		1017	88	9874	255	5687	19
2-5	32	330	8	69	9768	138		1124	89	10587	248	6135	26
5-10	32	376	9	71	9880	138		994	74	10697	244	6187	27
10-15	31	384	8	88	9860	144		987	69	10876	242	6135	26
15-20	29	397	8	74	9880	146		985	82	10859	239	6122	26
20-25	32	389	7	78	9646	154		956	41	11038	241	6245	22
25-35	29	411	5	69	9774	148		964	41	11122	232	6287	19
35-45	28	346	7	55	9637	151		952	46	11248	225	6288	19
45-55	28	297	7	62	9688	162		951	31	11496	228	6299	11
55-65	31	320	8	69	9587	159		934	31	11987	201	6188	12
65-75	28	366	8	91	9578	152		925	35	11789	222	6412	12
E4													
0-2	31	328	8	22	9879	132		1124	72	9877	287	5489	12
2-5	31	335	8	69	9687	128		1123	54	10345	285	5943	17
5-10	32	364	9	71	9857	127		976	53	10258	267	6012	29
10-15	31	388	8	82	9863	122		987	49	10467	259	6085	28
15-20	31	398	8	88	9846	138		985	48	10986	248	6142	27
20-25	33	379	8	81	9785	137		972	48	11289	246	6135	27
25-35	28	412	6	91	9716	139		964	45	11362	237	6189	25
35-45	28	358	8	55	9768	141		945	42	11258	229	6278	21
45-55	28	297	7	63	9791	149		945	46	11653	228	6278	21
55-65	31	344	6	79	9571	151		936	38	11896	221	6289	13
65-75	26	369	7	62	9538	158		942	38	11875	221	6238	13

Table 5 continue.....

	Si		Al		Na		K		Ca		Mg	
	S	IW	S	IW	S	IW	S	IW	S	IW	S	IW
E5												
0-2	31	341	8	19	9785	122	1017	69	9967	274	5598	18
2-5	32	361	9	76	9897	122	1035	64	10109	268	5649	21
5-10	32	381	7	78	9768	126	992	66	10245	252	5863	21
10-15	29	332	8	81	9892	127	987	59	10358	243	6054	19
15-20	32	412	8	76	9768	129	976	52	10598	241	6123	17
20-25	32	412	9	79	9788	129	962	47	10876	239	6185	16
25-35	28	488	6	62	9624	137	958	43	11128	228	6223	16
35-45	27	386	7	55	9713	138	954	39	11287	221	6342	15
45-55	28	324	7	76	9785	141	959	34	11454	211	6297	15
55-65	29	314	6	77	9712	145	942	32	11687	215	6312	14
65-75	27	345	7	82	9712	155	939	32	11798	214	6354	13
E6												
0-2	28	336	9	21	9874	129	998	87	9886	241	5897	16
2-5	29	349	9	69	9976	121	987	81	10454	248	5914	16
5-10	33	386	7	84	9846	121	988	76	10683	249	6038	17
10-15	33	387	8	81	9814	125	986	72	10882	246	6059	16
15-20	32	413	8	78	9936	129	987	64	10597	237	6152	15
20-25	32	412	9	81	9123	134	974	64	11652	236	6183	14
25-35	29	438	6	91	9612	139	971	41	11263	231	6183	12
35-45	28	289	7	91	9645	141	967	43	11387	229	6214	12
45-55	29	262	6	68	9794	142	956	38	11488	222	6227	9
55-65	28	311	7	88	9825	148	946	32	11878	221	6233	9
65-75	30	326	6	87	9823	147	937	29	11946	218	6245	9
E7												
0-2	33	351	8	14	9825	121	978	58	10143	251	6011	26
2-5	32	349	9	38	9978	126	996	58	10217	248	6054	28
5-10	32	362	8	64	9914	128	982	62	10312	247	6112	27
10-15	31	388	8	68	9862	128	981	62	10367	240	6117	27
15-20	31	411	9	67	9845	132	968	61	10487	239	6117	27
20-25	32	412	8	82	9738	137	976	57	11254	235	6224	26
25-35	29	423	7	74	9767	142	972	57	11537	228	6228	26
35-45	29	359	7	66	9765	146	951	52	11812	225	6228	21
45-55	28	357	7	68	9763	146	950	48	11798	221	6289	21
55-65	31	398	7	72	9687	149	949	43	11882	220	6245	18
65-75	28	411	8	76	9613	149	948	43	11935	220	6214	18
E8												
0-2	31	351	8	31	9945	121	987	88	9847	287	6012	24
2-5	33	353	8	56	9932	121	986	88	9883	263	6088	24
5-10	33	387	9	72	9867	124	996	83	10125	253	6124	25
10-15	32	368	8	81	9834	126	992	82	10248	259	6128	24
15-20	31	397	8	88	9831	132	986	77	10356	248	6245	23
20-25	32	398	9	79	9701	133	974	63	11456	241	6283	22
25-35	29	412	6	74	9614	137	968	61	11583	232	6288	19
35-45	29	412	8	62	9732	141	967	48	11576	232	6273	19
45-55	32	387	7	88	9791	141	953	33	11692	212	6281	18
55-65	31	389	8	88	9678	138	953	28	11714	231	6288	15
65-75	28	387	8	91	9632	146	952	22	11812	245	6273	15

Table 5 continue.....

	Si		Al		Na		K	Ca		Mg		
	S	IW	S	IW	S	IW	S	IW	S	IW	S	IW
M1												
0-2	28	343	8	41	11985	155	997	92	9887	292	6012	18
2-5	28	348	8	48	11964	159	983	99	9863	294	6014	18
5-10	27	351	8	56	11922	167	922	96	10245	296	6035	16
10-15	27	368	7	61	11934	168	864	94	10317	285	6047	15
15-20	28	387	8	72	11912	172	623	89	10366	273	6187	15
20-25	28	388	7	72	11819	177	714	83	10589	268	6126	16
25-35	25	415	6	88	11846	194	712	85	10245	245	6138	15
35-45	26	415	7	79	11874	198	768	84	11254	259	6155	14
45-55	27	422	7	83	11689	211	711	72	11356	244	6114	15
55-65	26	411	6	88	11678	236	716	66	11454	238	6174	14
65-75	24	412	6	96	11645	255	722	62	11878	231	6177	11
M2												
0-2	28	352	7	64	11890	156	989	96	9765	287	5989	22
2-5	29	387	8	55	11980	155	863	97	10145	288	6015	26
5-10	28	367	8	62	11783	159	846	97	10277	264	6022	25
10-15	27	388	7	88	11644	161	839	89	10345	253	6038	26
15-20	29	349	6	96	11456	171	839	82	10562	245	6087	23
20-25	29	397	6	74	11487	182	796	82	10786	238	6145	18
25-35	28	376	8	79	11356	194	751	78	11263	235	6178	18
35-45	28	412	7	82	11286	209	726	73	11487	228	6180	14
45-55	26	392	8	88	11286	223	712	71	11314	227	6179	14
55-65	26	412	8	88	11222	234	745	69	11455	215	6188	14
65-75	27	379	6	76	11232	236	713	65	11450	215	6190	12
M3												
0-2	27	324	8	33	11875	161	878	94	10100	247	6114	23
2-5	28	245	9	46	11800	166	816	83	10155	249	6023	25
5-10	28	355	9	52	11763	172	798	88	10212	247	6044	25
10-15	29	367	8	88	11787	177	780	79	10487	260	6087	24
15-20	28	349	8	65	11684	184	766	76	10244	252	6144	24
20-25	27	328	8	83	11612	192	768	77	11254	244	6154	21
25-35	28	388	6	96	11545	211	758	72	11378	256	6187	17
35-45	28	379	8	76	11454	228	714	73	11201	234	6188	16
45-55	27	368	7	84	11585	241	727	66	11406	234	6173	14
55-65	27	346	8	84	11612	248	712	64	11515	226	6145	15
65-75	27	382	6	82	11215	244	704	64	11454	229	6188	15
M4												
0-2	28	345	6	33	11876	160	786	89	9886	244	6112	19
2-5	29	362	8	59	11945	162	879	88	9874	246	6045	24
5-10	29	348	6	62	11825	168	845	83	10124	235	6087	24
10-15	26	355	7	71	11941	171	826	79	10145	233	6055	24
15-20	26	371	8	78	11812	186	822	76	10452	230	6087	24
20-25	28	388	7	88	11724	189	798	75	10612	212	6145	25
25-35	29	391	7	79	11654	195	764	69	10770	235	6124	23
35-45	27	411	8	84	11456	213	782	67	10882	233	6163	23
45-55	28	452	6	86	11256	217	780	62	11243	231	6188	21
55-65	28	387	8	88	11423	228	764	21	11360	229	6187	21
65-75	27	385	8	78	11235	235	772	61	11344	222	6185	18

Table 5 continue.....

M5

0-2	31	351	8	31	11749	158	927	86	10125	247	6012	26
2-5	33	353	8	56	11836	159	918	88	10137	247	6027	26
5-10	33	387	9	72	11929	167	889	85	10464	246	6035	24
10-15	32	368	8	81	11873	169	847	79	10456	246	6039	24
15-20	31	397	8	88	11884	173	819	79	10398	243	6078	21
20-25	32	398	9	79	11857	174	811	76	10521	243	6083	21
25-35	29	412	6	74	11283	177	797	71	10522	238	6094	19
35-45	29	412	8	62	11465	181	782	68	10632	238	6145	19
45-55	32	387	7	88	11520	184	775	65	11102	231	6154	12
55-65	31	389	8	88	11390	191	760	61	11279	231	6182	11
65-75	28	387	8	91	11417	213	722	67	11321	229	6179	8

M6

0-2	28	348	8	32	11887	156	927	85	10124	247	6020	22
2-5	28	344	8	48	11876	156	848	85	10240	247	6024	22
5-10	27	348	9	61	11924	157	861	81	10265	246	6028	25
10-15	28	346	8	69	11945	162	812	76	10349	241	6033	24
15-20	27	347	8	77	11928	161	822	76	10434	241	6150	24
20-25	28	351	9	83	11812	167	748	72	10487	238	6160	24
25-35	28	359	6	85	11836	170	792	72	10677	234	6174	19
35-45	27	361	8	87	11648	179	736	69	10675	229	6185	19
45-55	27	367	7	87	11639	187	781	67	11124	227	6188	15
55-65	27	354	8	85	11534	189	792	67	11256	227	6192	12
65-75	27	362	8	89	11453	198	746	66	11255	225	6192	12

content in estuarine and marine cores are relatively very low (Table 3) the Si content is also low and therefore the sand content of sediments has a direct bearing on Si values. In nearshore marine sediments off Cochin a high positive correlation with sand and negative loadings with silt and clay have been observed by Ramachandran (1992). Hartmann et al., (1976) and Zwolsman et al., (1993) have reported the strong association of Si with the coarse (sandy) fraction of sediments.

High content of dissolved Si (Fig.9a & b) is mainly attributed to the dissolution of both amorphous and biogenic silica. Significant Si concentration by diatom has been established by Kamatani and Takano(1984). Further, the concentration of Si particularly at depth (Fig. 9a & b) may be due to leaching of detrital quartz grain under the reducing condition giving rise to reaction structures (Plates 5 and 6), such reaction structures are not seen at the surficial quartz (Plates 1 and 2). Further, it has also been found that during adsorption of metals onto Fe-oxy hydroxides phases Al and Si are replaced so that to form Fe rich smectite in the sediment column (Hein et al., 1979; Graybeal and heath, 1984). Brumsack and Gieskes (1983) have observed a general increase of Si with depth in interstitial waters of the sediments of Gulf of California, Mexico. In contrast, higher interstitial Si concentrations have also been observed at the surficial level in laminated sediments unaffected by bioturbation. Willey (1978) has suggested two possibilities for the low Si in interstitial waters: i) some removal processes such as uptake of Si by clays and ii) the biogenic Si is prevented from dissolution by some physical or chemical mechanisms. However, in this study since the interstitial Si is uniformly high throughout the core, dissolution would be the main cause for such an enrichment.

In Vembanad estuarine and other areas sediments Al is derived principally from alumino-silicate minerals of detrital in origin and clay minerals though some of them could be from

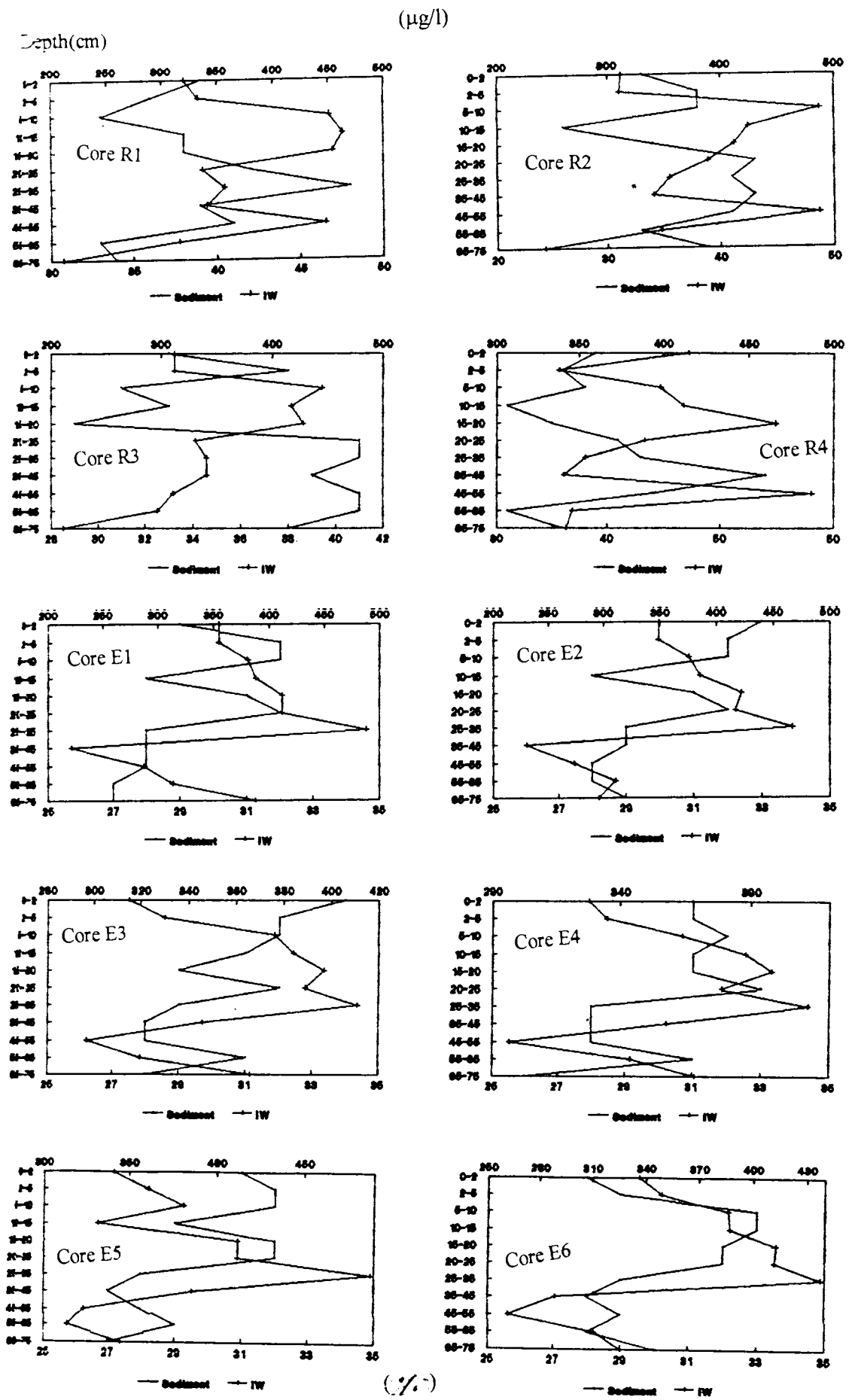


Fig. 9(a) Vertical variations of Si in sediments ($\%$) and interstitial waters ($\mu\text{g/l}$)

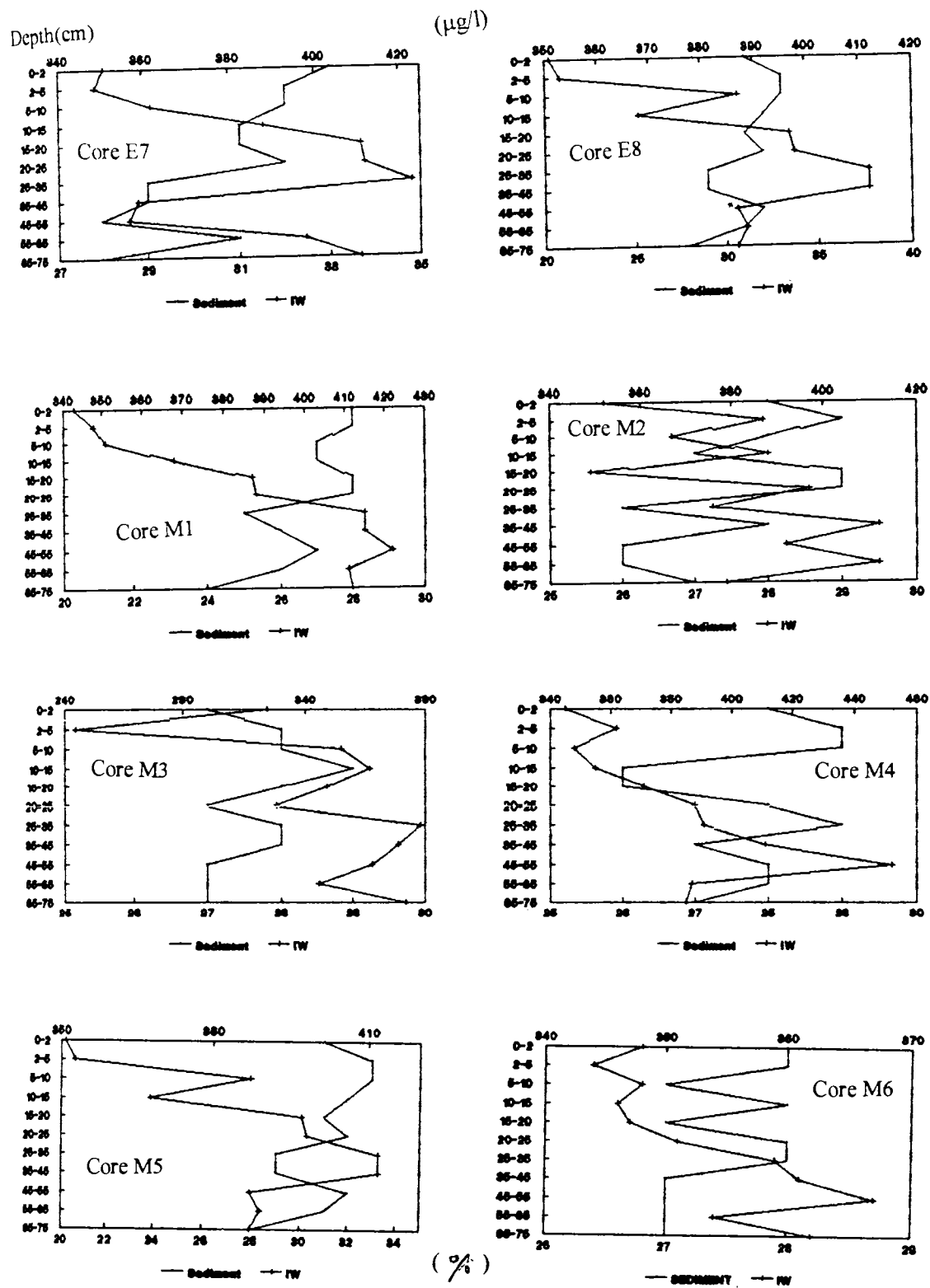


Fig. 9(b) Vertical variations of Si in sediments (%) and interstitial waters ($\mu\text{g/l}$)

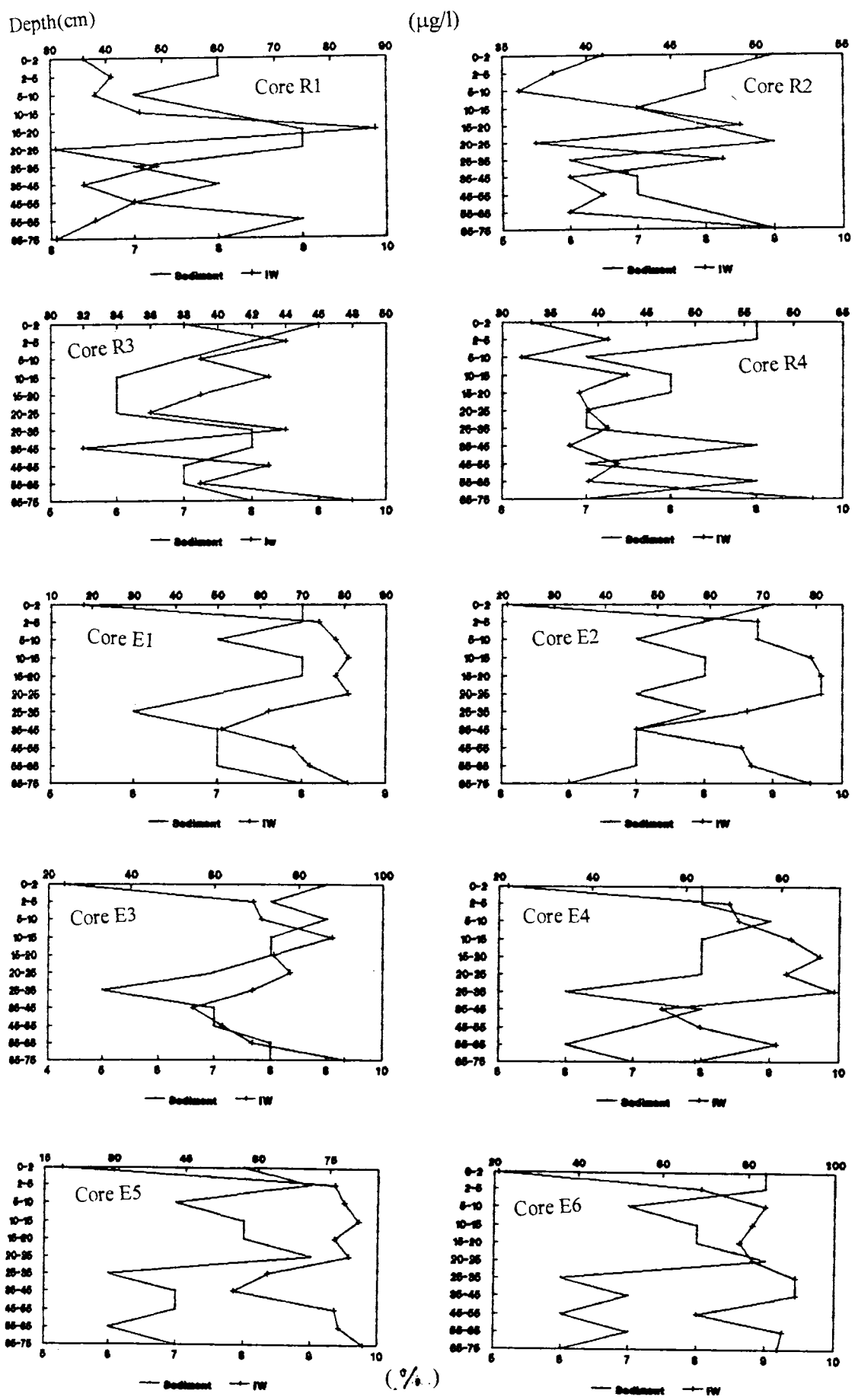


Fig. 10(a) Vertical variations of Al in sediments (%) and interstitial waters (µg/l)

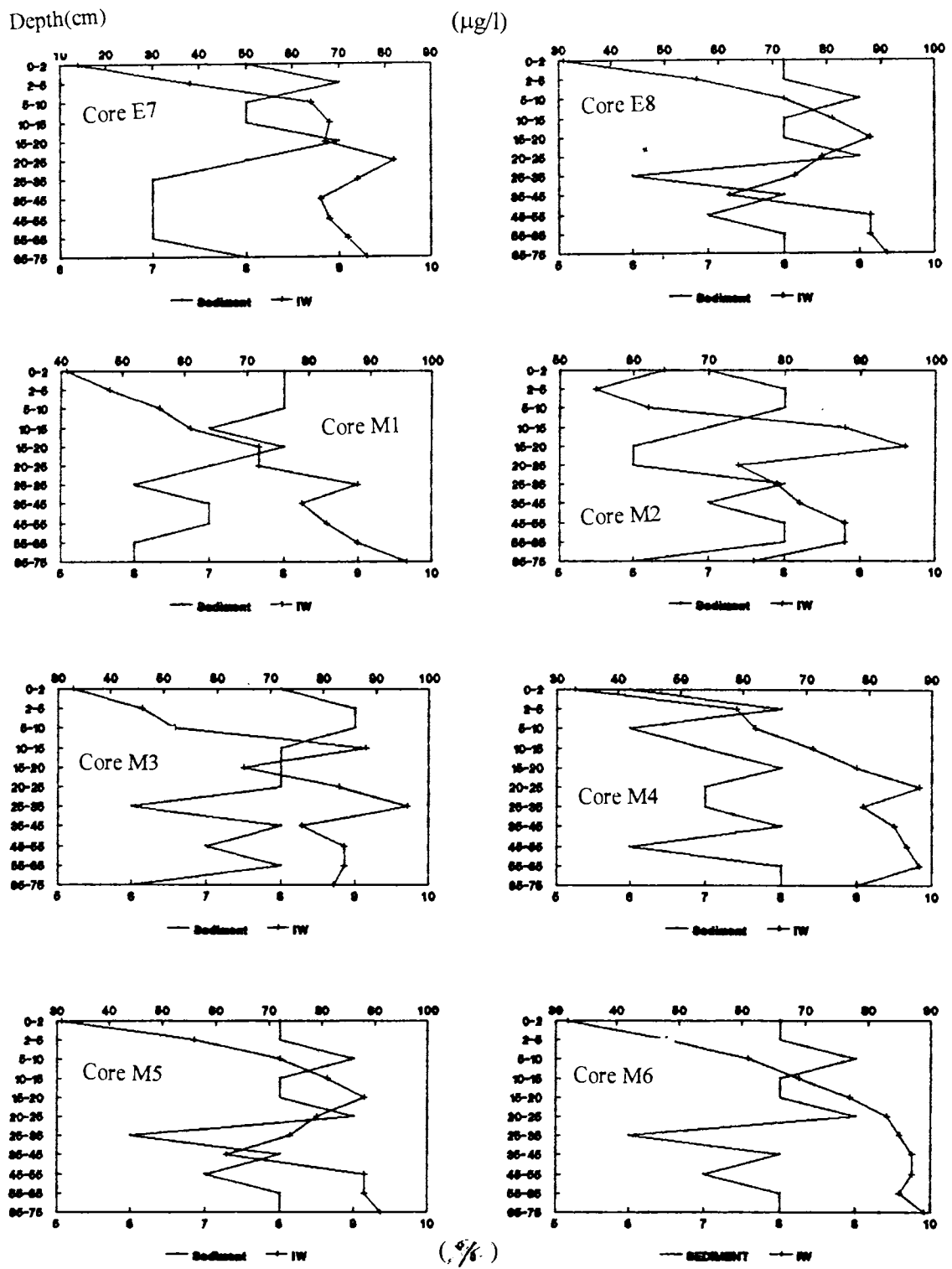


Fig. 10(b) Vertical variations of Al in sediments (%) and interstitial waters ($\mu\text{g/l}$)

authigenic processes (Cronan, 1980). Murty et al., (1983) have attributed a clay mineral control to the Al content of the core sediments. Odada (1986, 1990) has recorded high Al content in clay rich sediments but less values where low input of terrigenous material. Paropkari (1990) has stated that the Al is mainly held in clay mineral lattices. He also established a relationship between the distribution pattern of Al_2O_3 and textural distribution of sediments. In the inner shelf off Cochin a positive correlation of Al_2O_3 with silt and clay has been reported by Ramachandran (1992).

Unlike other metals, data on Al in interstitial waters are still relatively less, partly due to analytical difficulties. Generally Al values in interstitial waters are considerably higher than in the overlying bottom waters. In sediments, dissolution of clastic particles would give sufficient Al content to interstitial waters. Feldspar dissolution at depth has been shown through SEM photos (Plates 7 and 8). On the other hand from SEM photo (Plate 6) authigenic precipitation with a feldspar composition (identified from EDX spectrum) has also been found over a quartz grain. Such precipitations would affect the interstitial Al values. Brumsack and Gieskes (1983) have stated that the formation of authigenic clay minerals can be an ultimate sink for dissolved Al. Therefore, the Al profile both in sediments and interstitial waters of this study do not show a regular trend (Table 5, Figs. 10a & b). Stoffyn-Elgi (1982) has observed a strong correlation between dissolved Si and Al at the surface sediments but Brumsack and Gieskes (1983) have observed no correlation between them in core sediments. Presence of significant Al in marine plankton has been confirmed by leaching experiments (Collier and Edmond, 1981) and therefore the decomposition of biogenic material would contribute Al to interstitial waters

Sodium, potassium, calcium and magnesium

It is an established fact that the four ions - Na^+ , K^+ , Ca^{++}

and Mg^{++} - account for more than 99% of the positive charges in sea water salts. They are the major constituents of river water salts, the earth's crust and body fluids of the organisms. Weathering of rocks, adsorption/desorption process etc.. can greatly alter the concentration of these cations in a sedimentary environment. Therefore, understanding their behaviors is important for understanding the overall chemistry of the estuarine/marine hydrosphere. Sediment - interstitial water chemistry offers a method of assessing the extend of enrichment or depletion of these ions in sediments.

Results:

Depth profiles variation of major cations in marine interstitial waters has been reported earlier (Manheim, 1976; Presley and Trefry, 1980; de Lange, 1986). However, in this study the concentration of Na, K, Ca and Mg both in interstitial waters and sediments are presented (Table 6 and Figs. 11 to 14). The Na content in the interstitial waters of river sediments is very less ranging between 10 and 20 ppm whereas higher values with a range of 118 and 167 ppm in estuary and from 155 to 255 ppm in marine area are recorded. An increase of interstitial Na is noticed with depth (Figs. 11a & b). At the core top the maximum Na concentration is 7989 ppm in river, 9989 ppm in estuary and 11985 ppm in marine sediments. A slight decrease in sediment Na with depth is recorded. Unlike Na, interstitial K values decrease with depth in all the cores (Figs. 12a & b). There are many reports available on the decrease of interstitial K (Presley and Kaplan, 1970; Sayles et al., 1973; Presley and Trefry, 1980). In riverine cores the interstitial content of K ranges from 10 to 25 ppm while in estuary the range is between 22 and 121 ppm and in marine from 21 to 99 ppm. In sediments, the maximum K at the core top is 11987 ppm in river, 1124 ppm in estuary and 997 ppm in marine cores. Sediment K shows a decreasing trend with depth (Figs. 12a & b).

The Ca content in the riverine interstitial waters ranges

between 112 and 158 ppm, while the range in estuarine (201 - 287 ppm) and marine (212 - 296 ppm) is more or less similar. A decrease of Ca content with depth is noticed in interstitial waters of all the cores whereas the trend in sediment core is just reverse (Table 5, Figs. 13a & b). Arie et al., (1972) have recorded nearly 75% Ca decrease in interstitial waters with depth in Saanich inlet, British Columbia. Similarly Sholkovitz (1973) has observed Ca depletion in interstitial waters of Santa Barbara basin. In sediment Ca in riverine core top is 8143 ppm while the Ca in estuarine (10214 ppm) and marine (10125 ppm) sediments are appreciably high. Mg content in riverine interstitial waters ranges between 20 ppm and 105 ppm, while the range in estuarine (9 - 31 ppm) and marine (11 - 26 ppm) region is very narrow. In sediments, the maximum content of Mg at the surficial sediments of the river is 5142 ppm whereas in estuarine (6012 ppm) and marine (6114 ppm) area the content is slightly more (Table 5). In all the cores the Mg content of interstitial waters decreases with depth whereas in the sediments its content slightly increases (Fig. 14a & b). Earlier Sholkovitz (1973) and Presley and Trefry (1980) have observed large depletion of Mg in interstitial waters. Ramachandran (1992) has observed an average of 2.81% Na₂O in the sediments off Cochin whereas the K₂O content is 0.89%. The average values of CaO and MgO in the surficial sediments off Cochin are 4.83% and 3.81% respectively (Ramachandran, 1992). The average contents of Na, K and Ca in the bulk sediments of Cochin estuary as reported by Padmalal (1992) are 1.51%, 1.16% and 1.05% respectively.

Discussion:

Review of literature shows that enrichment or depletion of the four cations Na, K, Ca and Mg in sediments and interstitial waters are mainly attributed to clay mineral uptake or removal processes. Other processes play a less dominant role.

As Na and K are not precipitated by hydrolysis it is conceivable that they are tied up in clay minerals either by

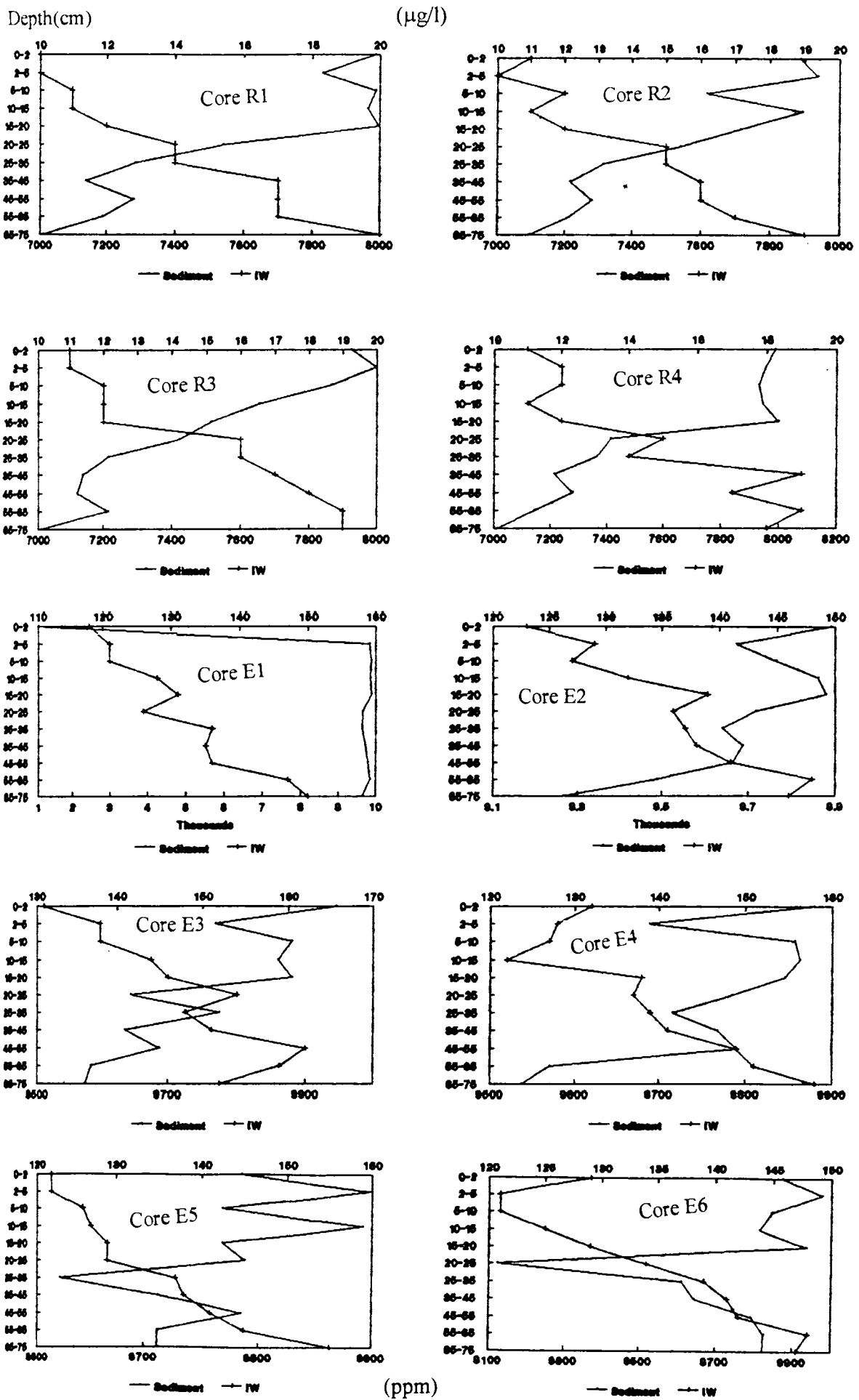


Fig. 11(a) Vertical variations of Na in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

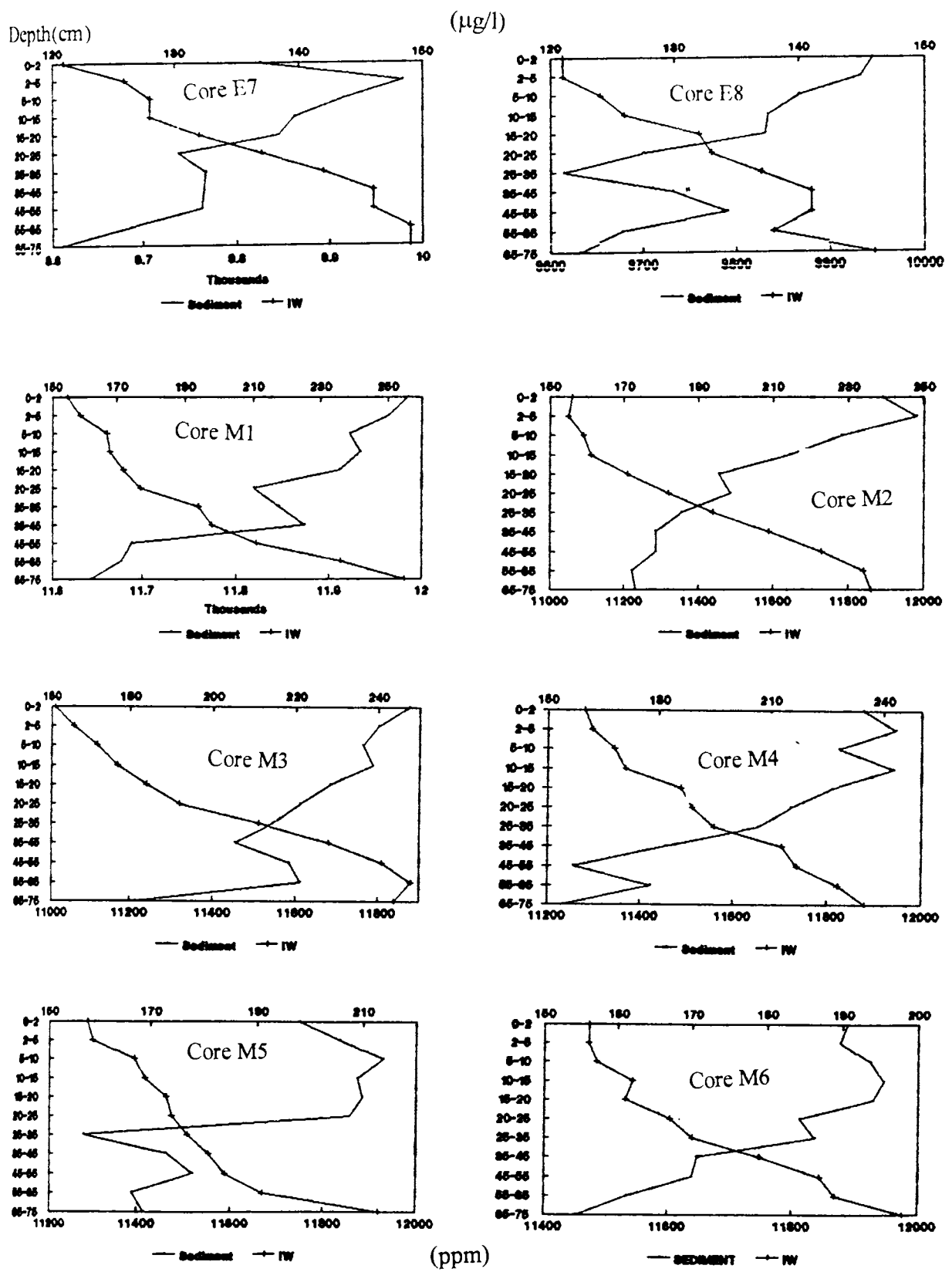


Fig. 11(b) Vertical variations of Na in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

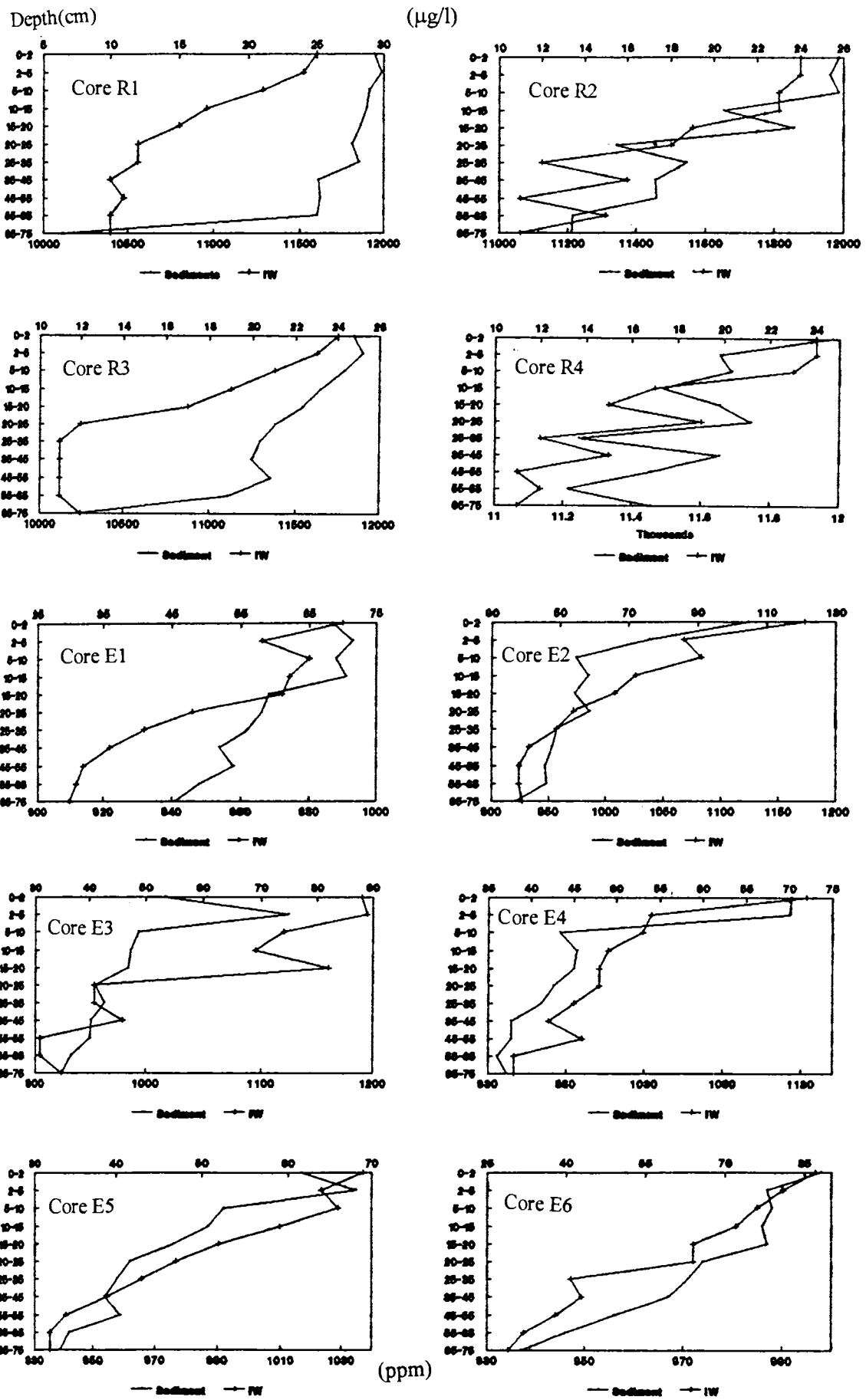


Fig. 12(a) Vertical variations of K in sediments (ppm) and interstitial waters (µg/l)

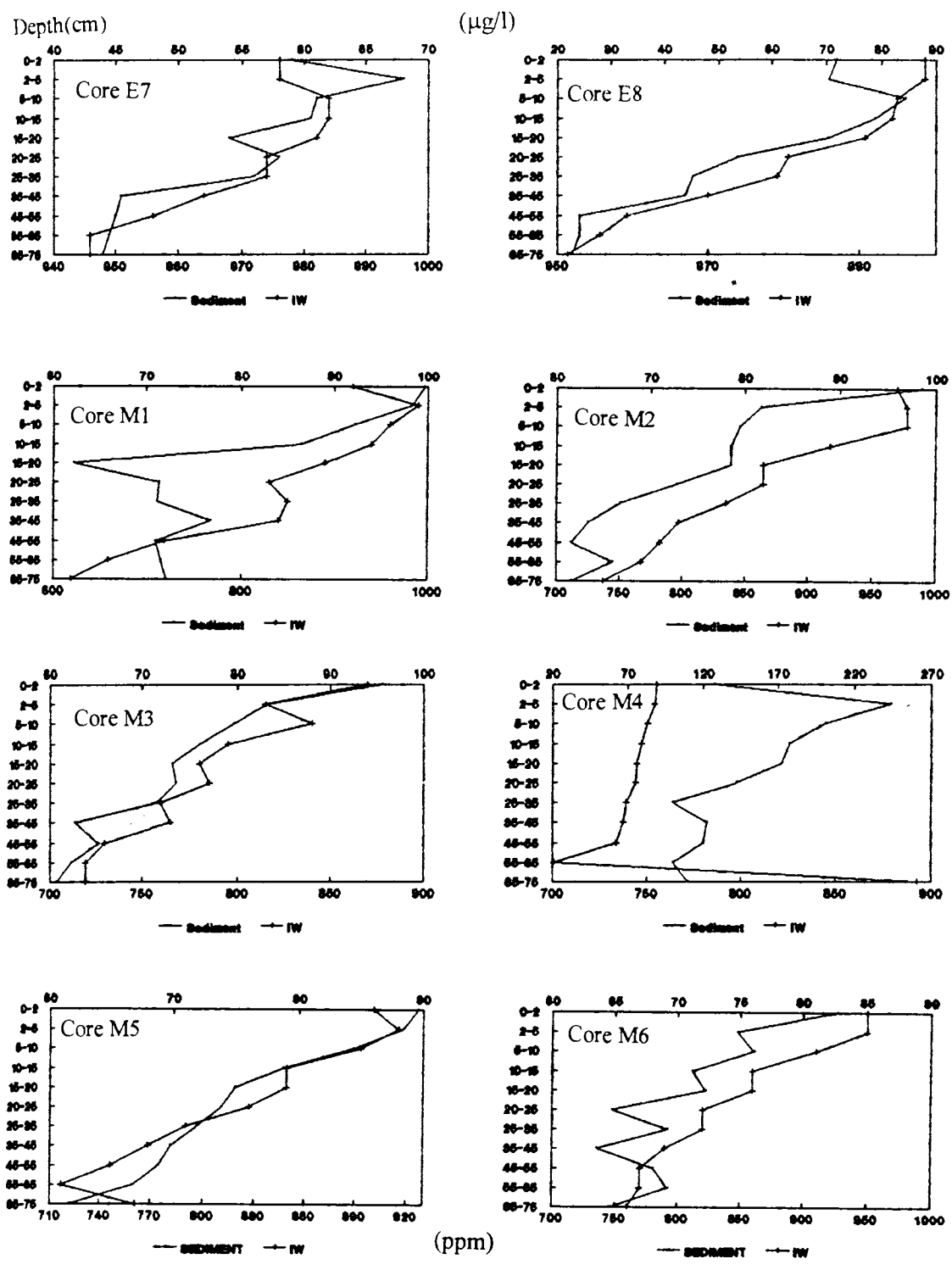


Fig. 12(b) Vertical variations of K in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

adsorption and/or cation exchange. Sediment Na and K shows a decreasing trend with depth indicating breakdown and dissolution of feldspars and other silicate minerals under reducing conditions. Padmalal (1992) has stated that K feldspar constitutes about 20 - 30% of total light minerals in this sediments and is next to quartz content. The relatively high K content in riverine sediments may be due to coarse feldspar content. More over, dissolved K in river region is less than marine and estuarine regions. In contrast the increasing high Na content in estuarine and marine sediments than riverine clearly indicates that Na ion is competing more successfully than K ion to vacant exchange sites in clay minerals. Sayles and Mangelsdorf (1976) has stated that in saline regions Na can even replace Ca in clay minerals. Therefore, the higher content of Na in sediments of estuarine and marine region may be a texturally controlled one. As these sediments are highly muddy in nature with high clay content than river, Na would be fixed more in clay minerals.

Interstitial K depletions are characteristics of nearly all stations and the values are even lower than overlying waters (Table 5). The decreasing interstitial water K concentration with depth is attributed to ion exchange reaction on clay mineral surfaces and with interlayers (Russell, 1970) but it might also be related to authigenic formation or diagenesis of clay minerals (Kastner and Gieskes, 1976; Manheim, 1976). High K depletion in interstitial waters is found especially in continentally derived sediments. Absorption of K by illite is highly possible in estuary as the illite content in this estuary (27%) is significant (Padmalal, 1992). Precipitation of authigenic mineral with a feldspar composition has also been predicted through SEM (Plate 6).

Sediment Ca and Mg show increasing concentration with depth but in interstitial waters a reverse trend is observed. Weathering of plagioclase feldspar would release Ca; similarly uptake of Mg by clay minerals is always found to be accompanied

by release of Ca (Kastner and Gieskes, 1976; Perry et al., 1976; Lawrence et al., 1979). These released Ca has been quantitatively removed from solution by several mechanisms. In this investigation precipitation as CaCO_3 is a likely process where in the required carbonate is being derived from the sulphate reduction process (see Chapter 3). With a large SO_4^{2-} depletion in interstitial waters and a concomitant steady increase in alkalinity with depth, precipitation of CaCO_3 is a distinct possibility (Presley and Kaplan, 1968; Sholkovitz, 1973; Nissenbaum et al., 1972). Sholkovitz (1973) has stated that a small part of sedimentary carbonate should be of authigenic origin. Above all, precipitation of CaSO_4 is a dominant mechanism in removing Ca from interstitial waters (Plates 9 and 10). Therefore, the sediment Ca would remain high at the bottom. At the surficial level both Ca and phosphate would have been precipitated out of solution as calcium phosphate because of high redox potential.

Just like this study, large depletion of Mg in interstitial waters have been reported particularly in nearshore sediments (Drever, 1971; Sholkovitz, 1973; Presley and Trefry, 1980). The concentration of Mg in interstitial waters is even lower than overlying waters (Table 5) and this depletion is attributed to a probable uptake or exchange of Mg with clay minerals and carbonates respectively (Siever et al., 1965). Muller (1969) has found that Ca rich fresh water clays preferentially adsorb Mg in brackish water. The marginal enrichment of Mg in estuarine and marine sediments compared to the riverine is probably attributed to a progressively larger fixation of Mg by clay minerals especially in smectite and chlorite. Weaver (1967) has stated that clay minerals are adsorbing more Na and Mg from the sea water. Sayles and Mangelsdorf (1976) have stated that Mg is an important exchangeable cation in sea water next to Na. Experimental data given by Russel (1970) indicates that upon prolonged soaking montmorillonite will take up Mg from sea water especially when Ph values are greater than 8. On the other hand Sholkovitz (1973) has attributed that the cation uptake capacity

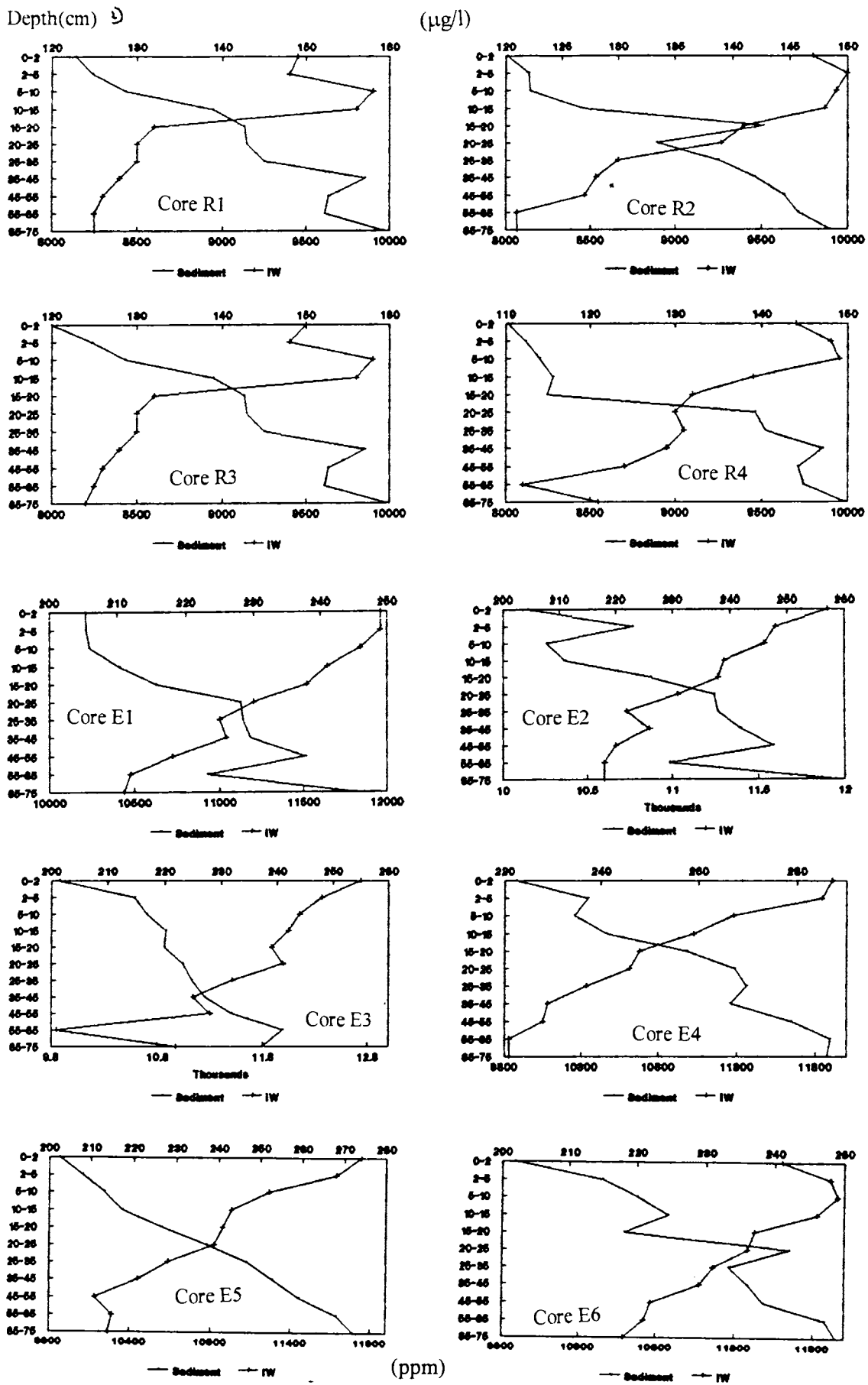


Fig. 13(a) Vertical variations of Ca in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

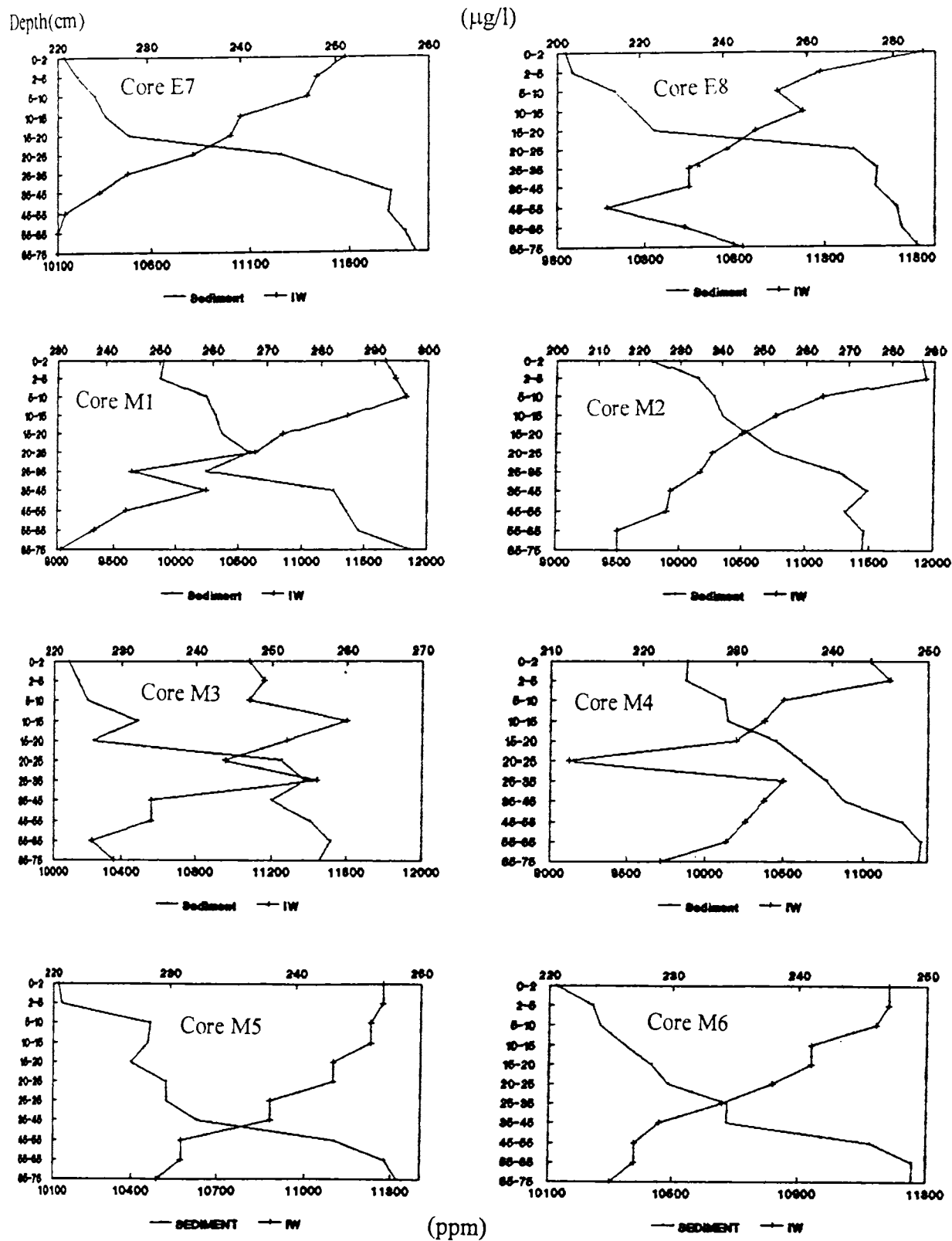


Fig. 13(b) Vertical variations of Ca in sediments (ppm) and interstitial waters (μg/l)

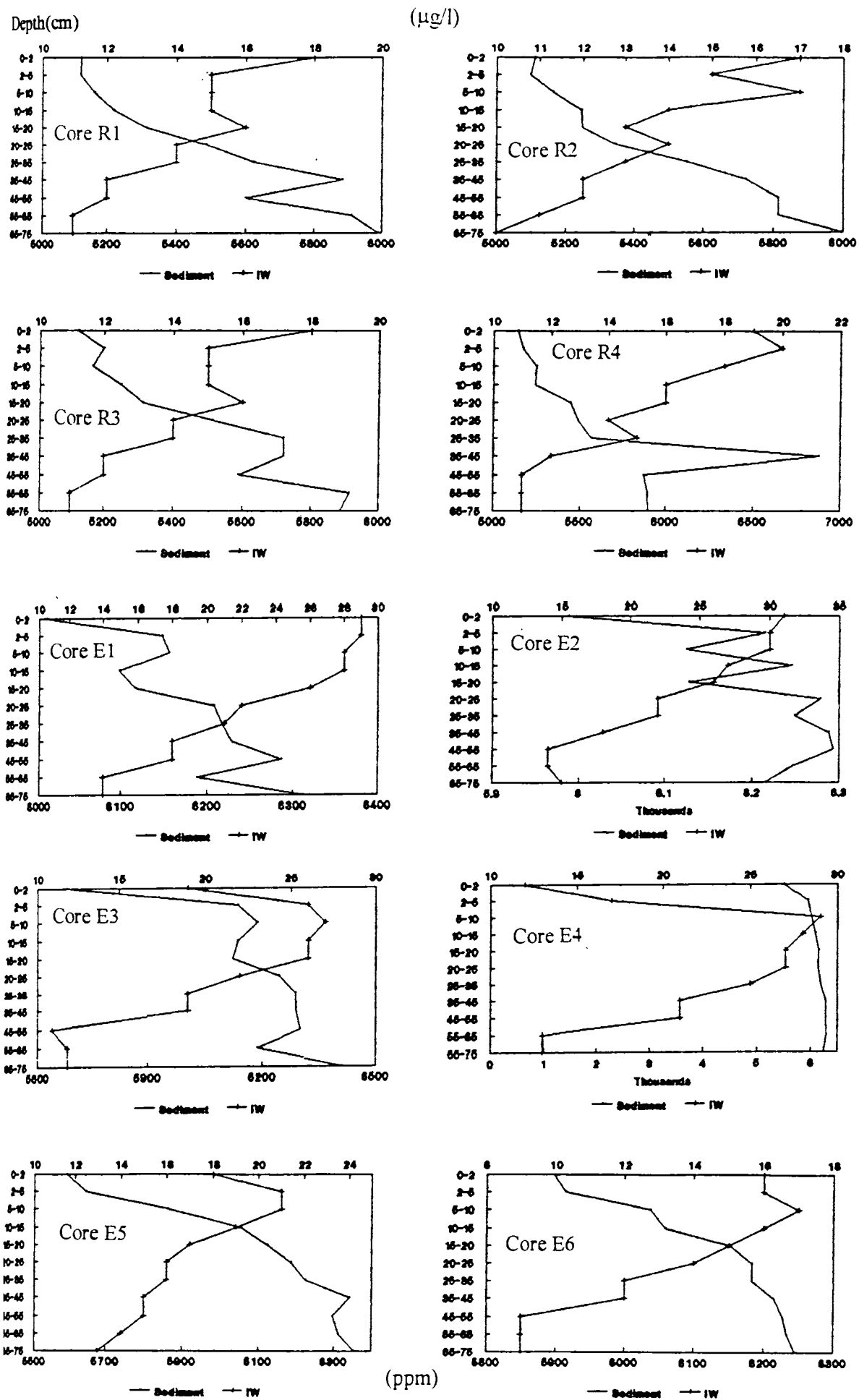


Fig. 14(a) Vertical variations of Mg in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

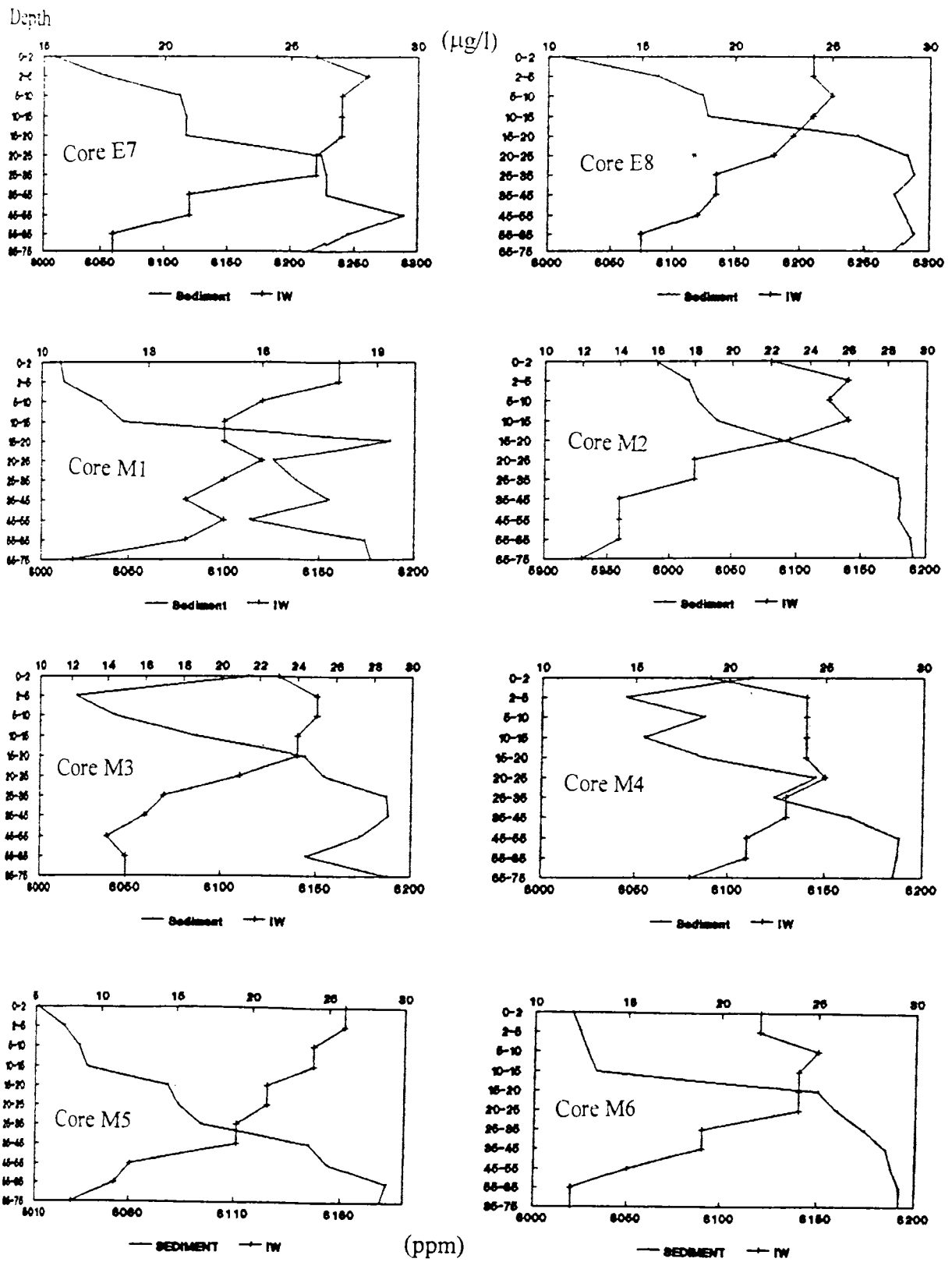


Fig. 14(b) Vertical variations of Mg in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

of clay minerals is very high under reducing conditions because iron oxide coatings absorbed on clay minerals and/or iron-hydroxy interlayers are removed to form iron sulfides, thereby making previously blocked sites available for Mg uptake. Accordingly the bottom core sediments invariably show high Mg content in this study (Table 5 and Figs. 14a & b).

Fe and Mn: The distribution of Fe and Mn in the sediments depends primarily on the rate of flux of particulate and dissolved Fe and Mn, sedimentation rate, biological contribution, the migration of Fe and Mn which in turn controlled by Eh conditions. Mineralogical control and oxide coatings over solid particles would also play a significant role. Fe and Mn also act as major carriers for many trace metals in sediments.

Results:

Concentrations of Fe and Mn are given in Table 6 and plotted in Figs. 15 and 16 respectively. Sediment Fe contents show much fluctuation in the river core. On the otherhand the estuarine and marine sediments show a systematic decreasing trend with depth. Certain cores (eg. E1, E3, E8) show a slight higher Fe values around 2-10 cm level than at core top. Interstitial Fe exhibits a sharp increasing trend with depth (Figs. 15a & b). Ramachandran (1992) has observed an average of 7.76% Fe_2O_3 in surficial sediments off Cochin. The observed average Fe values in surficial bulk sediments of Cochin estuary is 4.39% (Padmalal, 1992). A similar value of Fe has also been observed by Jayasree and Nair (1995).

In sediments Mn reveals a decreasing trend with depth (Figs. 16a & b). In many cores high concentrations are observed just below the surface layers (eg. R2, R4, E1, E3, E6, E7 etc.). In contrast interstitial Mn is very high at the bottom of core (Table 6). The average Mn content in the sediments off Cochin is 177 ppm (Ramachandran, 1992). In the estuarine bulk sediments of

Table 6. Elemental concentrations in sediments (Sed), overlying waters (OW) and interstitial waters (IW)
 (Concentration of waters in ug/l and sediments in ppm except Fe which is in wt.%)

Core B1

Depth(cm)	Fe		Mn		Cu		Co		Cr		Ni		Zn		Cd		Pb		Sr	
	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW
OW	12.0		198		10		12		8		28		65		4		8		21	
0-2	4.2	175	451	20	48	0	38	12	134	2	180	75	94	22	3.2	1.2	56	4	12	11
2-5	4.3	200	473	92	54	1	27	12	104	1	177	160	104	94	4.2	1.4	70	2	6	12
5-10	3.9	114	499	34	36	14	34	13	125	2	195	170	100	39	4.9	1.4	59	4	8	12
10-15	3.2	201	432	17	33	9	19	12	65	1	145	180	98	49	4.6	1.4	65	2	12	12
15-20	3.0	413	480	17	36	16	20	13	88	2	138	370	84	82	4.4	1.2	63	3	29	12
20-25	5.3	411	174	17	64	24	22	13	109	2	156	230	82	81	4.5	2.1	48	2	25	13
25-35	5.5	528	446	20	58	17	24	12	165	2	140	280	83	100	5.2	1.2	52	3	18	12
35-45	6.0	307	455	18	56	14	20	11	150	2	150	390	86	150	7.3	1.2	46	2	18	12
45-55	6.6	355	423	22	38	34	13	12	109	3	155	510	75	122	4.6	1.2	64	3	25	13
55-65	5.5	411	390	25	50	25	15	12	160	4	140	450	75	360	4.5	2.1	67	3	35	12
65-75	5.5	300	450	60	55	22	13	13	96	3	146	410	70	365	2.7	2.1	65	4	58	12

Core B2

OW	13.0		218		8		11		9		27		82		5		11		32	
0-2	3.9	215	478	35	45	2	52	12	274	4	101	32	88	12	2.5	2.8	48	4	22	12
2-5	4.2	350	576	154	48	4	166	62	190	5	124	65	112	54	4.5	2.8	68	6	12	12
5-10	3.9	136	545	200	36	12	132	43	182	4	114	65	108	48	4.9	2.1	59	7	15	14
10-15	3.2	201	450	263	32	10	70	14	137	6	125	100	106	49	4.2	2.1	62	6	10	14
15-20	3.0	413	475	178	36	15	40	32	182	8	114	150	98	68	4.4	1.9	63	5	32	15
20-25	5.3	365	510	153	52	18	35	36	152	4	120	200	98	81	4.5	1.7	48	6	23	14
25-35	5.5	342	411	118	58	17	78	24	160	6	114	300	92	91	4.8	2.5	49	5	19	12
35-45	5.2	326	494	123	56	21	68	12	190	8	50	100	91	138	5.8	2.6	49	7	18	13
45-55	6.6	355	456	120	48	28	52	9	198	4	115	200	85	165	5.1	2.1	64	6	23	14
55-65	5.5	352	434	117	50	25	47	51	152	6	115	190	70	241	4.5	2.4	68	6	35	12
65-75	5.2	325	435	125	48	25	40	55	120	4	115	350	60	290	2.5	2.1	68	6	58	12

Core B3

OW	18.0		193		11		14		10		31		96		6		12		27	
0-2	5.1	12	472	12	51	8	40	13	140	3	160	22	110	14	2.2	2.1	49	4	10	22
2-5	5.4	66	473	43	54	5	35	15	110	5	186	152	104	22	4.2	3.6	71	4	9	12
5-10	3.9	160	499	52	41	14	34	24	117	4	195	168	100	39	4.8	2.1	63	4	11	25
10-15	3.2	125	420	17	36	10	21	24	89	5	162	191	107	48	4.6	3.4	65	5	12	32
15-20	3.8	236	462	25	38	16	20	29	89	5	138	230	101	86	4.2	3.4	63	6	26	28
20-25	5.1	352	247	22	52	24	22	31	112	3	156	230	98	99	4.5	3.4	59	4	25	21
25-35	5.1	352	465	20	58	17	24	25	185	5	186	280	99	102	4.9	2.8	52	5	21	19
35-45	5.6	307	440	18	56	14	18	42	149	5	150	385	96	150	6.7	2.8	45	6	25	18
45-55	6.5	355	423	22	45	22	13	45	122	6	149	498	92	127	4.6	2.7	64	5	25	21
55-65	5.3	368	390	25	50	25	12	39	131	5	140	426	85	360	4.2	2.7	68	5	35	22
65-75	5.1	365	424	36	49	28	12	45	110	5	151	412	79	357	3.8	2.7	62	5	46	22

Core B4

OW	22.0		137		12		13		11		36		88		6		12		31	
0-2	4.1	184	460	96	48	9	110	21	258	4	121	19	112	12	2.8	1.1	52	2	33	12
2-5	4.1	235	576	249	48	9	142	49	198	4	124	22	126	15	4.8	2.1	62	2	38	12
5-10	3.9	136	522	197	39	8	132	43	182	4	112	22	110	15	4.8	2.6	59	4	41	45
10-15	3.6	201	450	263	36	8	88	41	137	6	118	96	110	22	4.2	2.7	61	4	51	36
15-20	3.2	285	465	222	38	12	76	32	186	6	114	128	98	68	4.6	2.7	61	3	56	41
20-25	4.8	225	490	235	51	18	35	36	152	5	126	189	99	68	4.5	2.9	47	5	56	43
25-35	5.2	254	412	181	58	17	78	24	160	6	114	256	96	88	4.8	3.4	49	6	59	35
35-45	5.2	289	464	223	56	22	68	18	177	6	114	256	96	129	4.8	3.4	49	5	62	35
45-55	6.2	312	456	189	48	28	58	12	198	5	115	200	68	180	4.8	3.6	42	5	58	46
55-65	5.8	314	434	87	48	31	47	38	148	6	115	211	61	180	3.6	3.6	42	6	65	46
65-75	5.6	312	423	125	48	31	51	35	126	6	112	325	62	185	2.6	3.7	43	6	60	48

Table 6 continue.....

Core E1

Depth(cm)	Fe		Mn		Cu		Co		Cr		Ni		Zn		Cd		Pb		Sr	
	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW
OW		28		65		4		6		6		8		41		3		6		65
0-2	5.0	0	390	95	67	18	25	23	154	21	156	20	447	24	6	4	91	41	12	36
2-5	5.2	2	470	208	71	57	22	107	143	100	135	520	486	-217	11	22	108	430	26	245
5-10	4.9	5	449	153	66	65	25	110	126	130	118	730	490	235	11	32	92	480	22	345
10-15	5.3	5	350	154	73	65	19	119	167	80	120	570	440	284	11	29	107	410	29	287
15-20	3.9	10	340	172	54	67	15	124	102	80	86	520	274	286	11	33	84	360	71	255
20-25	3.6	10	350	206	64	70	16	121	126	50	108	650	243	322	9	38	87	380	70	239
25-35	4.0	15	340	223	62	70	15	128	110	60	95	510	283	386	9	41	85	360	120	204
35-45	3.8	15	350	250	73	77	12	122	122	70	82	530	220	370	8	48	84	410	145	207
45-55	2.6	15	193	250	64	75	13	113	72	30	88	730	234	375	8	51	58	320	200	241
55-65	3.5	15	305	258	46	71	9	127	81	60	60	610	176	398	7	55	60	380	281	200
65-75	3.3	14	300	250	56	75	2	125	83	70	78	650	192	402	6	56	49	300	282	225

Core E2

OW	31.0		59		5		7		8		7		38		4		5		49	
0-2	6.5	0	415	60	70	18	27	20	150	22	143	16	460	21	8	2	88	33	23	43
2-5	5.2	0	465	150	65	57	25	120	131	98	150	420	480	230	9	12	110	330	26	239
5-10	4.9	5	449	153	61	65	24	125	129	115	121	615	490	235	11	18	100	397	28	249
10-15	5.3	5	355	165	63	63	24	122	129	98	118	570	487	235	8	22	111	395	29	273
15-20	3.9	10	340	172	54	66	21	120	102	80	95	540	374	226	6	23	95	360	62	255
20-25	3.6	10	355	206	65	70	28	106	118	65	108	535	328	288	6	31	98	360	70	241
25-35	4.0	15	340	223	58	70	15	116	110	60	69	510	302	286	5	34	85	347	118	204
35-45	3.8	15	350	265	61	73	16	111	112	70	82	530	302	294	6	38	72	339	145	214
45-55	3.5	15	225	270	64	73	11	158	72	35	88	880	294	318	5	41	58	317	198	223
55-65	3.5	15	295	258	49	81	11	129	81	59	55	610	220	329	5	45	61	311	281	210
65-75	3.4	14	280	280	54	85	11	135	89	62	52	675	225	348	6	52	53	312	291	219

Core E3

OW	27.0		48		6		8		7		8		44		3		6		37	
0-2	5.1	0	387	21	73	21	33	36	167	12	127	21	507	7	18	4	91	28	81	48
2-5	7.8	20	520	20	65	45	35	88	168	30	125	325	529	615	19	42	112	425	86	75
5-10	7.7	30	470	18	66	48	33	94	168	35	124	330	525	545	18	51	109	470	89	40
10-15	6.9	20	358	20	58	52	29	110	159	31	112	330	506	514	18	58	103	450	101	562
15-20	6.9	20	315	40	52	47	31	121	152	35	112	337	510	635	19	54	87	452	101	520
20-25	6.5	20	289	36	52	57	32	121	147	30	109	338	501	540	18	34	87	448	107	559
25-35	6.2	25	217	34	49	55	28	133	152	28	118	329	482	640	17	31	88	450	109	568
35-45	6.2	20	208	41	54	60	28	137	148	28	110	351	456	565	16	30	88	420	111	572
45-55	6.1	35	208	45	54	62	25	139	161	25	98	357	456	938	13	35	73	425	113	567
55-65	6.1	25	191	47	48	67	21	141	151	22	101	360	387	889	13	40	73	450	114	585
65-75	6.1	27	187	51	43	71	21	148	148	22	89	364	356	920	14	45	71	460	114	588

Core E4

OW	28		58		4		6		7		11		41		3		6		37	
0-2	8.1	4	364	18	82	12	37	26	167	24	114	18	558	6	12	3	77	22	61	52
2-5	6.4	7	380	20	79	49	41	112	190	100	110	520	550	117	11	31	75	27	70	245
5-10	6.4	7	385	22	77	49	35	112	198	120	109	500	523	220	9	31	90	117	75	255
10-15	5.9	11	341	87	65	45	35	123	170	130	99	525	447	300	8	37	92	320	65	275
15-20	5.9	18	320	103	65	51	34	123	167	100	87	554	425	335	7	37	95	313	75	305
20-25	5.8	23	320	154	64	53	33	127	121	90	97	580	387	380	7	41	88	310	78	345
25-35	5.7	37	295	172	60	57	29	131	175	80	94	625	390	380	5	41	87	298	70	300
35-45	5.7	36	300	206	60	59	29	133	200	70	95	670	349	380	4	42	86	298	80	287
45-55	5.1	39	305	223	59	63	31	140	225	60	95	670	321	398	4	42	80	287	85	255
55-65	5.2	41	301	123	55	63	31	155	198	35	88	675	315	389	5	42	77	287	90	239
65-75	5.1	40	301	258	55	67	30	155	152	30	82	687	318	401	5	42	73	283	70	200

Table 6 continue.....

Core E5

0V		32		66		5		7		12		12		53		2		8		43
0-2	7.9	5	384	12	33	8	28	12	166	18	127	19	435	24	11	2	69	17	40	64
2-5	6.5	18	398	33	36	41	36	28	185	80	131	84	498	180	12	18	65	27	68	235
5-10	6.4	19	385	49	31	44	35	85	183	187	122	255	450	211	11	29	66	417	78	238
10-15	5.9	26	360	187	28	45	34	112	170	180	111	489	420	300	9	34	72	440	77	234
15-20	5.8	28	357	211	28	51	33	123	167	161	98	500	325	323	9	37	79	397	83	227
20-25	5.8	33	357	254	22	52	33	127	157	128	98	620	326	311	8	41	78	380	88	226
25-35	5.7	37	346	272	22	56	31	131	151	120	96	625	290	329	8	41	87	366	90	221
35-45	5.7	36	320	306	20	59	29	133	151	112	89	620	250	345	5	43	86	323	90	221
45-55	5.4	39	305	308	21	61	31	142	149	98	86	658	210	362	4	42	82	330	98	220
55-65	5.2	41	308	311	20	63	31	153	143	63	80	670	190	371	4	45	76	287	111	220
65-75	5.2	40	304	321	21	63	31	155	152	60	76	698	165	378	4	45	77	280	116	220

Core E6

0V		17		49		8		8		7		11		63		3		9		54
0-2	5.5	6	276	14	91	9	42	8	286	21	101	9	382	31	8	3	66	8	95	38
2-5	5.1	6	391	20	97	22	53	0	295	156	98	87	335	202	11	4	80	8	82	215
5-10	5.1	6	357	28	84	29	53	31	285	287	96	220	333	220	12	4	80	11	85	220
10-15	4.9	27	317	189	82	88	41	46	275	300	90	217	324	300	10	11	71	16	100	243
15-20	4.9	30	280	246	79	91	42	68	264	301	88	225	312	335	10	19	71	56	105	235
20-25	4.8	37	274	280	75	112	41	69	262	280	88	219	287	380	8	24	63	59	109	245
25-35	4.7	38	275	284	75	116	41	96	248	220	60	220	288	387	8	24	62	79	105	220
35-45	4.5	45	265	280	77	121	38	111	231	187	56	180	263	381	7	25	64	215	112	180
45-55	4.5	45	262	285	75	128	38	117	203	173	51	170	254	370	7	32	58	215	125	170
55-65	4.3	51	260	320	74	126	37	117	201	162	50	120	250	388	8	36	55	320	130	163
65-75	4.1	55	254	310	73	129	32	128	211	109	51	118	255	388	8	37	52	320	130	117

0

Core E7

	Fe		Mn		Cu		Co		Cr		Ni		Zn		Cd		Pb		Sr	
	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW
0V		13		42		5		7		11		12		57		2		14		68
Depth(cm)																				
0-2	4.1	4	347	22	84	8	31	6	182	19	88	7	418	36	8	2	75	8	69	31
2-5	4.2	5	408	26	89	9	35	8	212	187	110	29	440	216	12	2	81	27	88	245
5-10	4.1	2	396	34	77	45	29	8	206	168	115	35	425	237	12	12	75	219	90	220
10-15	4.1	18	387	245	75	45	29	57	198	166	111	201	410	289	8	28	70	221	70	218
15-20	3.9	20	380	281	75	51	26	111	198	157	108	227	328	335	8	31	65	201	85	218
20-25	3.9	23	362	280	71	57	25	117	187	168	101	249	321	380	7	37	64	189	97	215
25-35	3.9	38	350	320	69	57	28	123	161	159	105	254	286	397	7	37	64	188	75	220
35-45	3.8	39	355	324	65	62	25	128	153	151	101	262	282	421	5	41	61	176	57	180
45-55	3.6	47	320	370	62	63	24	135	155	146	105	267	241	443	5	41	55	175	91	170
55-65	3.6	47	315	374	61	65	23	135	148	120	102	286	360	421	5	47	53	164	85	120
65-75	3.3	53	315	381	58	65	22	147	148	110	101	284	360	440	5	47	41	165	85	118

Core E8

0V		16		36		8		9		13		14		61		3		12		88
0-2	6.2	5	221	12	78	6	30	5	178	12	66	7	118	28	8	2	63	5	56	23
2-5	6.8	4	298	36	89	10	34	12	166	118	122	88	440	88	11	3	78	5	89	129
5-10	6.7	4	286	48	77	22	29	28	160	222	115	112	428	97	11	8	75	5	90	220
10-15	6.7	21	280	127	76	41	29	57	162	286	112	153	423	156	9	22	70	17	110	284
15-20	6.5	30	280	200	75	45	26	112	158	292	109	159	412	235	5	31	66	125	112	285
20-25	6.5	33	271	211	68	48	27	121	159	280	101	189	389	280	7	37	62	128	118	246
25-35	6.4	41	270	286	69	52	28	118	146	253	98	211	354	280	5	39	64	211	126	220
35-45	6.3	44	262	279	64	56	25	128	146	241	99	222	345	298	5	41	61	317	121	183
45-55	6.3	44	240	280	64	63	24	136	132	189	85	245	321	298	5	41	58	388	129	171
55-65	6.1	47	245	311	61	66	24	135	132	180	85	245	315	311	5	51	53	389	130	149

Table 6 continue.....

Core M1

Depth(cm)	Fe		Mn		Cu		Co		Cr		Ni		Zn		Cd		Pb		Sr	
	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW
0V		31		57		5		5		6		7		43		2		7		48
0-2	6.5	12	380	36	26	5	22	12	145	21	127	13	380	15	8	3	54	12	17	82
2-5	5.1	30	385	103	32	12	35	86	155	70	130	129	370	-85	10	12	92	450	27	292
5-10	4.8	35	317	120	25	26	21	88	142	60	130	132	365	55	8	15	83	430	38	282
10-15	4.4	40	314	134	25	34	22	98	143	55	121	138	367	80	8	29	85	500	49	263
15-20	4.4	50	310	154	24	38	20	94	137	52	117	135	361	97	7	46	79	475	55	243
20-25	4.2	45	322	162	21	39	20	103	137	55	117	140	351	112	5	57	64	450	55	255
25-35	4.2	50	287	170	20	42	18	105	129	49	96	142	332	136	5	66	64	425	87	262
35-45	4.1	40	286	189	18	44	18	112	128	56	96	155	325	148	8	65	59	400	96	279
45-55	4.0	30	290	190	18	48	18	116	129	42	95	155	332	153	5	69	59	425	115	222
55-65	4.0	45	274	195	19	52	19	120	125	41	87	161	328	168	5	72	58	450	115	212
65-75	3.9	30	276	200	19	53	19	122	112	45	83	162	304	180	5	77	56	450	128	290

Core M2

0V		24		62		6		7		5		8		44		3		7		38
0-2	7.1	12	276	26	25	3	80	14	182	20	76	12	112	31	6	2	52	14	31	68
2-5	5.1	21	384	94	25	5	54	62	182	89	100	65	250	44	12	2	72	16	145	217
5-10	4.8	21	370	105	20	5	73	87	190	94	114	126	122	187	11	5	70	21	141	220
10-15	4.8	30	391	124	20	40	11	112	198	112	108	187	171	193	11	8	65	27	121	300
15-20	4.3	41	375	144	18	45	82	124	182	128	101	215	153	202	9	17	64	40	110	335
20-25	4.3	47	321	187	18	45	59	145	190	137	99	268	145	207	9	20	65	114	100	280
25-35	4.1	50	300	196	17	47	80	187	182	137	90	270	170	219	8	22	59	127	104	220
35-45	4.2	55	287	205	17	48	95	187	185	145	89	285	175	246	9	28	59	215	107	180
45-55	4.1	55	290	222	15	49	85	214	180	149	89	299	185	287	8	32	55	215	113	170
55-65	4.1	51	281	160	15	56	85	228	182	158	90	287	180	294	8	37	55	370	110	120
65-75	4.1	61	274	287	15	55	95	230	171	155	73	288	185	299	8	44	55	414	120	110

Core M3

0V		31		65		5		8		5		7		51		2		8		42
0-2	6.5	65	276	32	20	2	74	8	175	22	101	8	182	33	5	3	55	12	95	82
2-5	6.4	145	395	80	25	12	85	12	185	37	80	12	234	88	12	2	68	15	82	114
5-10	6.5	248	375	120	20	12	75	28	160	64	89	20	233	121	11	4	65	17	85	186
10-15	6.4	292	363	245	20	20	75	89	165	225	90	30	214	148	11	8	58	89	100	210
15-20	6.3	315	354	286	18	23	70	114	167	235	63	35	172	163	9	11	55	105	105	215
20-25	6.1	315	304	280	18	29	67	156	180	280	62	230	161	157	9	17	49	109	95	280
25-35	5.8	328	275	320	17	37	59	174	185	220	90	220	168	179	8	17	49	109	105	220
35-45	5.8	337	255	345	13	45	59	198	175	180	76	225	173	202	9	24	49	127	90	180
45-55	5.8	349	246	370	12	54	59	187	160	170	65	261	175	214	5	25	43	138	85	170
55-65	5.7	355	286	374	12	54	54	190	162	120	89	270	152	219	5	32	49	145	100	120
65-75	5.7	371	208	391	11	54	54	199	162	120	62	290	155	246	4	32	44	196	102	110

Core M4

0V		36		58		7		9		4		8		44		3		7		53
0-2	5.2	20	290	12	18	5	85	3	201	18	87	14	107	28	7	2	50	11	173	88
2-5	5.2	30	300	62	24	58	91	12	220	27	95	129	214	135	8	8	55	36	180	164
5-10	5.1	35	287	120	18	45	90	101	201	48	95	132	236	156	12	31	53	430	167	282
10-15	5.1	40	265	134	15	42	82	98	200	65	80	138	245	158	12	60	48	500	164	263
15-20	4.8	50	237	154	13	48	76	94	174	61	81	135	257	187	10	62	45	475	160	243
20-25	4.6	45	243	162	13	56	70	103	174	55	78	140	269	188	8	70	44	450	155	255
25-35	4.6	65	245	170	12	62	71	95	162	49	70	142	269	196	8	75	44	425	148	262
35-45	4.6	80	220	189	11	64	69	85	165	44	65	155	277	185	8	65	35	400	148	279
45-55	4.3	95	220	190	15	71	60	95	168	41	65	169	298	212	7	57	35	425	148	222
55-65	4.3	105	217	195	16	72	54	109	158	35	64	170	298	215	8	55	33	355	151	212
65-75	4.1	109	217	200	15	53	54	122	151	33	64	177	289	220	8	55	35	354	151	290

Table 6 continue.....

Core K5

Depth(cm)	Fe		Mn		Cu		Co		Cr		Ni		Zn		Cd		Pb		Sr	
	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW
0V		41		64		8		6		7		6		51		4		8		43
0-2	4.1	21	280	22	17	8	84	6	182	12	18	11	217	28	8	2	47	12	87	81
2-5	4.7	29	290	28	27	12	89	85	197	16	80	18	215	71	9	5	53	48	64	97
5-10	4.7	36	275	64	30	5	65	89	160	19	82	65	202	127	8	6	45	86	63	112
10-15	4.1	27	274	130	28	40	64	112	161	20	71	112	187	127	7	14	37	112	62	121
15-20	4.1	45	265	137	28	47	63	107	160	27	65	127	164	151	7	20	35	108	60	120
20-25	3.8	44	284	140	21	49	52	117	185	36	65	127	150	155	8	35	33	103	60	125
25-35	3.9	49	265	151	21	49	51	121	155	47	64	130	154	176	8	43	30	96	54	145
35-45	3.9	62	292	157	18	55	48	121	154	80	63	128	165	187	7	49	30	88	54	143
45-55	4.0	62	217	163	18	70	45	132	164	85	62	141	145	167	7	54	32	67	60	143
55-65	4.0	55	214	174	19	71	49	137	134	85	60	145	135	186	6	59	32	63	60	167
65-75	3.5	54	215	179	20	69	51	137	130	79	50	153	130	184	5	62	32	59	53	167

Core K6

Depth(cm)	Fe		Mn		Cu		Co		Cr		Ni		Zn		Cd		Pb		Sr	
	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW	Sed	IW
0V		45		73		7		8		7		8		55		5		11		46
0-2	4.8	18	280	31	26	8	68	8	215	14	27	12	187	33	4	2	37	9	80	59
2-5	4.7	21	280	46	26	18	75	14	228	16	87	18	194	67	12	6	52	29	61	86
5-10	4.3	27	280	67	28	20	70	39	223	21	87	31	185	88	9	8	51	112	15	97
10-15	4.1	28	250	87	24	21	64	82	212	20	63	52	185	112	7	14	47	98	13	114
15-20	4.2	37	240	96	24	21	63	124	212	24	62	85	163	118	7	14	49	97	22	144
20-25	4.0	43	238	120	21	28	69	127	185	28	54	87	167	139	5	27	41	87	13	137
25-35	4.0	55	238	120	21	29	58	132	185	42	54	95	184	134	4	84	37	65	14	140
35-45	4.0	55	240	141	20	31	62	135	177	48	58	120	135	149	4	85	36	66	31	136
45-55	3.8	62	235	197	20	34	65	135	165	87	62	125	137	151	5	63	35	58	29	127
55-65	3.9	68	237	186	18	38	48	141	182	84	52	127	141	157	4	85	36	51	27	110
65-75	3.8	70	217	200	17	40	45	145	184	65	52	135	145	168	3	67	37	50	26	103

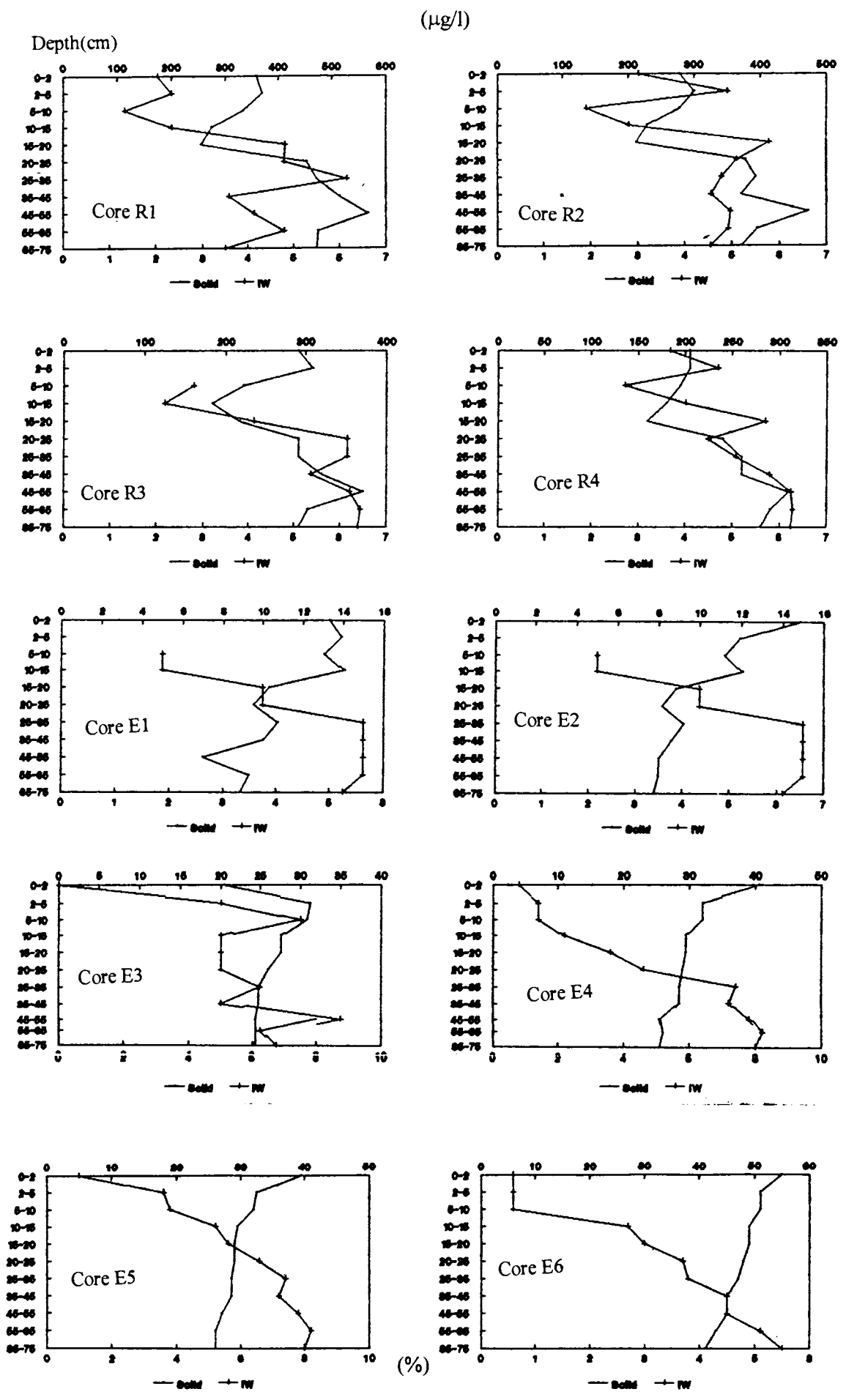


Fig. 15(a) Vertical variations of Fe in sediments (%) and interstitial waters ($\mu\text{g/l}$)

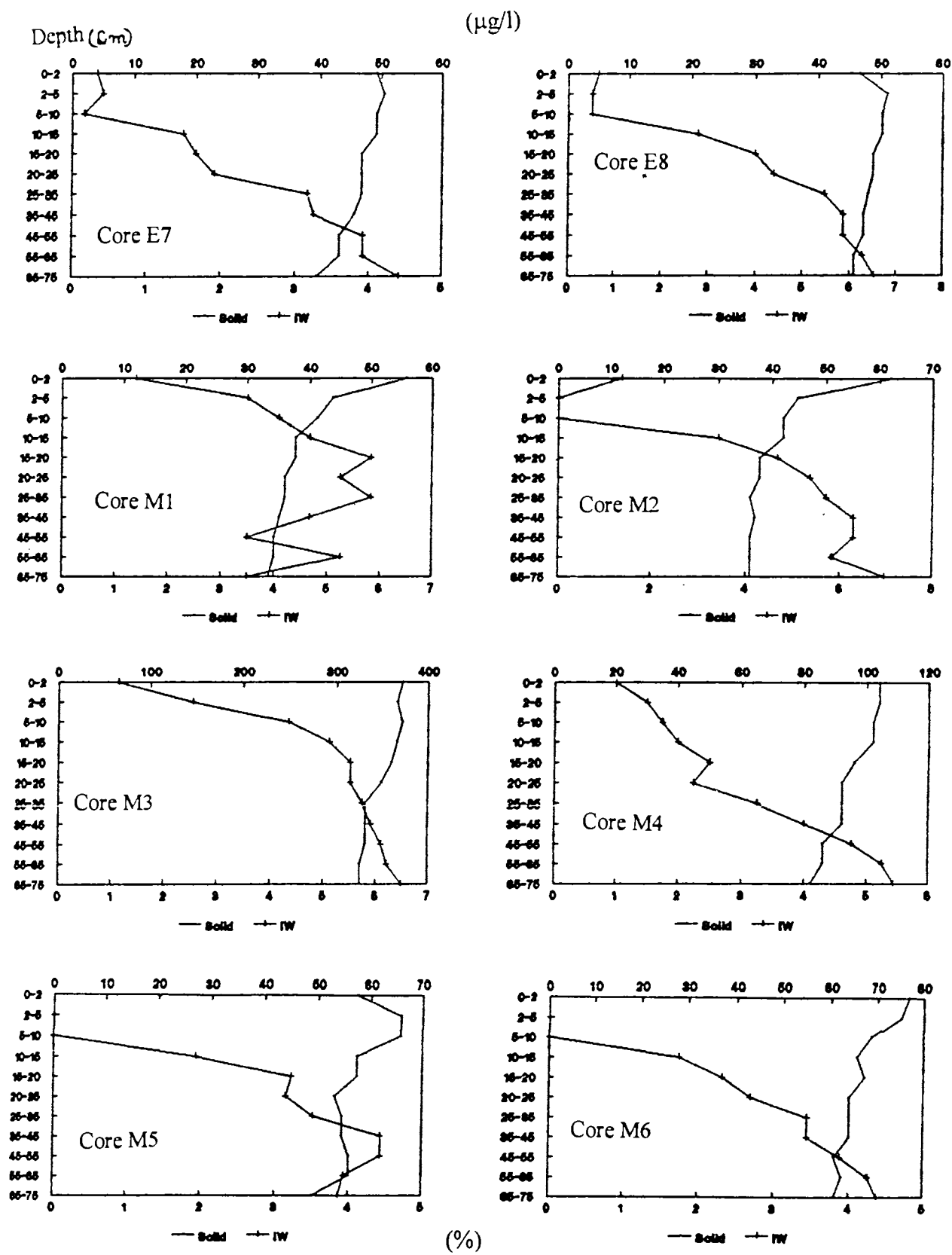


Fig. 15(b) Vertical variations of Fe in sediments (%) and interstitial waters ($\mu\text{g/l}$)

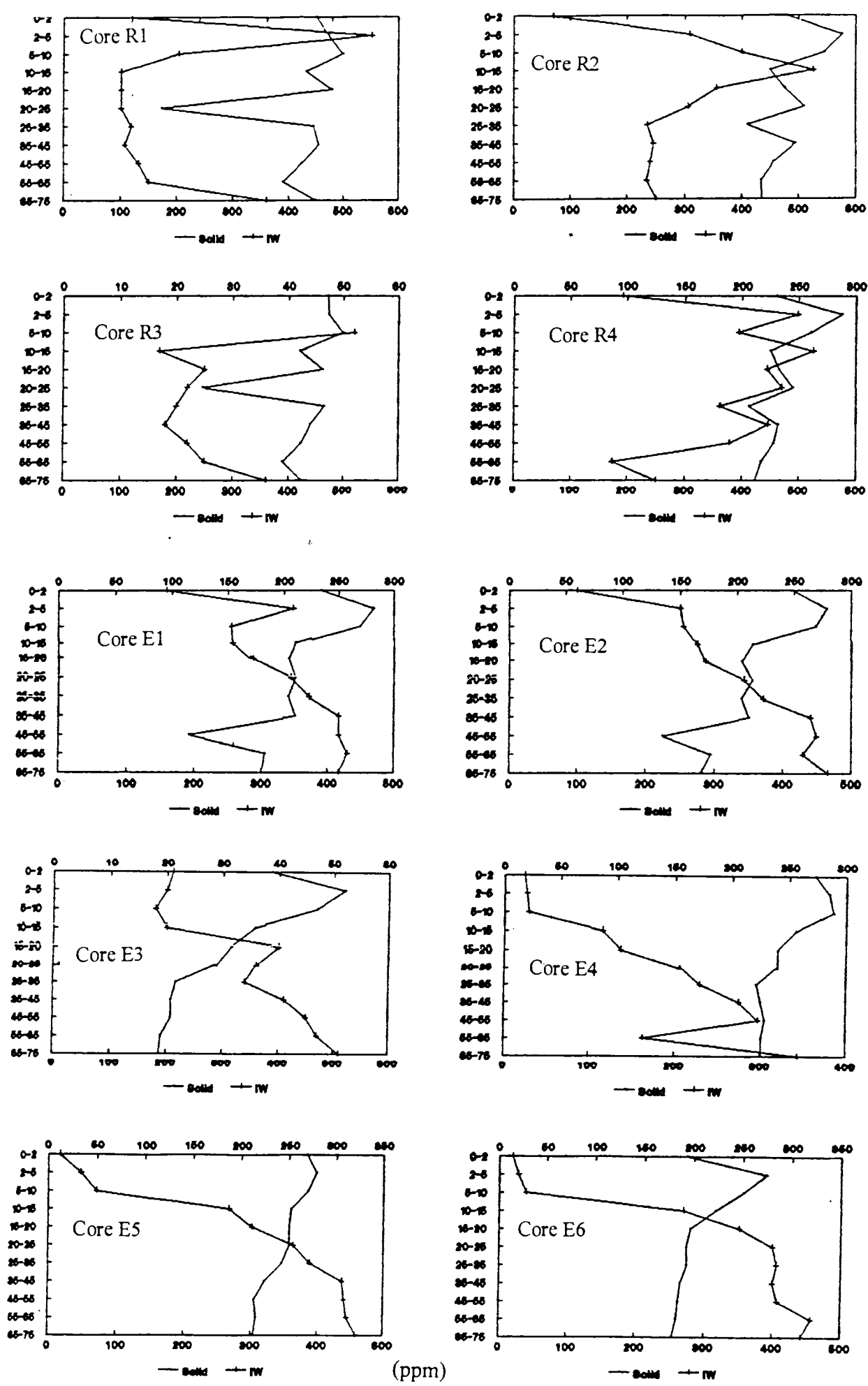


Fig. 16(a) Vertical variations of Mn in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

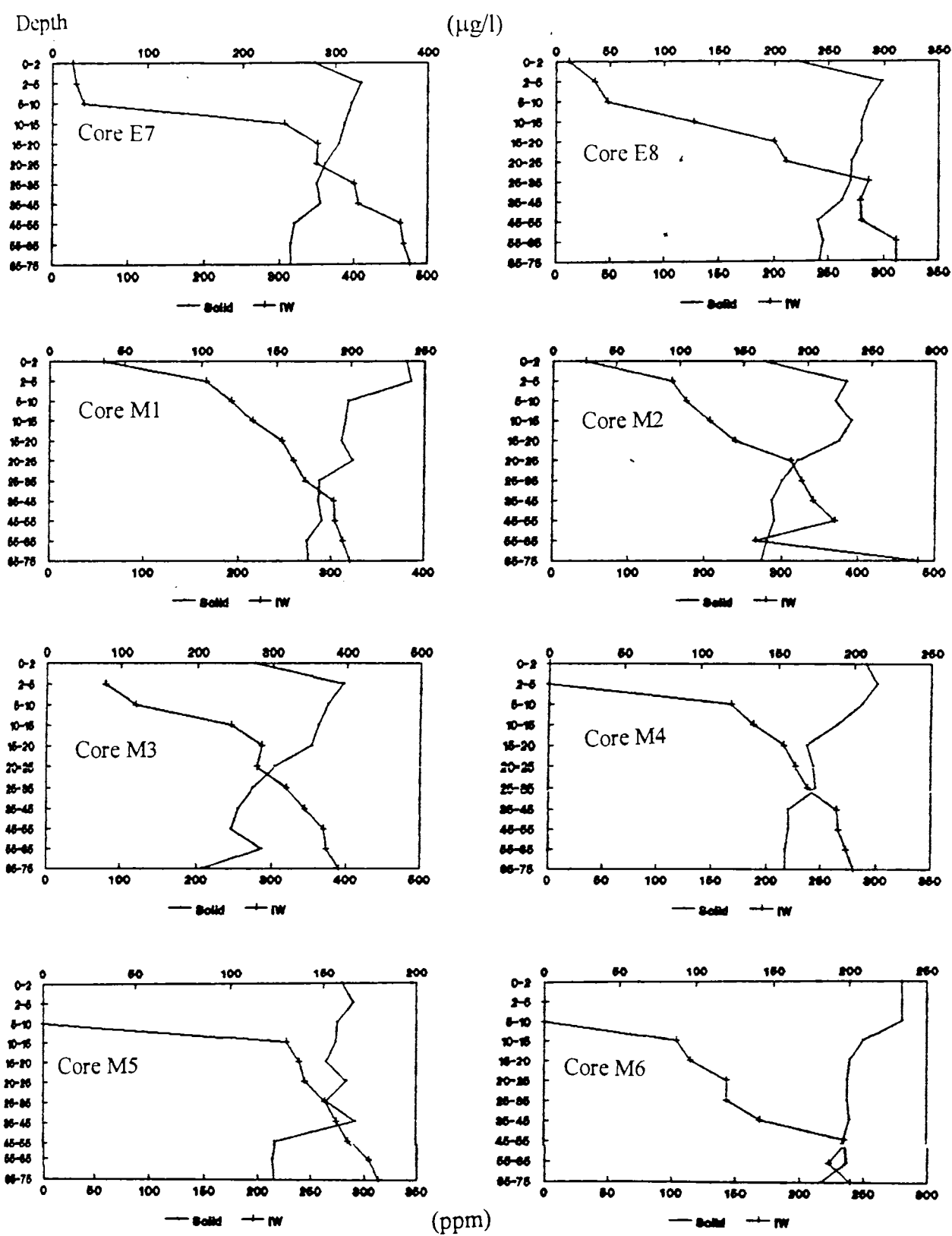


Fig. 16(b) Vertical variations of Mn in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

Cochin the average Mn according to Padmalal (1992) is 366 ppm. However, Jayasree and Nair (1995) have reported a low Mn content (av. 54 ppm) during pre monsoon season.

Discussion:

Concentrations of Fe and Mn in estuarine interstitial waters are often reported to be very high and this is due to the dissolution of sediment Fe and Mn under reducing condition (Holderen et al., 1975; Lu and Chen, 1977). Presley and Trefry (1980) have stated that where interstitial O_2 and NO_3^- deplete, concentration of dissolved Fe and Mn clearly increase and vice versa. Similar increasing trends of Fe and Mn have been observed by Gaillard et al., (1986).

In the Vembanad estuarine sediments, where the penetration of oxygen is very much restricted to the top few cm of the cores and thereby very low Eh even at the surficial level, existence of reducing condition very close to the sediment-water interface is evident (Chapter 3). The effect of Eh on metal diagenesis can be seen through the high interstitial Fe and Mn which are highly susceptible to dissolution under reducing condition. From low levels at the sediment-water interface, the concentrations of dissolved Fe and Mn increase sharply with depth to values which are several orders higher than in core top layers.

The high Fe and Mn build up in interstitial water below the depth of oxygen penetration/bioturbation zone is caused by reduction processes. In anoxic sediments enzymatic reduction of Mn (Froelich et al., 1979) and Fe (Stumm and Morgan, 1981) has been postulated. Also under low NO_3^- concentrations, Fe can be reduced by denitrifying bacteria (Ehrlich, 1981). As in this study NO_3^- decrease sharply down the sediment column reduction of Fe and Mn can be accelerated. The released Fe and Mn diffuse into the oxic portion of the sediment column and are removed again from the interstitial waters at or near the sediment-water interface and therefore their concentration in the core top sediments or just below it are always higher. The removal is by

the precipitation of Fe and Mn oxides or oxyhydroxides (Frolich et al., 1979; Klinkhammer, 1980; Emerson et al., 1980; Klinkhammer et al., 1982; Bender and Heggie, 1984; Heggie et al., 1986; Shaw, 1988; Shaw et al., 1990). Since the surficial sediments show relatively higher pH than at sub bottom, spontaneous oxidation is very much possible as far as Fe is concerned. The oxidation rate increases 100 fold per unit pH increase (Stumm and Morgan, 1981). On the other hand Mn oxidation at the surficial level is mediated enzymatically by microorganisms. For spontaneous oxidation of Mn the required pH is over 9 (van-Veen et al., 1978). Further, the released Mn can be re-adsorbed at the surficial level onto pre-existing/freshly formed Mn oxide phases either by inorganically or through microbiological processes (Santschi, et al., 1990).

The significant enrichment of Fe and Mn down the core indicates that a major portion of these metals are bound within the sediment other than oxide form. Through reduction process only a part of Fe and Mn are remobilized to the top layers. On the other hand a major part of the remobilized metals can once again be regulated by formation of other sparingly soluble compounds in an anoxic environments. Santschi et al., (1990) have stated that Fe^{2+} production rates are no measures of the reduction rates as some of the Fe^{2+} produced can be formed as sulfide, phosphate and carbonate minerals. So also Emerson (1976) has found $MnCO_3$ to be the solubility limiting in an anoxic sediments of Lake Greifen in Switzerland. Mastisoff et al., (1980) have found MnS to be limiting in Lake Erie. A detailed account on the dissolution/ reprecipitation mechanism has been given by Calvert and Price (1972). Heavy mineral contribution of Fe and Mn are also very significant (Rajendran et al., 1996).

Cu, Co, Ni, Zn, Pb, Cd, Cr and Sr:

Results:

The concentrations of Cu, Co, Ni, Zn, Pb, Cd, Cr and Sr

both in sediments and interstitial waters are given in Table 6 and plotted in Figs. 17 to 24. The concentration of Cu, Co, Ni, Zn, Pb, Cd and Cr show a general decreasing trend with depth in sediments. However, in interstitial waters a reverse pattern is noted (Table 6) except Cr. Just like Fe and Mn, most of the metals show an enrichment just below top of core. Sr content in sediments increases with depth but in interstitial waters decreases. In the nearshore surficial sediments of Cochin Ramachandran (1992) has observed an average of 15.4 ppm Cu, 64.4 ppm Co, 146.5 ppm Ni, 79.6 ppm Zn, 50.3 ppm Pb, 27.4 ppm Cd 84 ppm Cr and 272.6 ppm Sr respectively. In the Vembanad estuarine bulk sediments Padmalal (1992) has observed an average of 31 ppm Cu, 20 ppm Co, 109 ppm Ni, 90 ppm Zn, 14 ppm Pb, 4 ppm Cd and 125 ppm Cr respectively. Recently Jayasree and Nair (1995) have observed during pre monsoon period an average of 0.35 ppm Cu, 2.1 ppm Co, 3 ppm Ni, 14 ppm Zn, 2.7 ppm Pb, 5 ppm Cd and 1 ppm Cr. The wide variations of the above metals within surficial levels are often attributed to metal pollution from various sources and more particularly from industries. Several pockets of high concentration of metals are also observed (Padmalal, 1992) indicating point sources.

DISCUSSION:

Cu, Co, Ni, Zn and Pb: The concentration of Cu, Co, Ni, Zn and Pb metals in interstitial waters generally increase with depth. In a few cores concentrations in interstitial waters show an increasing trend towards top of core (Table 6). Sawlan and Murray (1983) have shown several patterns for Cu and Ni in sediments of red clay, hemipelagic and highly reducing shelf area. Similarly irregular variations of Cu, Co, Ni, Zn and Pb has been reported by Duchart et al., (1973). On the other hand their values in sediments increase towards sediment-water interface. In this study all the trace metals generally follow the same pattern shown by Fe and Mn. Earlier Sawlan and Murray (1983) has observed that where nitrate is present Cu is also maintained in solution. Since denitrification and sulphate

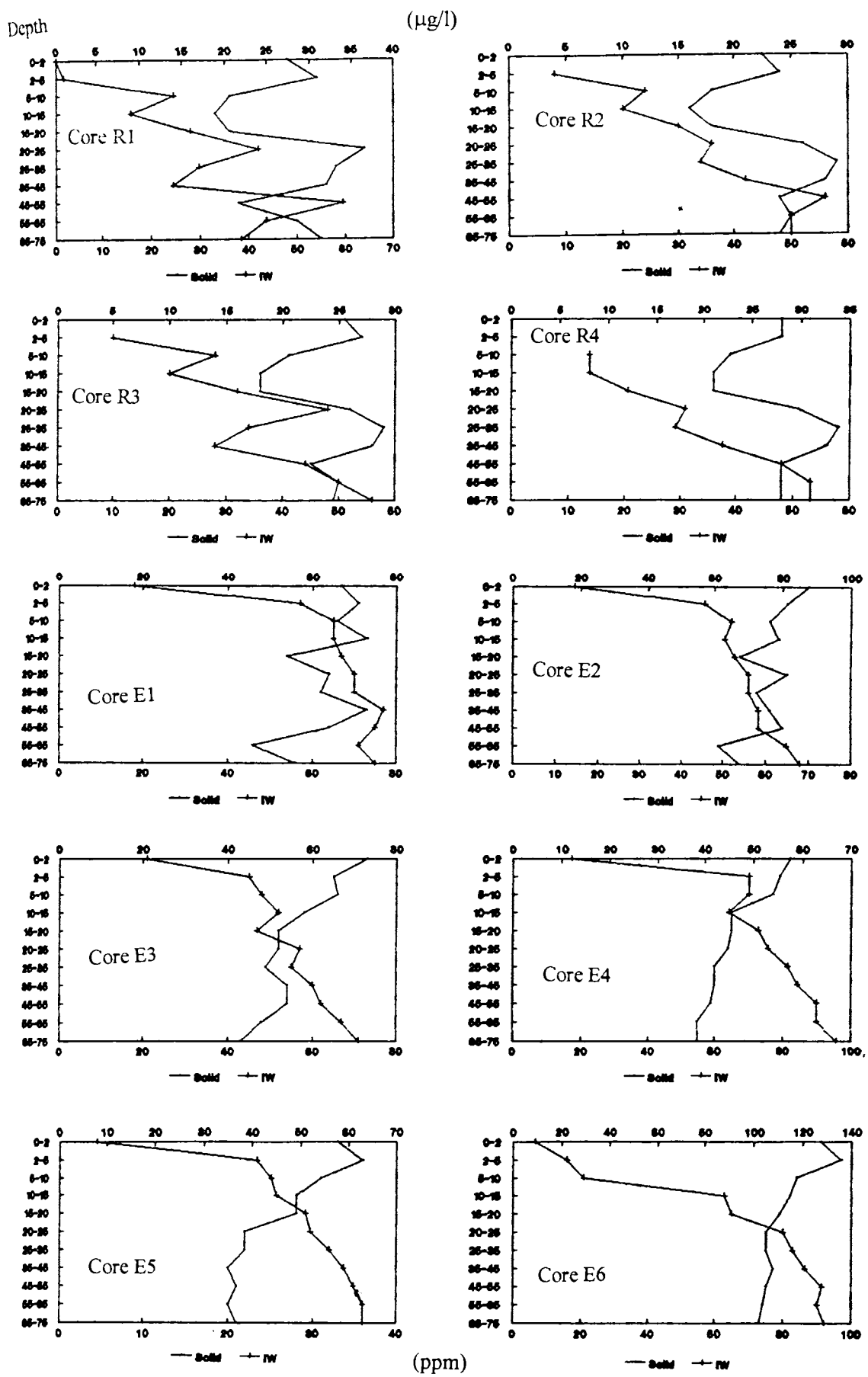


Fig. 17(a) Vertical variations of Cu in sediments (ppm) and interstitial waters (µg/l)

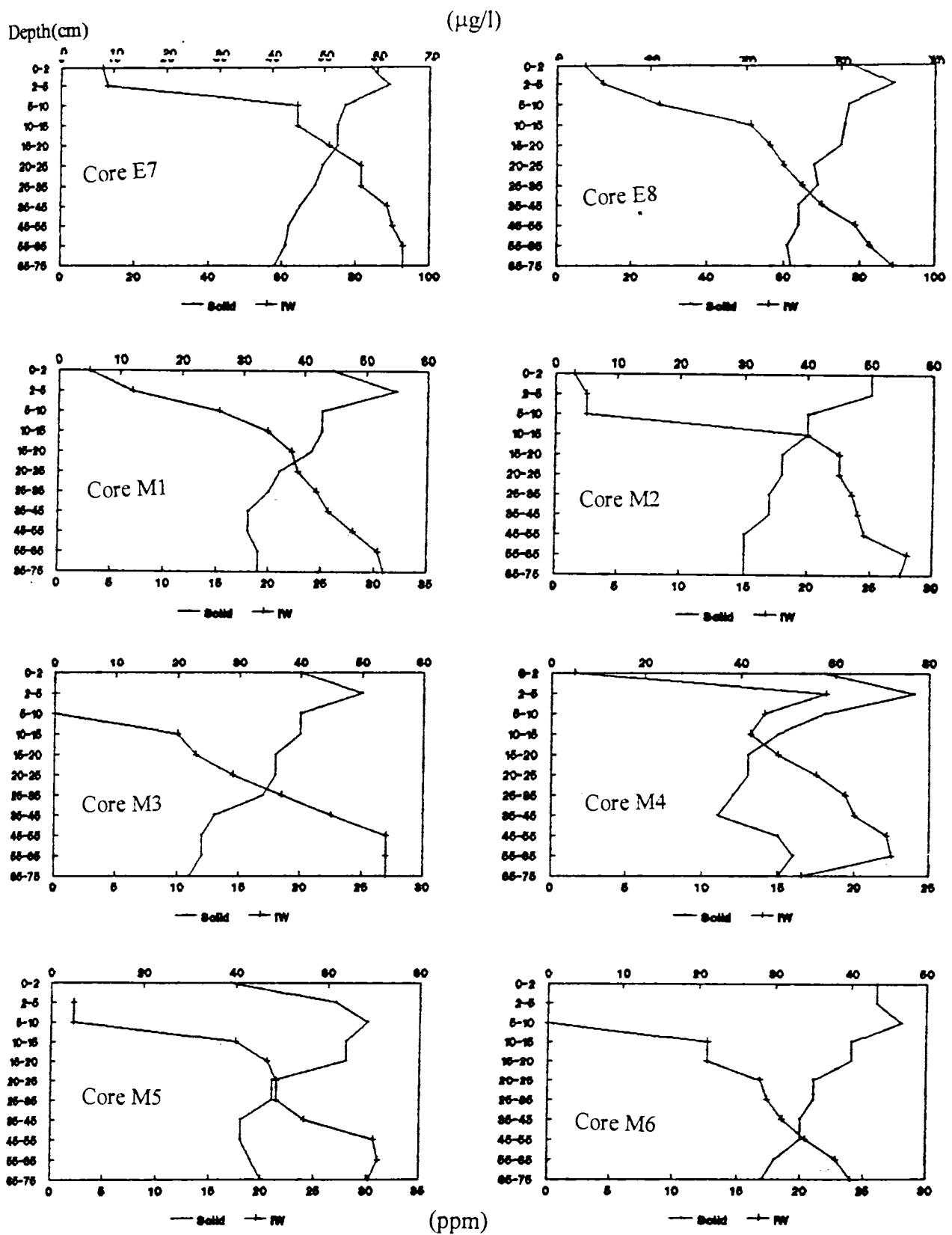


Fig. 17(b) Vertical variations of Cu in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

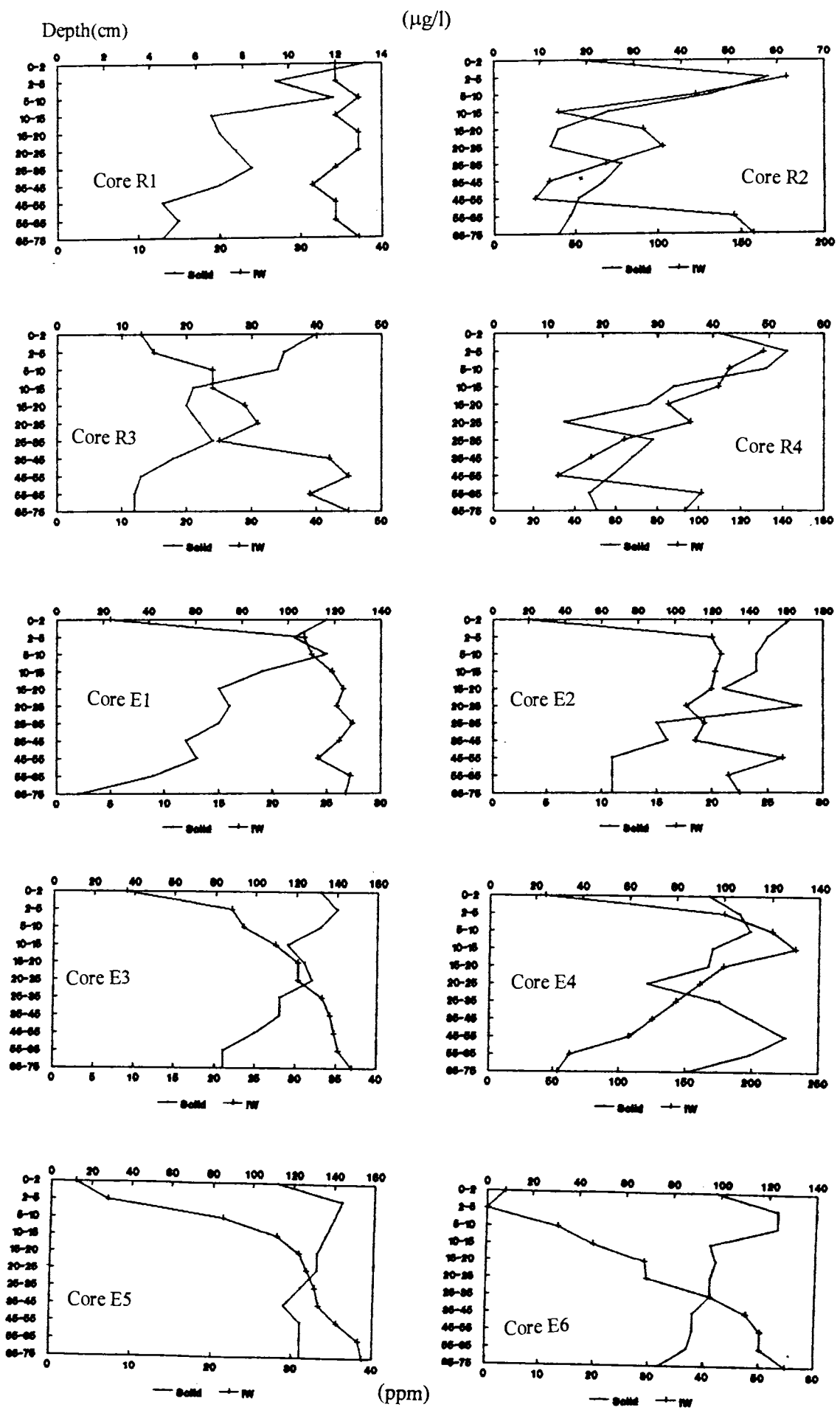


Fig. 18(a) Vertical variations of Co in sediments (ppm) and interstitial waters (µg/l)

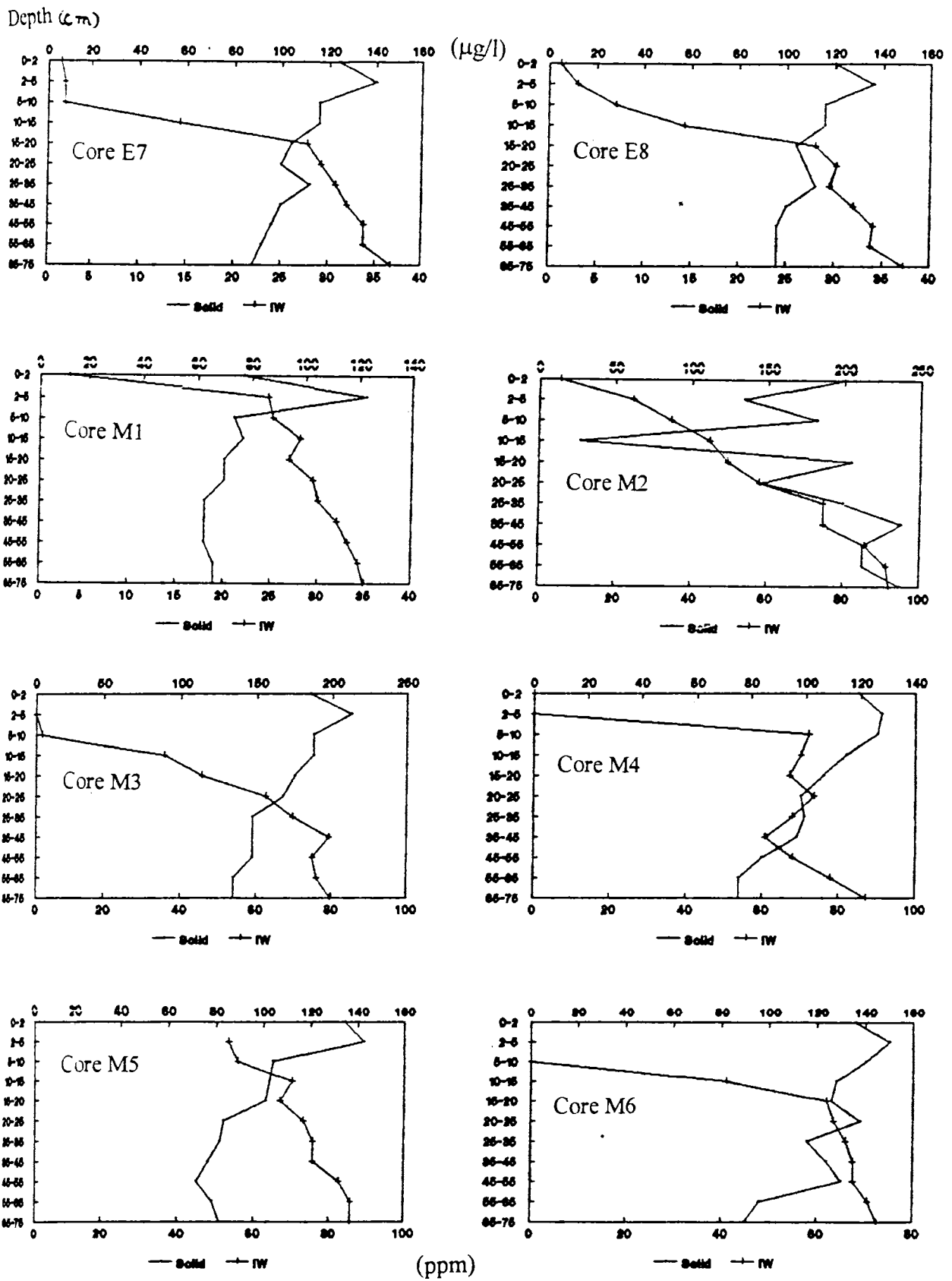


Fig. 18(b) Vertical variations of Co in sediments (ppm) and interstitial waters (µg/l)

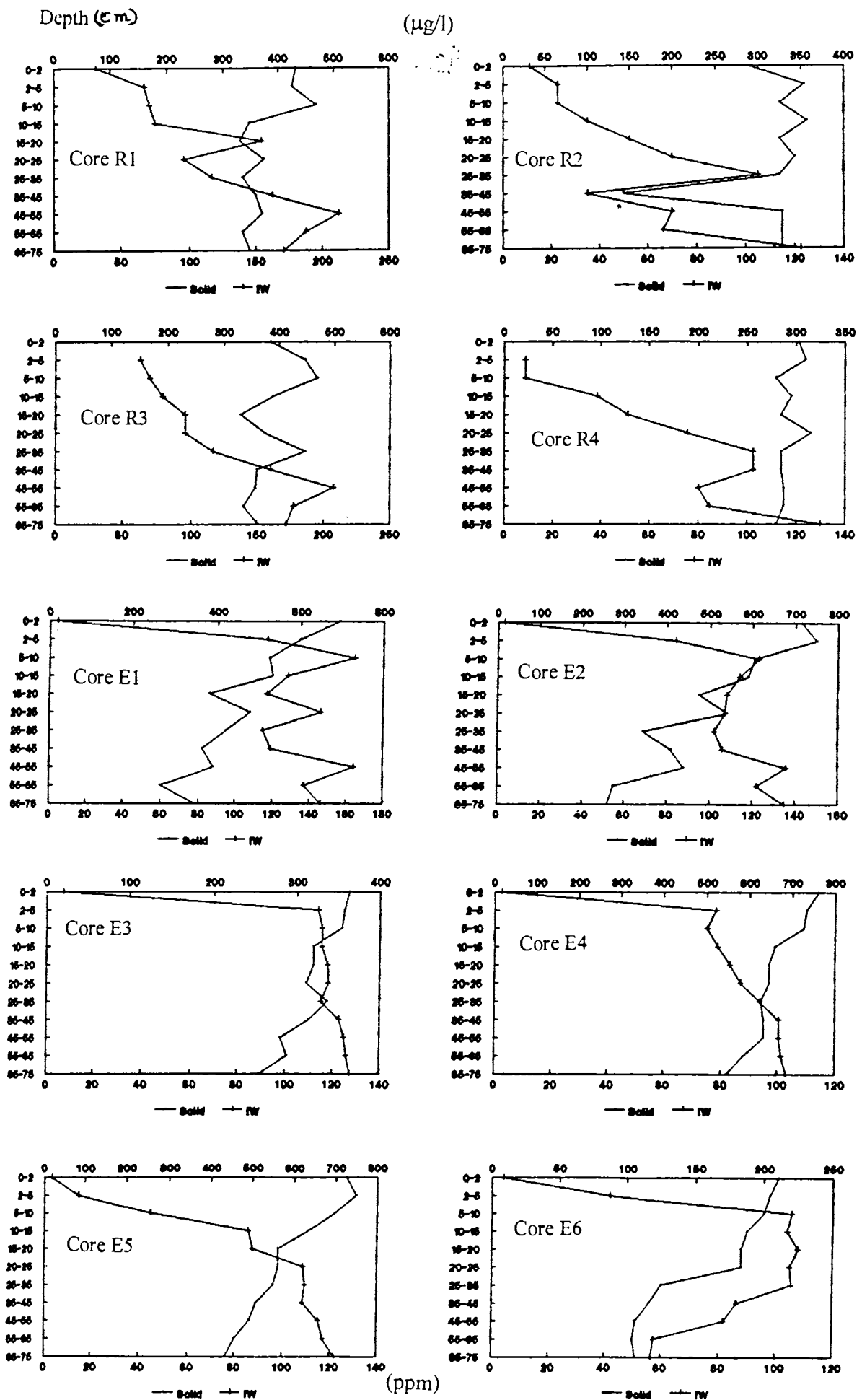


Fig. 19(a) Vertical variations of Ni in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

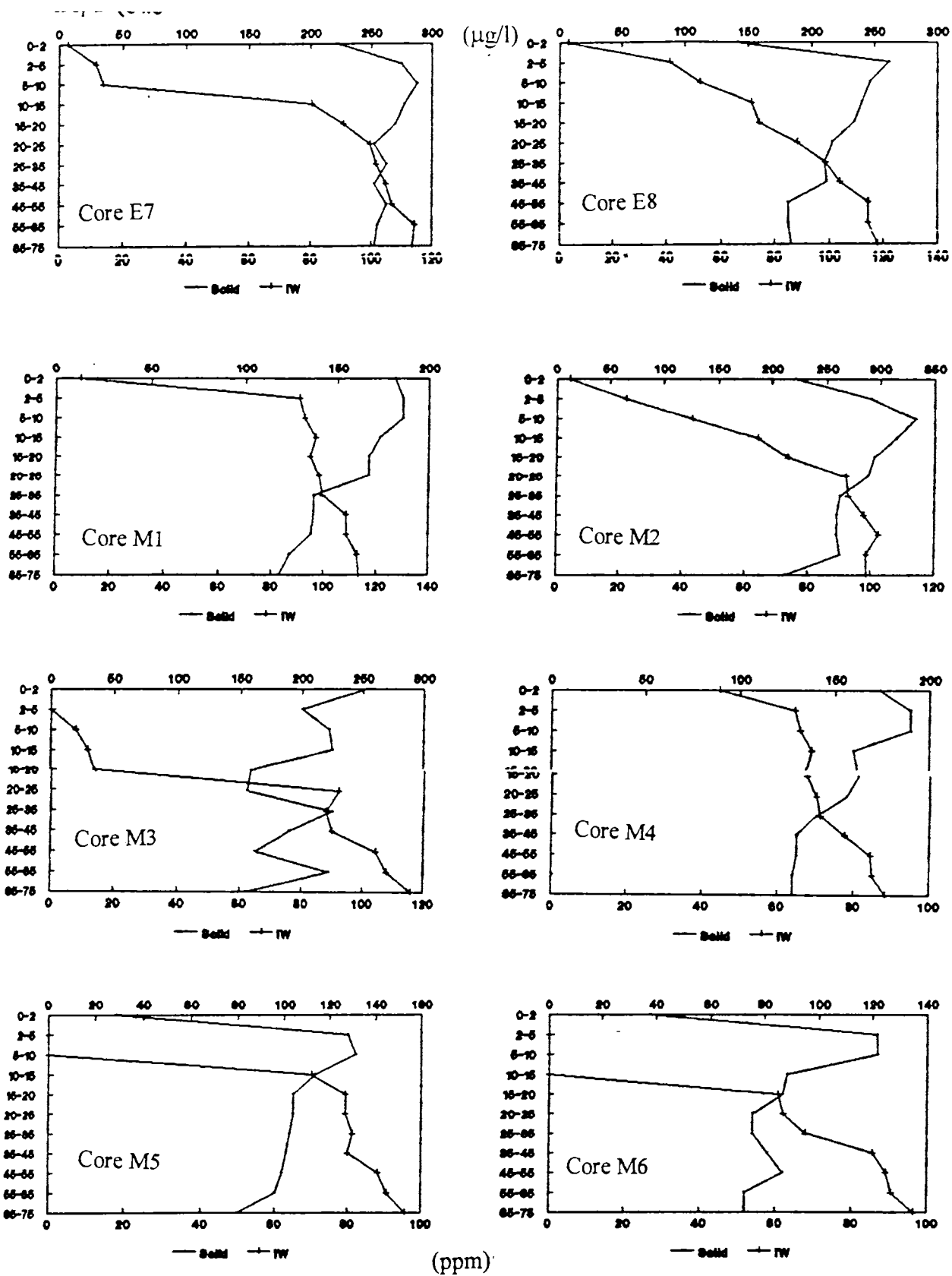


Fig. 19(b) Vertical variations of Ni in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

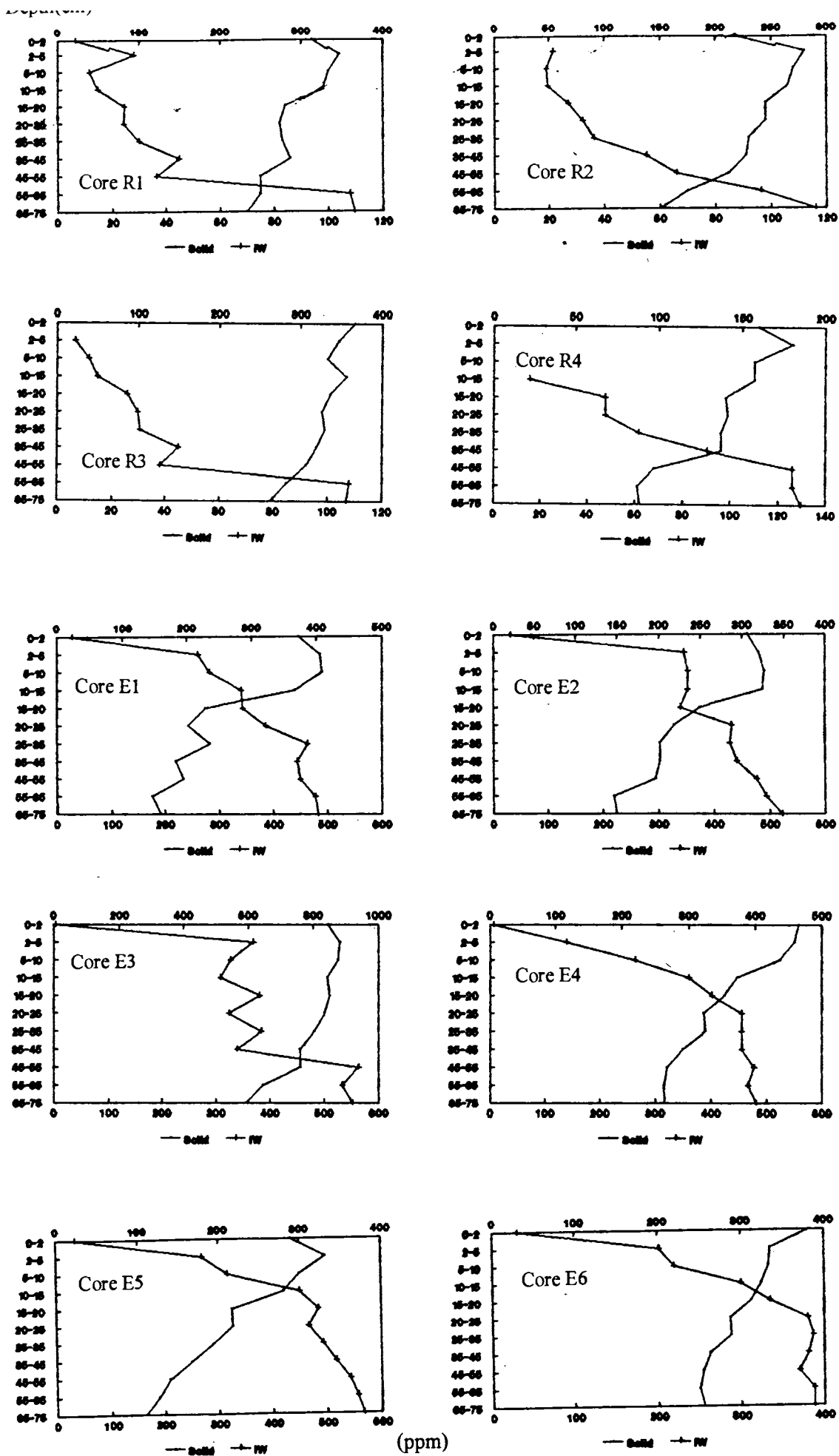


Fig. 20(a) Vertical variations of Zn in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

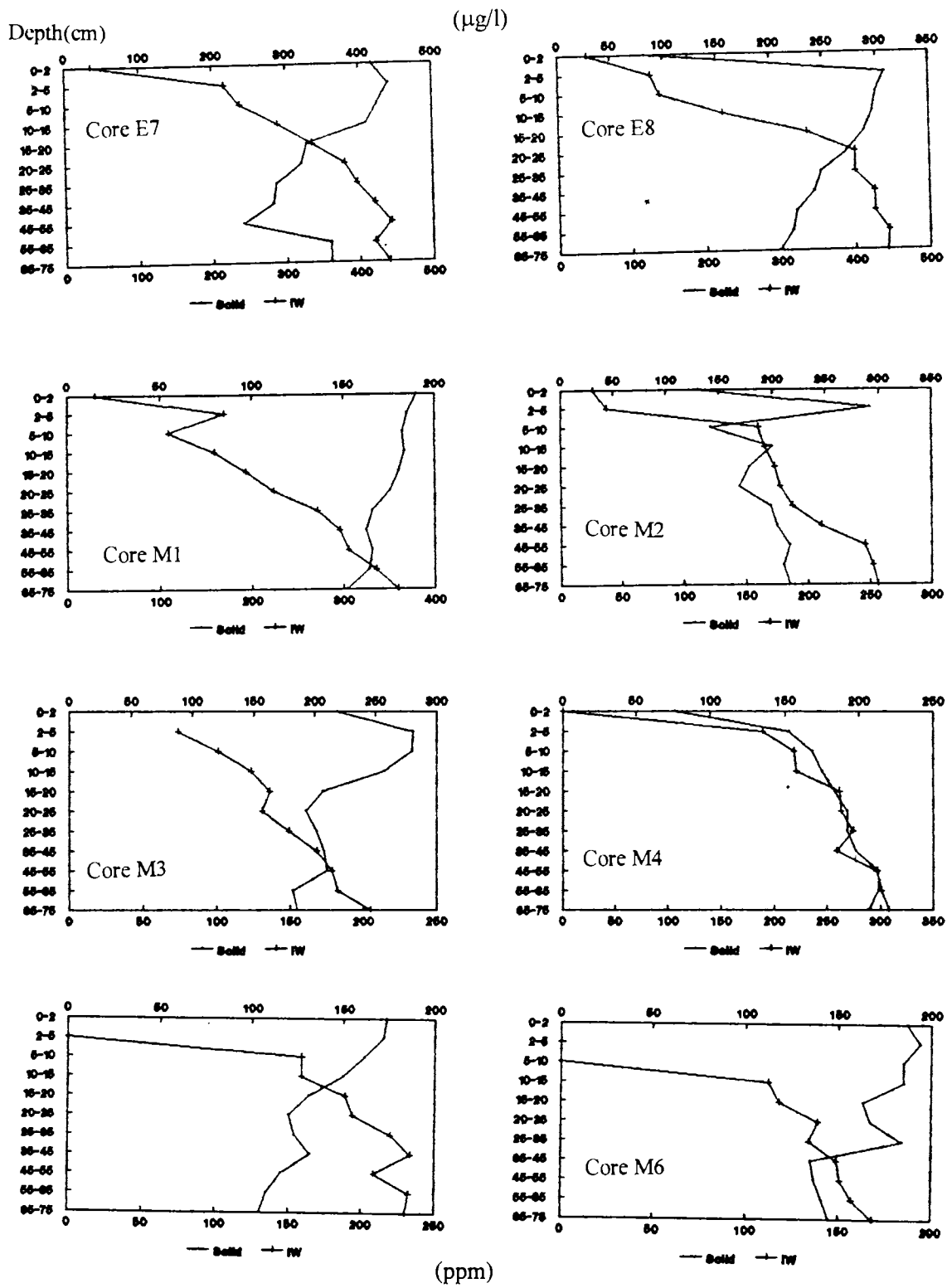


Fig. 20(b) Vertical variations of Zn in sediments (ppm) and interstitial waters (µg/l)

Depth (cm)

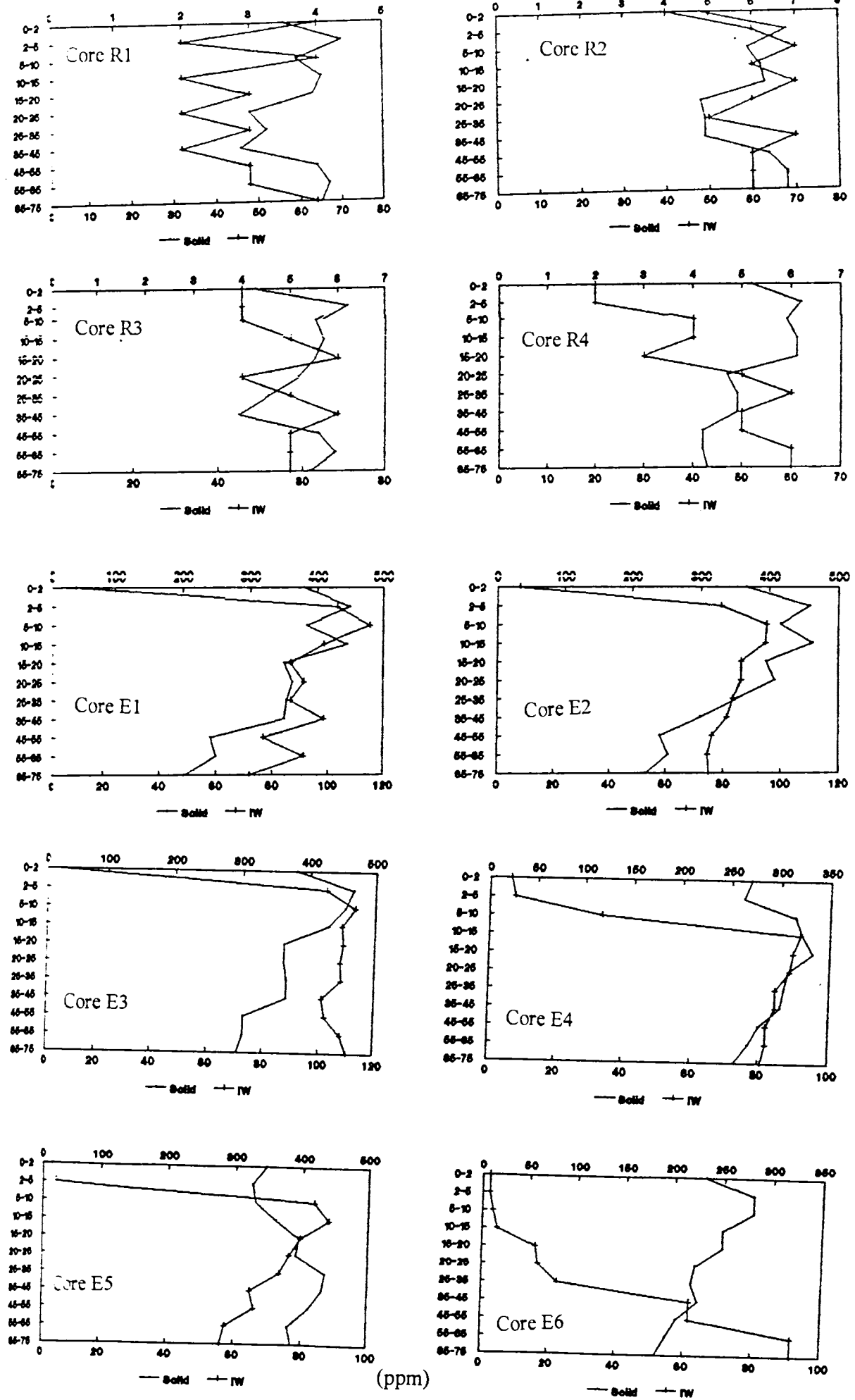


Fig. 21(a) Vertical variations of Pb in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

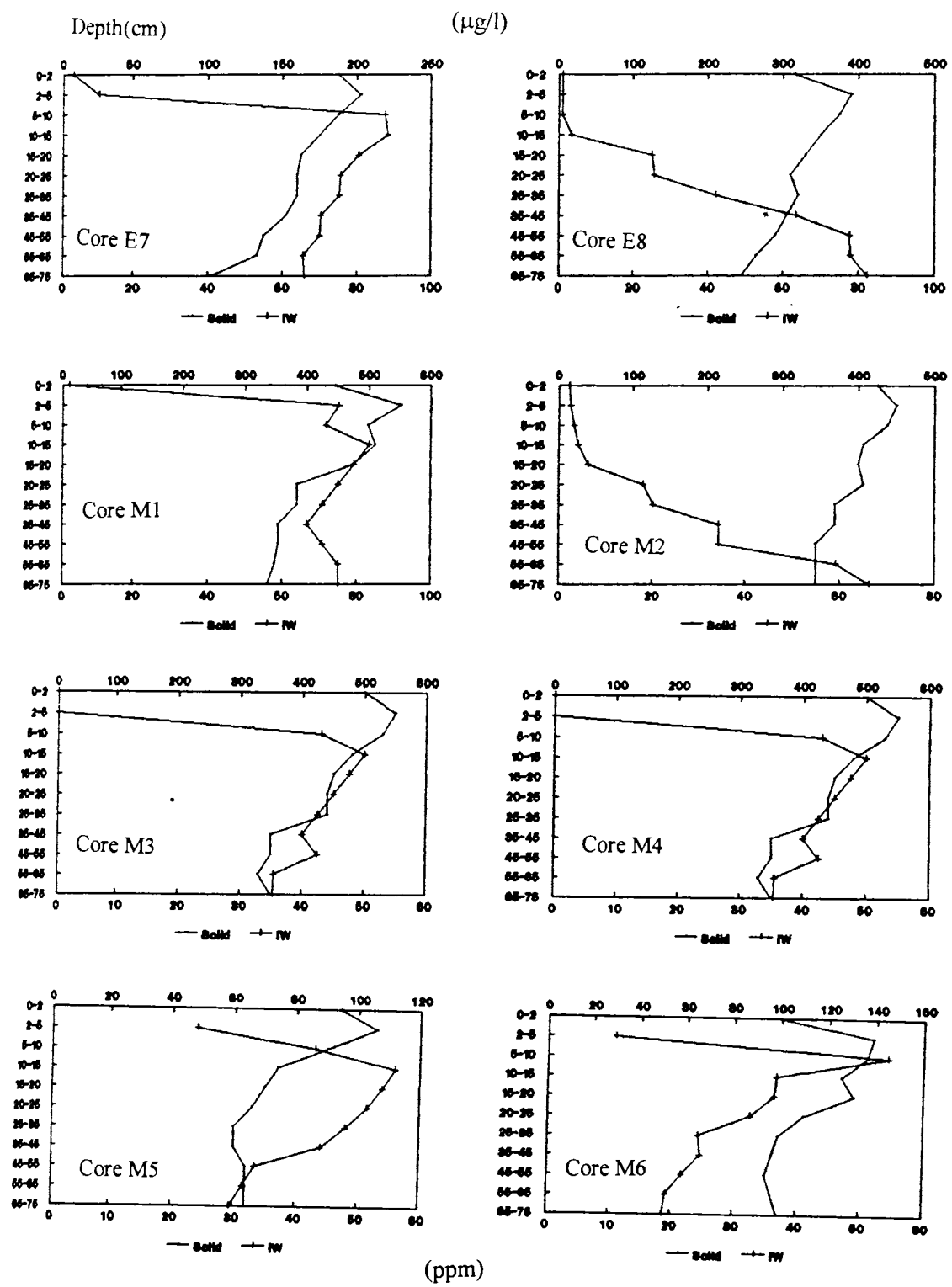


Fig. 21(b) Vertical variations of Pb in sediments (ppm) and interstitial waters (µg/l)

reduction are important processes in this area (Chapter 3) simultaneous reduction of Fe and Mn is also evident. In many cores a significant concentration gradients of metals in sediments are observed just below sediment water interface either at 2-5 cm or 5-10 cm level. On the other hand maximum dissolution of metals take place in the bottom layers of the sediments. Such dissolution or remobilization process has been reported (Presley et al., 1972, Duchart et al., 1973, Murray et al., 1978, Sawlan and Murray 1983, Gaillard et al., 1986). Metals bound in Mn and Fe oxyhydroxides would be first released under reducing conditions to interstitial waters by the microbially mediated reduction process (Graybeal and Heath 1984). Secondly during organic matter degradation organic bound metals are also released to the interstitial waters. Portion of these metals migrate towards the surface layers by diffusion where they again get precipitated under oxic condition. However, the relatively high concentrations of elements at the bottom layers indicate their fixation as sulfides. Through microprobe study Elderfield et al., (1979) have stated that trace metals are more likely scavenged by Fe sulfide than precipitated as pure sulfide minerals. Since Mn concentration is also high in the sediment and precipitation of Mn carbonates is predicted earlier, concentration of these metals by the carbonate phase is also significant.

Cd: Unlike other trace elements Cd is the least distributed metal in this area. Cd concentration is very low in the river sediments. On the other hand its concentrations in riverine and marine sediments are relatively very high. Cd in core E1, E2, E3, is uniformly high throughout the core, however all the cores show a decrease in concentration in sediments with depth. The high concentration just below sediment-water interface indicates precipitation as oxyhydroxide phases under oxic condition. However, at depths Cd is released to interstitial water by solubilization (Gaillard et al., 1986, Silverberg and Sundby 1990) bound mostly in oxide phases. Cd is highly enriched in the bottom interstitial waters. On the other hand

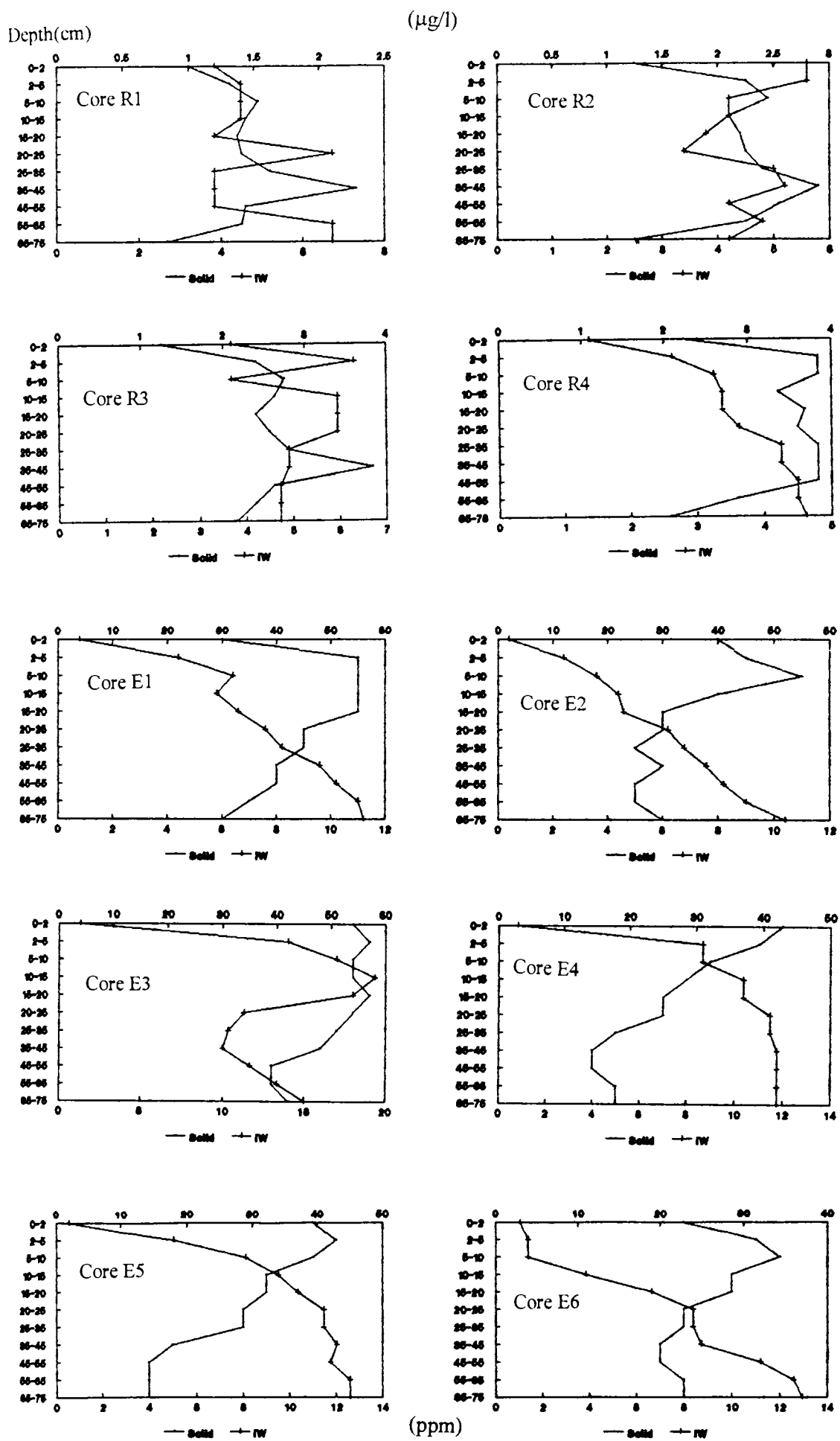


Fig. 22(a) Vertical variations of Cd in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

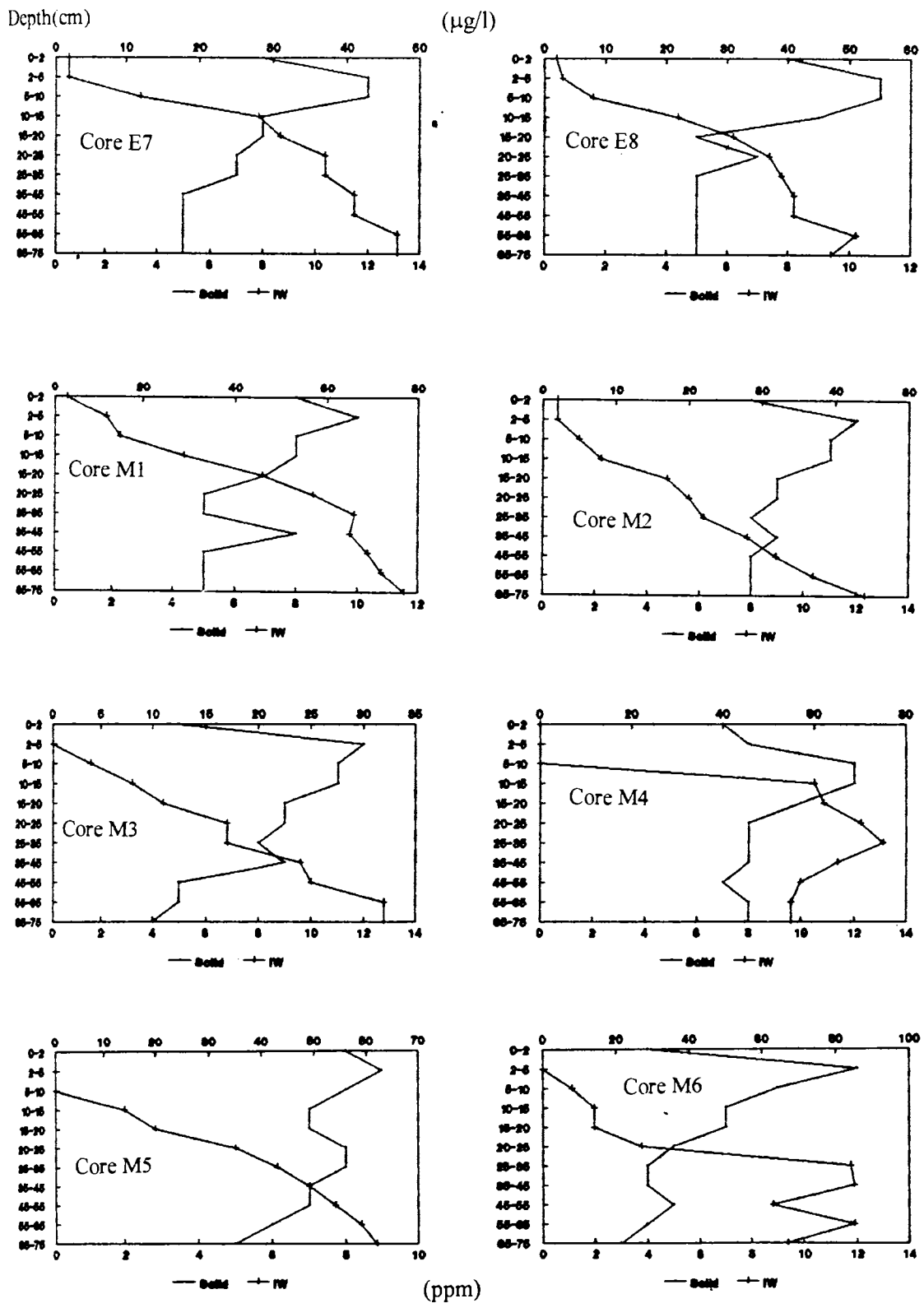


Fig. 22(b) Vertical variations of Cd in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

the relatively high concentrations of Cd in estuarine and marine sediments due to the re-fixation of solubilized Cd in the form of Cadmium carbonate and precipitation of sulfide phases. Similar observation has been made earlier (Gaillard et al., 1986). Since sulfide phases have very low solubility, Cd would remain immobile in reducing estuarine sediments (Presley and Trefrey 1980).

Similarly high Cd in interstitial waters at the top of some core with concomitant low in sediments indicates the dissolution of unstable Cd phases and organic bound under aerobic degradation. Lu and Chen (1977) have experimentally confirmed that Cd has been released from oxidized sediments.

Cr: Compared to Cu, Co, Ni, Zn, Cd and Pb, the concentrations of Cr show a slightly different pattern, both increasing and decreasing trends in sediments have been observed. Further cores E3, E4, E5, E6 and M2 do not show a clear trend. However, in maximum number of cores Cr decreases with depth in sediments. In interstitial waters Cr decreases with depth (Table 6 and Figs. 23a & b). The geochemical behavior of Cr during early diagenesis will be affected by its two oxidation states; Cr(III) and Cr(VI). Under oxic condition Cr (VI) is the dominant species and is much more soluble and mobile whereas Cr(III), which usually occurs in reducing condition, is not only less mobile but also rather insoluble and is strongly adsorbed particularly by organic matter (Cranston 1983) Therefore, the interstitial Cr to a larger extent depends primarily on the redox process: large interstitial water concentration primarily at the top layers will correspond to the presence of Cr(VI) whereas decreasing Cr towards deeper layers is due to the reduction and scavenging processes, eventually via a catalytic process involving HS^- (Schroeder and Lee, 1975).

Interstitial Cr enrichment near the sediment-water interface can be interpreted due to the decomposition of labile organics with concomitant regeneration of organically complexed

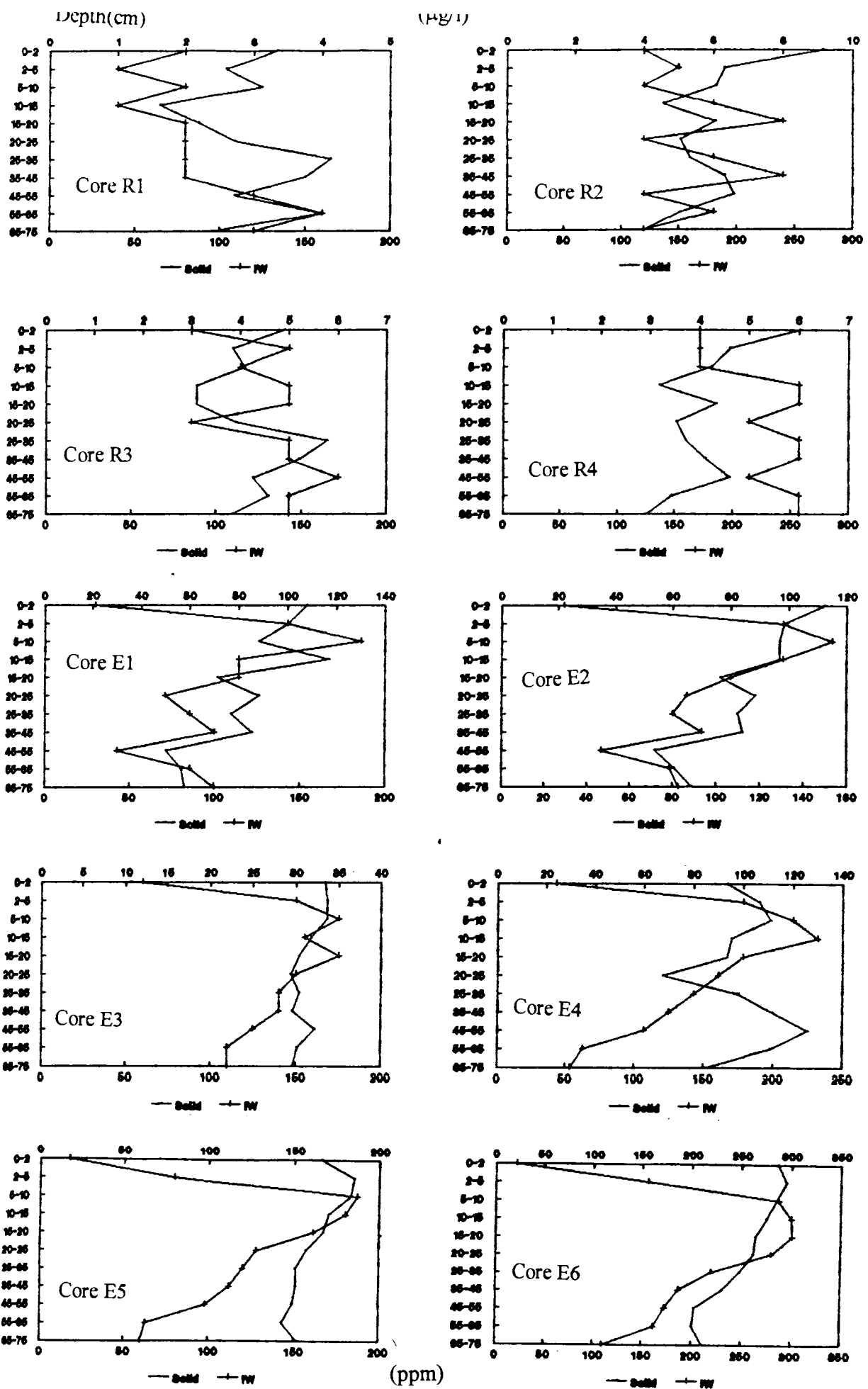


Fig. 23(a) Vertical variations of Cr in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

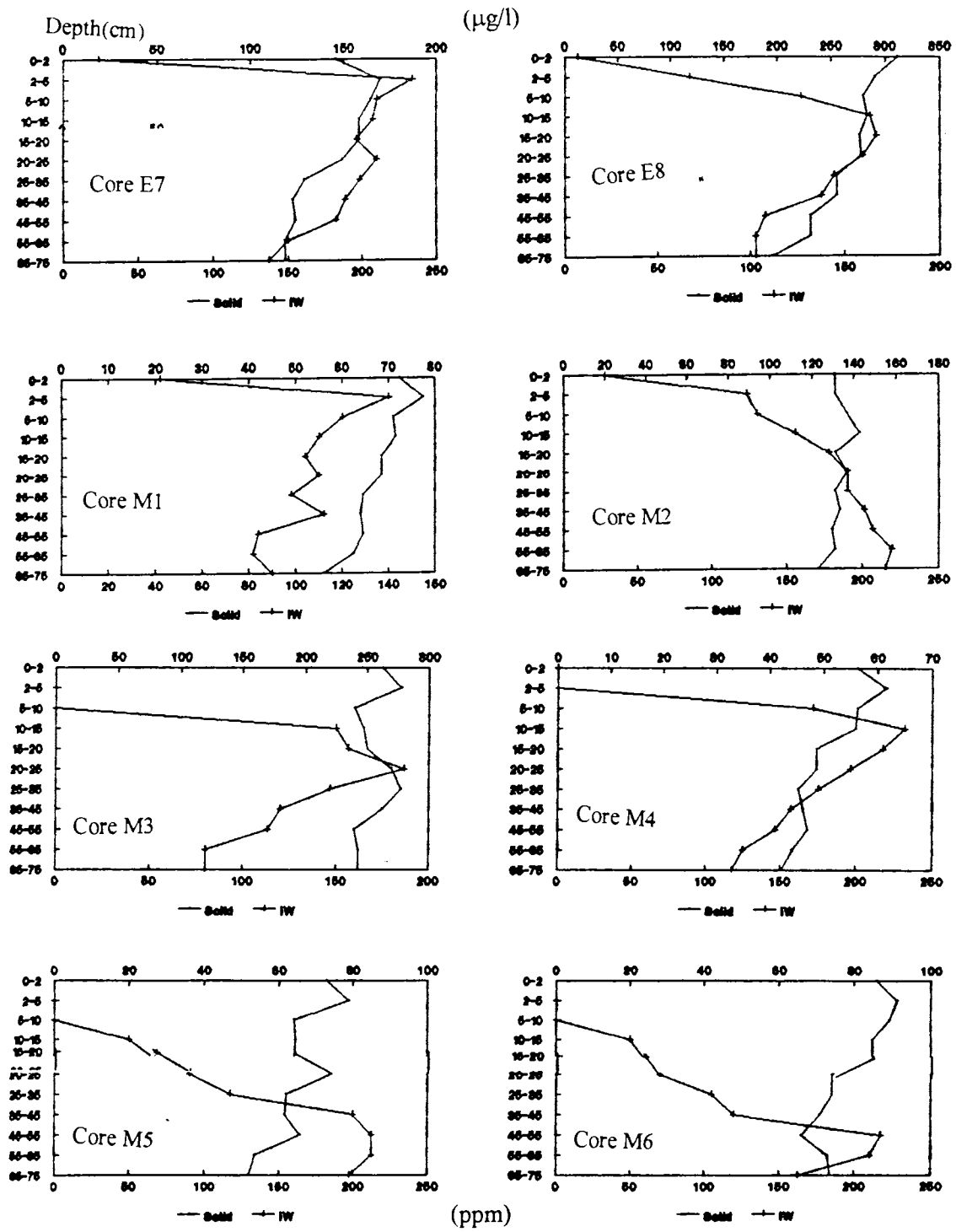


Fig. 23(b) Vertical variations of Cr in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

Cr(III) or biologically incorporated Cr(VI). At this stage, Cr(III) can be oxidised to Cr(VI), the kinetics of this reaction being enhanced by Mn-oxides (Nakayama et al., 1981; Gaillard et al., 1986). The interstitial water Mn profile of this study indicates the presence of Mn-oxides phases at the top of the core, as observed earlier (Michard, 1971; Holdren et al., 1975; Froelich et al., 1979; Gaillard et al., 1986). The above kind of process at the sediment-water interface may account for the high interstitial Cr at the sediment-water interface and represents a possible source of Cr to the overlying waters.

In sediments a major portion of Cr might be contributed through heavy mineral contents as abundant heavy minerals are reported in the sediments of Vembanad estuary (Padmalal, 1992).

Sr: Sr content in interstitial waters decreases with depth in most cores (Figs. 24a & b) and it follows the same pattern as that of interstitial Ca. Similarly in sediments Sr content increases with depth as Ca does. As precipitation CaCO_3 at depth has been suggested because of high alkaline values, the precipitating CaCO_3 can scavenge Sr (Nissenbaum et al., 1972). Precipitation of strontium carbonate and strontium sulphate can also increase the Sr content with depth. In the event of Sr carbonate precipitation in an anoxic condition with large sulphate reduction dissolution of strontium carbonate will not take place because of increase of bicarbonates. Further strontium carbonate is ten times less soluble than strontium sulphate (Brooks et al., 1968). Other possible source of Sr must be from the foraminiferal tests because of increased production.

Extraction Analysis:

The extraction analysis has clearly indicated the association of trace metals in various sediment phases (Core 5). Although partitioning techniques are not direct methods to detect diagenetic changes (Graybeal and Heath, 1984) within the

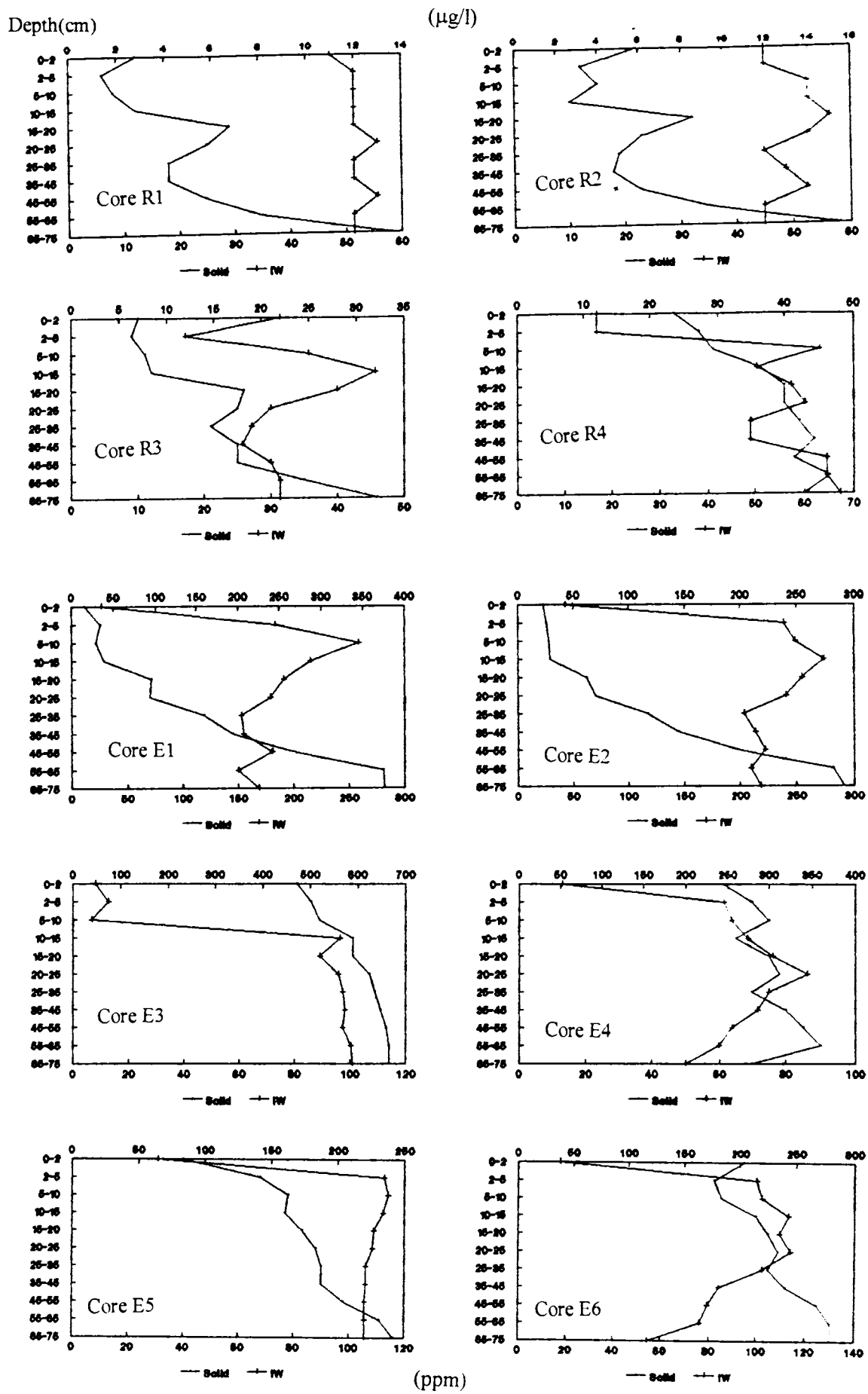


Fig. 24(a) Vertical variations of Sr in sediments (ppm) and interstitial waters ($\mu\text{g/l}$)

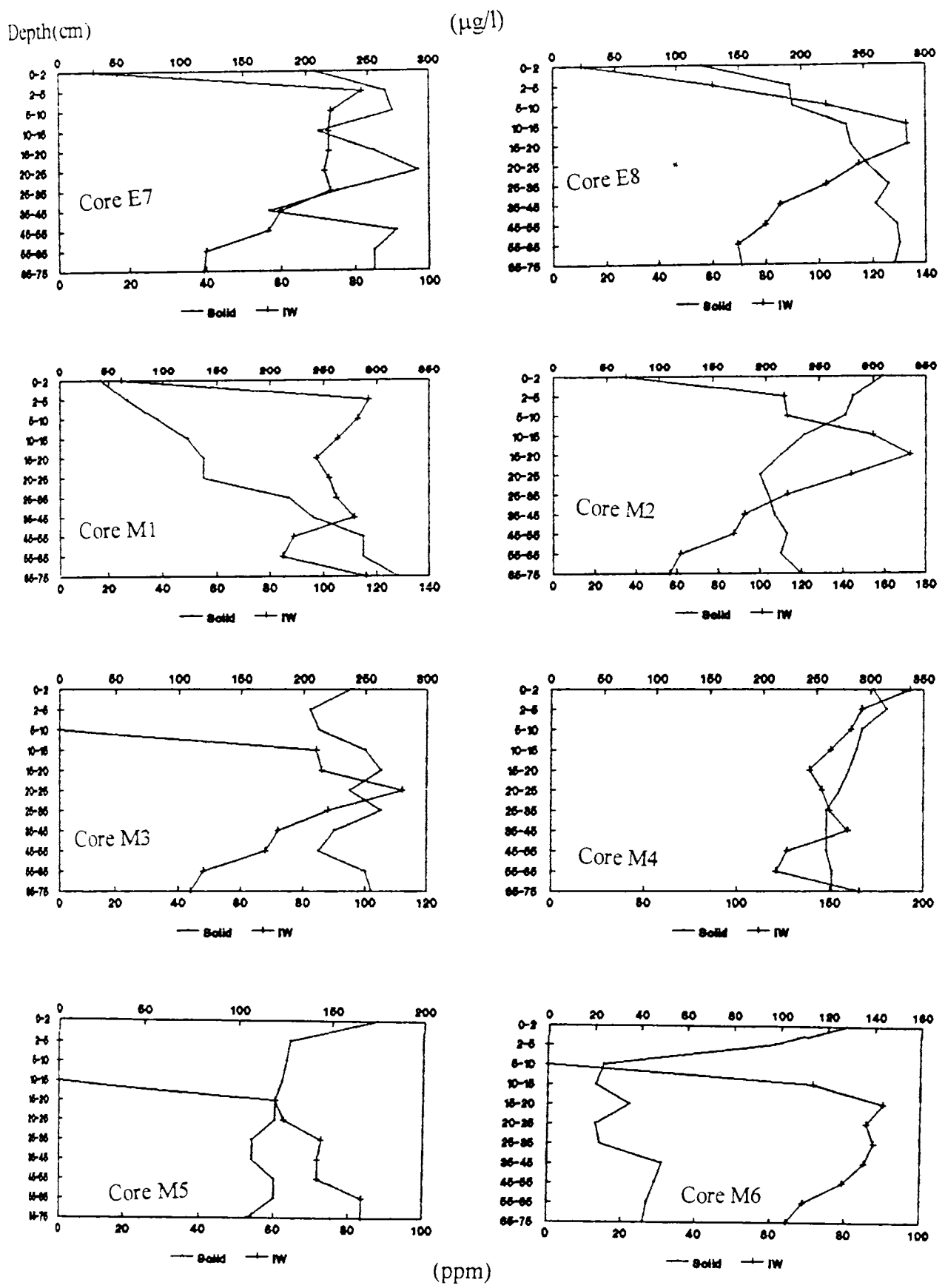


Fig. 24(b) Vertical variations of Sr in sediments (ppm) and interstitial waters (µg/l)

sediment column, they do help to infer indirectly by revealing anomalies relative to the initial composition of sediments. Table 8 reveals that major portions of the metals are associated with oxidizable and residual fractions. Except Mn and Zn the association of metals with the first three extractions are only marginal.

The metals associated with the first three extractions show nearly three grouping. A relatively very small percentage of Fe, Cu, Co, Cr and Ni are leached by the first three extractions. These leaching processes have yielded only around 2% of the total sediment concentration for Fe, Cu and Cr. However, about 2 to 5% of Co and Ni are associated with Fe-Mn oxide phases as reducible.

In the second grouping, concentration of Cd and Pb in these extracts are marginal; totalling to about 10%. On the other hand Mn and Zn (third group) association in each of the three extractions is very much significant. Only about 5 - 8% of total Mn is associated with the first extraction as easily exchangeable but the Mn content in carbonate and Fe-Mn oxide bound is very much significant together representing 20 - 30% of the total concentration. Zn also reveals more or less similar enrichment as that of Mn in the second and third extractions. This clearly shows that a considerable amount of Mn and Zn is associated with carbonate and Fe-Mn oxide fractions. Their contents are also slightly high at the surficial (0-5 cm) sediment where oxic condition prevails.

The hydrogen peroxide treatment, which was aimed to dissolve mainly sulphides and organic matter, accounts for a major part of the metal association in this area. Despite the difficulties in getting oxidized the whole of organic matter especially the detrital organic matter such tree fragments and other organic matter of organic life, the results indicate that a significant portions of the elements are association with oxidizable fraction. Further metals such as Fe, Co, Ni, Zn and Cd

associated with this fraction slightly increases with depth in accordance with the sulfate reduction process. Being a reducing environment precipitation of several sulphide complexes has been attributed while discussing the various metal distribution. This partitioning analysis clearly establish such precipitation of metals as sulphides with in the sediment column. Earlier Kunhikrishnan Nair (1992) has observed a relatively moderate proportion of trace metals in oxidizable fraction at the surficial level. However, in this investigation the oxidizable fraction is appreciably high for all metals and particularly for Cd (51-58%) and Zn (31-38%) (Table 8).

The last analysis i.e., the lithogenous fraction becomes the major type metal binding in this study except Cd. As the sediments contain appreciable heavy minerals such as magnetite, ilmenite and garnet (Padmalal, 1992) a good amount of metals might have contributed by heavy minerals. The importance of heavy mineral contribution to the bulk geochemistry of riverine and estuarine sediments has been stressed by Seralathan (1987) and Rajendran et al., (1996). Hirst (1962) has demonstrated through partition analysis that clay minerals such as illite, kaolinite and smectite transport Cu, Co, Ni, Cr and others to the Gulf of Peria held mainly in lattice structure. Earlier Nair et al., (1990) reported that residual fraction is the chief carrier of metals such as Cd, Cu, Pb and Zn. As in the present case Pb is primarily held in lithogenous fraction.

Hg: Hg is a good indicator of various forms of cultural activities (eg. agricultural use of fungicides, sewage input etc). Sediment cores from lakes, which ~~have~~ been investigated with respect to an assessment of historical changes and pollution intensities, mostly exhibit a characteristic increase of Hg concentration during the last several decades. Stronger increase in Hg concentrations originate from municipal sewage effluent and industrial wastes (Evans et al., 1973). Mc Mullen (1973) has reported a maximum of 32.6 ppm of Hg from Tennessee river sediments due to industrial pollution. Therefore a small

Table 7. Vertical distribution of Hg in sediment cores from various environments (ppm)

Depth	R1	R3	E3	E6	M2	M5
0-2	0.19	0.33	2.10	2.05	0.08	0.08
2-5	0.33	0.28	1.93	1.96	0.18	0.06
5-10	0.20	0.21	0.66	2.00	0.18	0.18
10-15	0.02	0.01	0.31	0.89	0.34	0.32
15-20	0.03	0.02	0.38	0.90	0.01	0.21
20-25	0.22	0.14	0.02	0.71	0.03	0.13
25-35	0.20	0.08	0.40	0.98	0.05	0.05
35-45	0.08	0.08	0.14	0.18	0.02	0.05
45-55	0.09	0.08	0.09	0.73	0.11	0.10
55-65	0.08	0.06	0.08	0.04	0.11	0.12
65-75	0.13	0.02	0.06	0.16	0.10	0.10

Table 9. Mean values of Ratio between concentrations

	Sed/wat.	Sed/IW	IW/wat.
NO2	4.00	1.55	2.58
NO3	0.60	0.24	2.50
NH4	0.96	0.09	10.00
PO4	1.15	1.04	1.10
Fe	1.78	2.27	0.07
Mn	6.00	4.11	1.46

Table 8 Metal concentration in each fraction of sediment (Core No.E5) as a percentage

Depth	Fe					Mn					Cu				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
0-2	0.04	0.28	4.5	17.9	77.3	6	12	18	19	45	1	1	1.0	14	83.0
2-5	0.04	0.28	2.8	18.6	78.3	8	12	19	23	38	1	1	0.2	18	79.8
5-10	0.04	0.28	1.9	18.5	79.3	7	13	15	25	40	1	1	0.2	17	80.8
10-15	0.04	0.28	1.6	18.8	79.3	7	12	14	25	42	1	1	0.2	17	80.8
15-20	0.03	0.27	1.5	19.1	79.1	7	12	14	25	42	1	1	0.2	16	81.8
20-25	0.03	0.27	1.5	19.6	78.6	6	12	13	24	45	1	1	0.2	17	80.8
25-35	0.03	0.26	1.4	19.1	79.2	6	11	13	22	48	1	1	0.2	16	81.8
35-45	0.03	0.26	1.3	21.6	76.8	6	12	12	22	48	1	1	0.2	15	82.8
45-55	0.03	0.25	1.4	21.5	76.8	5	12	12	21	50	1	1	0.2	17	80.8
55-65	0.03	0.21	1.4	22.4	76.0	5	11	11	21	52	1	1	0.1	15	82.9
65-75	0.03	0.22	1.4	22.6	75.8	5	12	12	21	50	1	1	0.1	15	82.9

Depth	Co					Cr					Ni				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
0-2	1.5	0.8	5	18	74.7	0.5	0.2	2.04	13	84.3	1.0	1.0	4	10	84.0
2-5	1.6	1.0	5	21	71.4	0.6	0.3	0.07	17	82.0	1.0	1.0	5	12	81.0
5-10	1.5	0.9	4	20	73.6	0.6	0.3	0.08	15	84.0	1.0	1.0	3	11	84.0
10-15	1.5	0.9	5	19	73.6	0.5	0.2	0.07	16	83.2	1.0	0.9	2	12	84.1
15-20	1.4	1.0	3	23	71.6	0.6	0.2	0.07	17	82.1	1.0	1.0	3	12	83.0
20-25	1.5	0.9	5	21	71.6	0.5	0.2	0.06	19	80.2	1.0	1.1	2	13	82.9
25-35	1.5	0.8	4	21	72.7	0.4	0.2	0.07	17	82.3	0.9	0.8	2	14	82.3
35-45	1.4	0.8	4	23	70.8	0.4	0.2	0.06	16	83.3	0.8	1.0	2	15	81.2
45-55	1.4	0.8	4	21	72.8	0.4	0.1	0.06	18	81.4	1.0	0.8	2	17	79.2
55-65	1.3	0.7	3	22	73.0	0.4	0.2	0.06	18	81.3	0.9	0.8	2	15	81.3
65-75	1.1	0.7	3	23	72.2	0.4	0.1	0.06	17	82.4	0.8	0.8	2	17	79.4

Depth	Zn					Cd					Pb				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
0-2	2.5	12	14	31	40.5	1.5	2	3	51	42.5	3	1.5	4	4	87.5
2-5	2.7	14	12	37	34.3	1.6	3	3	52	40.4	4	1.8	5	6	83.2
5-10	2.6	13	12	36	36.4	1.6	3	3	52	40.4	3	1.8	5	6	84.2
10-15	2.5	12	11	37	37.5	1.5	2	3	56	37.5	4	1.5	4	4	86.5
15-20	2.5	12	11	38	36.5	1.5	2	3	58	35.5	3	1.7	4	5	86.3
20-25	2.5	12	13	38	34.5	1.5	2	2	55	39.5	3	1.6	4	8	85.4
25-35	2.5	11	13	38	35.5	1.4	2	3	58	37.6	2	1.4	4	8	84.6
35-45	2.5	11	12	37	37.5	1.4	2	3	58	35.8	3	1.5	5	8	82.5
45-55	2.4	12	11	38	36.6	1.4	2	2	58	36.8	2	1.4	3	9	84.6
55-65	2.5	11	10	38	38.5	1.4	1	2	58	37.6	2	1.4	4	10	82.6
65-75	2.5	11	10	38	38.5	1.4	1	2	58	37.6	2	1.4	4	11	81.8

A - Exchangeable B - Carbonate bound C - Fe Mn oxides bound
D - Organic / Sulphide bound E - Lithogenous

attempt has been made here to study the variation of Hg in 6 sediment cores from different environments as several industries are located in this area.

Results:

Hg content in riverine cores varies between 0.01 and 0.33 ppm whereas in estuarine sediments the range is from 0.02 to 2.10 ppm. In marine sediments Hg ranges between 0.01 and 0.34 ppm. In all the cores the Hg content decreases with depth. Ouseph (1990) has reported 0.12 to 0.95 ppm of Hg from the Vembanad backwaters and also a good interrelationship of Hg with organic carbon, Fe and silt has been reported (Ouseph, 1990). Thomson et al., (1980) have also reported a range of 0.06 to 2.57 ppm and 0.2 to 4.4 ppm in the estuarine sediments.

In this study high Hg content at the surficial level may be due to dissolution and mobilization from the bottom to top of the core just as in the case of other metals. The relatively high Hg in core E6 can be attributed to high anthropogenic activity and industrial pollution. High values are ^{not} noted in the freshwater and marine regions and therefore ~~these~~ sediments are not affected by any Hg pollution.

Cluster analysis

Heavy metals both in solid and liquid phases in five estuarine cores (E1 to E5) were subjected to cluster analysis to understand the grouping of various metals. Dendogram obtained (Davis, 1973) for different cores show more or less similar grouping (Fig. 25)

In core E1, three intercorrelated groups of metals are identified: first group consists of Fe, Mn, Cd, Zn and Sr in liquid phase, second is solid phases of Fe, Mn, Cu, Ni, Co, Pb, Cr and Zn, and third one is of Co, Cd in solid phase and Cr, Sr, Pb and Cu in liquid phase. Liquid phase of Fe, Mn and Cd and solid

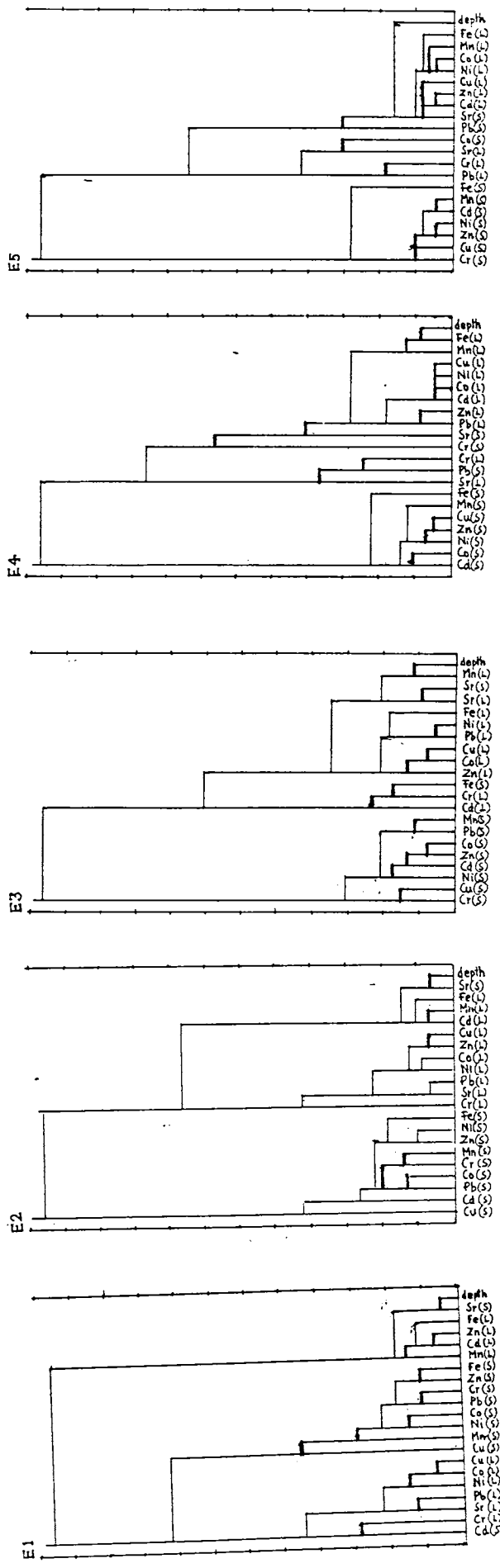


Fig.25 Dendrogram showing metal assemblages in sediments (S) and interstitial waters(L)

phase of Sr form first group in core E2 and second one consists of all other metals in liquid phase and third one is comprised of all other metals in solid phase. Three sub groups form a major group in core E3, . First subgroup consists of Mn in liquid phase and Sr in both phases and second sub group is of Fe, Ni,Cu,Co, Zn in liquid phase and Pb in solid phase. Third subgroup consists of Fe in solid phase and Cr and Cd in liquid phase. All other metals in solid phase forms the second major group. In core E4, Fe and Mn in liquid phase forms a sub group and Cr and Sr in liquid phase and lead in solid phase form a sub group and all other metals in solid and liquid phases forms respective groups. In E5 Co in solid phase and Sr, Cr and Pb in liquid phase form a sub group and all other metals in liquid phase and solid phase form their respective major groups.

In general all the five cores show more or less similar patterns as major grouping of solid and liquid phases. Except a few metals (eg. Sr, Cr, Pb in some cases), all the metals are controlled by Fe and Mn both in their solid and liquid phases. Vertical variations of Fe and Mn in cores are mainly controlled by the redox conditions of the sediment column. Interrelationships of the metals in sediment column depend on the metal mobility and preservation during early diagenesis of sediments (Shaw et al.,1990; Swalan and Murray, 1983).

CHAPTER 5

DIAGENETIC PROCESSES

Introduction

Diagenesis may be defined as those processes which bring about alteration in sediments after deposition (Berner, 1980). Sediments may be altered at, or close to, the sediment-water interface, or may suffer further at depths during continued burial. Studies on diagenetic reactions are very important in the light of chemical fluxes between the sediments and the overlying sea water. The extent of reactions between different elements contained in a sediment and those in interstitial water, as well as those contained in the overlying water, will provide much insight in understanding the importance of sediments as a control affecting the composition of sea water.

In many aspects the shallow water estuaries, continental shelves and platforms, which contain much organic matter and terrigenous detritus and thus may be inherently more susceptible to chemical and biological attack. Hence, sediments from transitional environments could be a more useful medium for observing and understanding chemical changes than deep sea sediments. A greater stress has been laid on chemical diagenesis of shallow water sediments. Nevertheless, many of the reactions occurring in these sediments can be translated to events happening in sediments from the deep sea. However, certain distinction between deep and shallow water sediments can be made which have some bearing on the degree and kinds of diagenesis within them.

Chemical diagenesis in sediments depends on a number of environmental factors all of which are directly or indirectly related, and it is difficult to attribute any change observed within sediments to any single factor. Total sediment accumulation rate, the amount and composition of organic matter within a sediment and its consumption by biological systems of different activity are predominant against these factors. Further, within anoxic systems the presence of dissolved

sulphide, produced by bacterial activity, not only influences metal sulphide formation, but to a larger extent may control the equilibria of other mineral species. Significant numbers of bacterial and allied organisms (eg. enzymes, actinomyces, yeasts, moulds and algae) are found in Recent sediments and seem capable of altering, perhaps biocatalytically, various substances, and of thus controlling the physico-chemical conditions within sediments. For this reason these organisms have a most important influence on chemical diagenesis in sediments. There is considerable evidence of a correlation between the number and kinds of bacteria and the physico-chemical conditions within a sediment (Rittenberg, 1940; Zobell, 1942; Bordoviskiy, 1965). The decrease in the rate of anaerobic bacterial sulphate reduction with depth has been shown by Sorokin (1962) to be due to the depletion of metabolizable organic compounds. Bacterial activity in oxic sediments is also likely to be dependent on the amount of metabolizable organic matter present, although pH, sediment particle size, temperature and the sequence of physical chemical changes caused by bacteria themselves may also have some influence. (Oppenheimer, 1960).

An increase in the flux of metabolizable organic carbon to the sediment leads generally to an increase in the rate of release of mineralized constituents to interstitial waters. Interstitial water concentrations of regenerated nutrients and carbon increases and concentration gradient across the sediment-water interface steepens (Klump and Martens, 1989).

In areas of low deposition rates the organic carbon content of the sediment would usually be low and, therefore, most of it material is oxidized in the upper few cm of the sediments by organisms utilizing dissolved oxygen as their main oxidant agent. This is sometimes reflected in the interstitial waters through an increase in dissolved NO_3^- content (Hartmann et al., 1973). But where there is a steady state of organic supply like the present one the degradation of organic matter, would remain incomplete (Table 4) even after denitrification and sulphate

reduction processes.

Sediment-water interactions

It is clear from the previous discussion in chapter III that many of the nutrient parameters are generated from the degradation of organic matter. The degradation of organic matter is very important for the survival of organic life. Klump and Martens (1987) have observed that nearly 80% of mineralization of labile organic matter occurs within eight months of deposition. By the process of diagenesis the soluble forms are transferred to interstitial waters. Later the various metal species are either reprecipitated at site as more stable forms possibly as sulphides, carbonates etc. or migrated to upper oxic layers and get precipitated as oxi-hydroxide forms. Fe and Mn are the best examples (Murray and Brewer 1977). During dissolution of unstable phases major elements at depths or at sediment water interface, many associated trace elements adsorbed into these oxide phases are also mobilized. Occurrence of diagenetic processes even near the sediment-water interface have been reported (Aller 1980 a & b).

In this study occurrence of several diagenetic changes are clear from the remobilisation of several nutrient parameters and elements. While some parameters show enrichment just below the sediment-water interface, the same is not recorded at the surficial layers. In some cores nitrification process takes place at 10-15cm level, whereas the values are very less at the surface. Similarly NO_2^- , NH_4^+ , PO_4^{3-} , SO_4^{2-} , SiO_2 and several major and trace metals are depleted at the top of core. Despite the favorable conditions at the sediment-water interface (high pH and positive Eh) nitrification is not noticed. So also oxidation of N and S is not found. Similarly reprecipitation of many elements are not recorded. In addition, there would be a steady supply of organic matter from the overlying waters and there by severe degradation processes. Similarly many kinds of metals deposition taking place in the form of suspended solid particles, oxi-hydroxide phases and biogenic forms.

In spite of the several factors favouring an enrichment of species at the top of core, the results show that not only in sediments but also in interstitial waters the concentration of several nutrient parameters and elements are depleted. This clearly shows that both nutrients and metals are recycled to the overlying water at the sediment-water interface. While NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} and SiO_2 can be transferred to the overlying waters through interstitial waters by diffusion; transfer of metals can take place not only through interstitial waters but also from sediments by adsorption-desorption processes.

The regeneration of nutrients and metals to the overlying waters from benthic sediments can be controlled by physical, biological and chemical factors, more particularly at the top 10-15cm level. Retardation of interstitial diffusion of nutrients through the top oxic sediments, if any, can be overcome by bottom current turbulence (Bray et al., 1973), bioturbation process and particulate reworking (Robbins et al., 1979), worm-tube irrigation (Hammond et al 1977) and methane gas bubbled ebullition (Klump and Martens 1981).

Proposed diagenetic Model

The sediments are considered to be the ultimate sink as well as the source of almost all of the bio and geochemical elements. The various diagenetic processes that operate in the sediment will thus have a profound effect in the maintenance of life in the sea. Though considerable effort were directed towards unveiling the nature and character of the diagenesis of various elements in the sediment, the kinetic and mechanism of the reactions are still poorly understood. The limitations in the sampling and analysis as well as the difficulties in developing effective in situ kinetic compartments are the major reasons for this.

To identify the probable nature and magnitude of the diagenetic processes, one has to first have a concrete idea on

the character of the sediment and the nature of the environment surrounding the sediment. Generally it is assumed that in coastal and estuarine systems the organic content of the sediments will be significantly higher. This condition will well suit for a biologically modulated diagenetic process, the result being the formation of a reducing or anoxic environment. The contribution from the turbulent overlying water and the consequent resuspension of sedimentary particles as well as the high porosity of the ill compacted structure will lead to an unstable potential in the surficial sediments. The intense microbiological activity in these layers all the same will keep these sediments at a negative potential. The deeper sediments, due to less microbiological activity, will have remineralisation as the major diagenetic process.

A number of mass transport models were given by various workers (Imboden, 1975; Berner, 1977; Vanderborght et al, 1977; Sayles, 1979, 1981) to explain the behavior of various elements during the diagenesis. All these works indicate a clear distinction between the first few cms of sediment (15 cm) and the deeper layers of the sediment. This is an attempt to elucidate a kinetic steady state model which will have a general character so that with minor substitution^{it} can be used for any element. To retain the general character the individual reactions of the elements and the effect of various biogeochemical processes are pooled together to a single kinetic equation.

The Model

Basic Assumptions

1. Though the reactivity in the first 2 to 5cm is considerably greater than the rest of the layers, the sediments upto 15cm is taken as a biologically reactive primary zone.

2. Though there are a number of processes contributing to the effective concentration of an individual element in the primary zone, sedimentation, resuspension, bioturbation, exchange

with water etc., the rate of change in concentration can be expressed as a function of the effective concentration.

3. Though there will be considerable variations in the actual concentration observed in the various components in the primary zone viz. the sediment, overlying water and interstitial water, the dynamicity of the zone retains the over all equilibrium.

4. The deeper layers of sediments will have exchange reactions with the interstitial waters and the contributors to the concentration of any element will be the sedimentary interaction and the diffusion from adjacent layers.

Based on the assumption the model proposed is

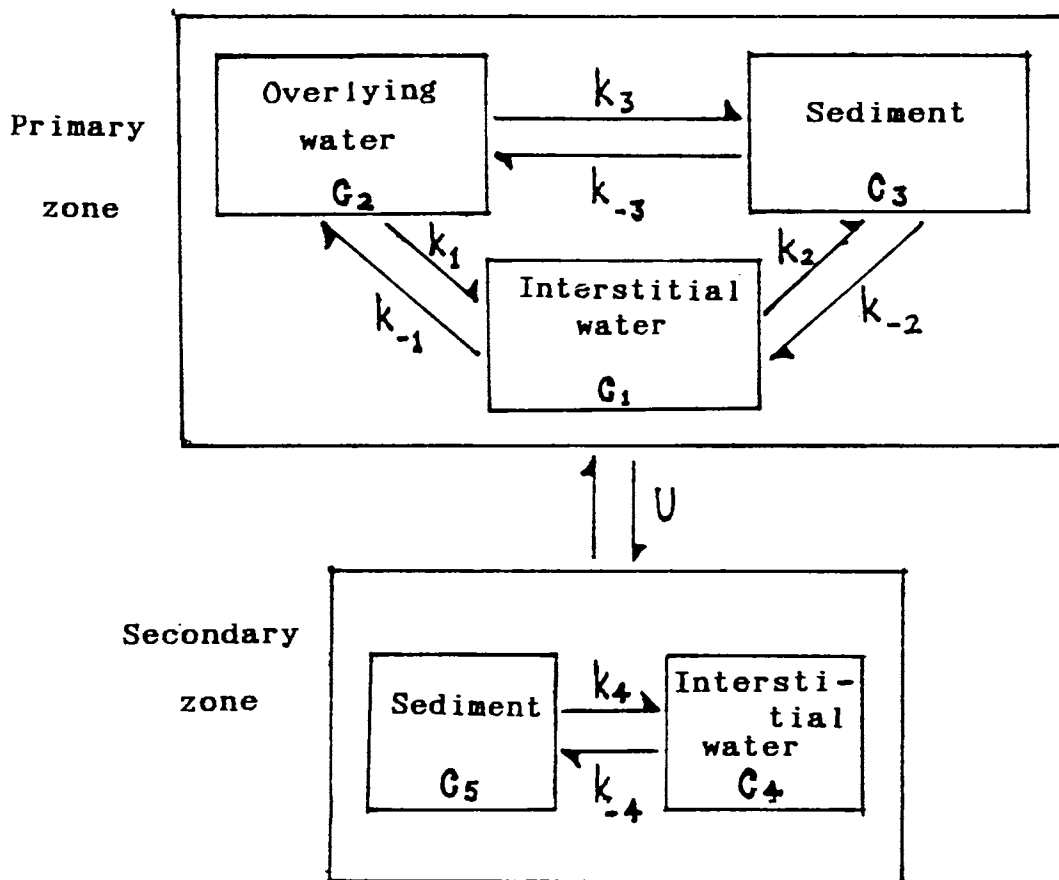


Fig. 26 Proposed diagenetic model

Terms

c_1, c_2 etc. represent the effective concentrations of any ion/element in the respective compartment

k_1, k_2 etc. represent the kinetic rate coefficient for the forward transformation.

k_{-1}, k_{-2} etc. represent the kinetic rate coefficient for the backward transformation

u the molar diffusion coefficient.

Evolution of the model

(a) The primary zone is a 3 compartment system. The change in concentration in the interstitial water can be represented by the general kinetic equation;

$$\text{At a steady state, } dc_1/dt = 0$$

or

$$k_1 c_2 - k_{-1} c_1 + k_2 c_3 - k_{-2} c_1 = 0$$

or

$$c_1 (k_{-1} + k_{-2}) = k_1 c_2 - k_2 c_3 \quad \text{---- (1)}$$

Similarly the change in concentration of the element in water can be given as

$$dc_2/dt = k_{-1} c_1 - k_1 c_2 + k_{-3} c_3 - k_3 c_1$$

Applying steady state,

$$k_{-1} c_1 - k_1 c_2 + k_{-3} c_3 - k_3 c_1 = 0$$

Assuming that the surficial sediment is uncompact and the porosity is high, leading to a well mixing with the water and the interstitial water is practically absent.

$$k_{-3} c_3 - k_3 c_1 = 0$$

or

$$c_3 = c_1 \cdot k_3 / k_{-3} \quad \text{----- (2)}$$

by substituting (2) in (1)

$$c_1 (k_{-1} + k_{-2}) = k_1 c_2 - k_2 (k_3 / k_{-3}) c_1$$

$$c_1 [k_{-1} + k_{-2} + k_2 (k_3 / k_{-3})] = k_1 c_2$$

or

$$c_1 \propto c_2$$

by a similar argument it can be seen that

$$c_1 \propto c_3$$

(b) The secondary zone

The remineralisation and the diffusion processes being the

major activities in this zone, the rate of change of concentration of any element can be given as

$$dc_4/dt = k_4c_5 - k_{-4}c_4 + u(dc/dz)$$

where dc/dz is the concentration gradient. In an atypical condition, by considering only the sediment-interstitial water interaction as a rate determining step

$$dc_4/dt = k_4c_5 - k_{-4}c_4$$

At an equilibrium, applying the steady state

$$k_4c_5 = k_{-4}c_4$$

or

$$c_4 = (k_4/k_{-4})c_5 = Ac_5,$$

where A is the equilibrium constant of the interaction.

Substituting this relation in equation

$$dc_4/dt = c_4(k_4/A - k_{-4}) + u(dc/dz)$$

A complete solution of this expressions is possible only with a definite value for either the molar diffusion coefficient or the rate coefficients k_4 and k_{-4} . Attempts towards this direction was not attempted here, mainly because of the emphasis of the study was on other parameters. Detailed study with radioactive tracers is essential for the complete elucidation of this final expression.

Proof for the model

The steady interrelations observed with each element in the different compartments in the primary zone clearly approves the proposed interaction pattern. The mean values of the ratios of a few parameters in water, sediment and interstitial water obtained in the present study is given in Table 9 for a reference.

The significantly high correlation obtained between the parameters ~~observed~~ within a sediment core (Figures in chapter III) and the varying trends observed with a different elements is an indication of a summation of more than one contributing factor to the effective concentration. The proposed model can very well explain the varying behaviour of the ions.

Scanning Electron Microscopic (SEM) Analysis:

Shapes of clastic particles and the microscopic textural patterns of surfaces are repositories of information about the physical and chemical processes to which the particles have been subjected (Marshall, 1987). In their external appearance, sand grains can record evidences of several sedimentological events. For example the gross shape of a grain may suggest a littoral cycle while minute textures superimposed upon the surfaces may indicate an aeolian origin, and into these textures may be etched features which can be of diagenesis. Thus, a single grain can be a remarkable store of information of several events. Thus SEM techniques give clear evidences for the identification of sources, interpretation of genesis, mechanical processes and diagenetic changes of various detrital sediments (Waugh, 1965, 1970). The surface features are regarded as important indicators of depositional characteristics of different environments (Krinsley and Donahue, 1968; Krinsley and Doornskamp, 1973; Georgiev and Stoffers, 1980)

Here, SEM techniques have been used to study the surface textures of quartz and feldspar grains to understand the changes taking place during burial and subsequent chemical reaction structures by diagenesis. The SEM photographs were taken at the Physical Research Laboratory, Ahmedabad, using Cambridge stereoscan S4-10 and the minerals were identified from EDX (Energy Dispersive X-ray) spectrum which were obtained using a KEVEX 500 μ X energy dispersive fluorescence X-ray system.

Quartz and feldspar grains collected at the surficial level of core E5 are subjected to SEM analysis and are presented in Plates 1, 2, 3 and 4. Sharp edges and conchoidal surfaces of the quartz grains (Plates 1 and 2) and a more or less perfect crystals of feldspar (Plates 3 and 4) indicate that the grains are not subjected to much chemical reaction. Quartz grain reveals some amount of angularity (Plate 1) which is an indication of recent detrital origin. Since they are embedded in

a clay rich environment, mechanical action under the impact of rolling and abrasion on the grain are less. This indicates the less diagenetic reactions at the surficial level.

Unlike the surficial quartz and feldspar, grains collected at a depth of 75 cm show clear reaction structures which are shown in Plates 5 and 6 (quartz) and Plates 7 and 8 (feldspar). Etching features and pitted surfaces and other unoriented etch pits would have resulted from diagenetic reactions at this depth. Because of very long residence time these structures would not have formed by mechanical processes. The diagenetic reactions have been affected severely even the refractory minerals like quartz. The intensity of leaching is further evidenced from high Si content in interstitial waters (see Chapter 4). Padmalal (1992) has stated that in addition to quartz, zircon also subjected to diagenetic changes, in the Vembanad estuarine (grab) sediments.

Further evidences for chemical dissolution have shown from authigenic precipitation. In Plate 6, an authigenic precipitation, obscuring the original/reaction structures, have been identified which could be of authigenic feldspars as identified from EDX spectrum (Fig. 27A). However, plates 9 and 10 are SEM photos of grains collected at the surface and 45 cm depth respectively. Since Ca and S are the prominent composition identified for those grains from EDX spectrum (Fig.27C) precipitation of calcium sulphate is possible. From the above photos it is clear that diagenetic processes are intensively taking place in this region. Ramachandran (1992) have observed silica precipitation even at the surface grab sediments off Cochin.

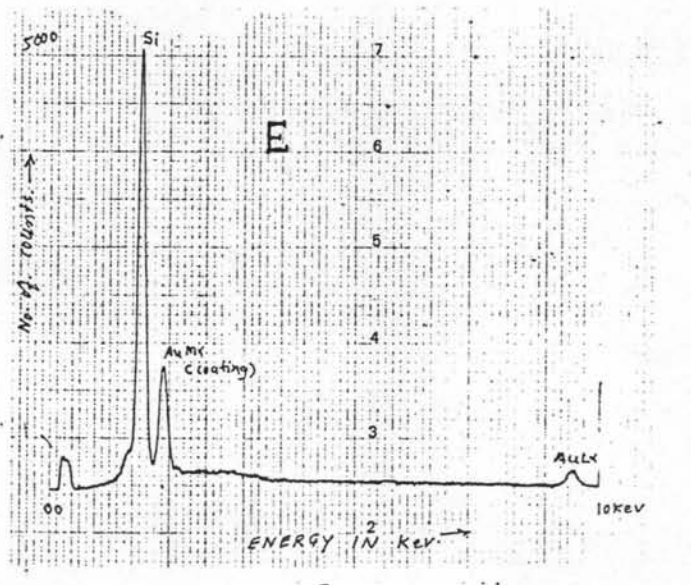
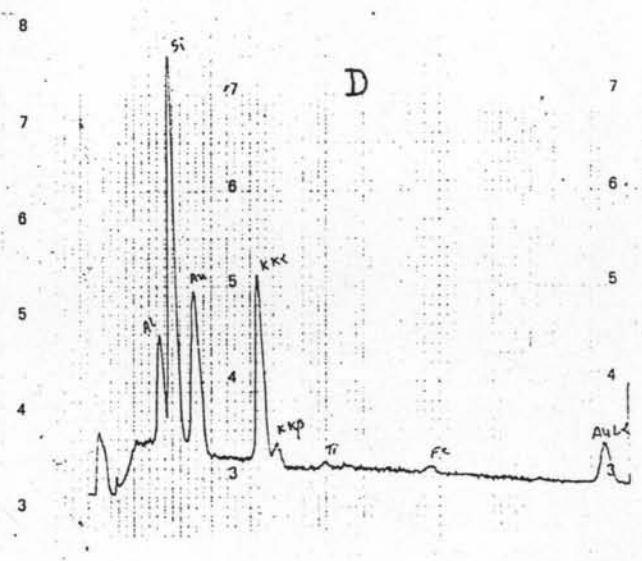
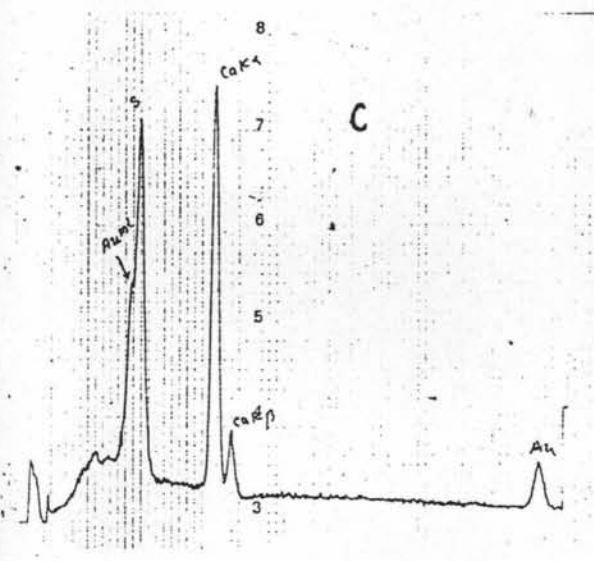
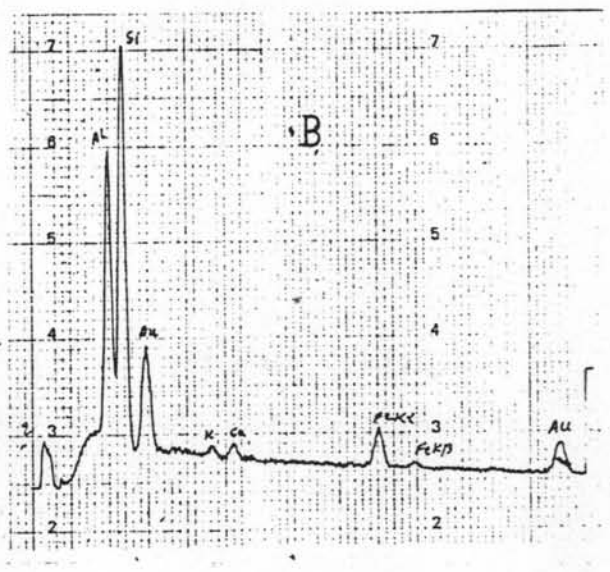
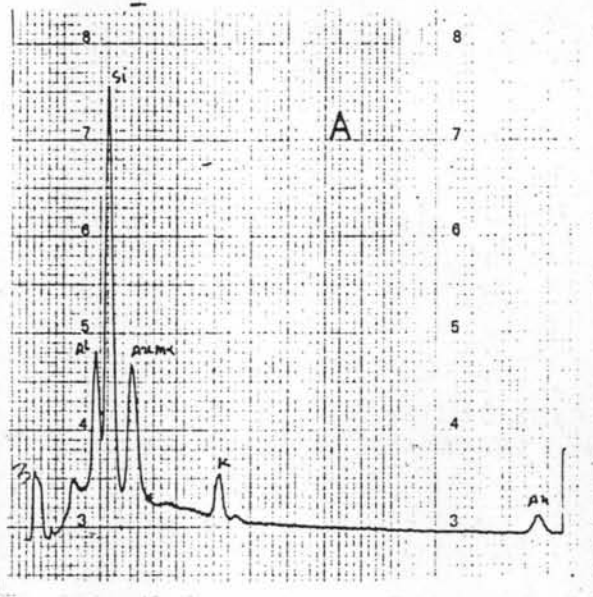


Fig. 27 EDX Spectra of the minerals

Plates 1 and 2

Quartz grains from the surficial sediments. Note the sharp edges and conchoidal fractures indicating least chemical action.

Plates 3 and 4

Feldspar grains from the surficial sediments showing sharp edges indicating less chemical action.

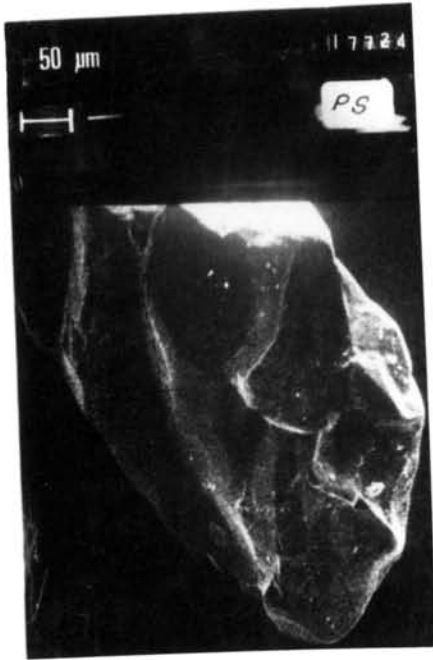


Plate 1

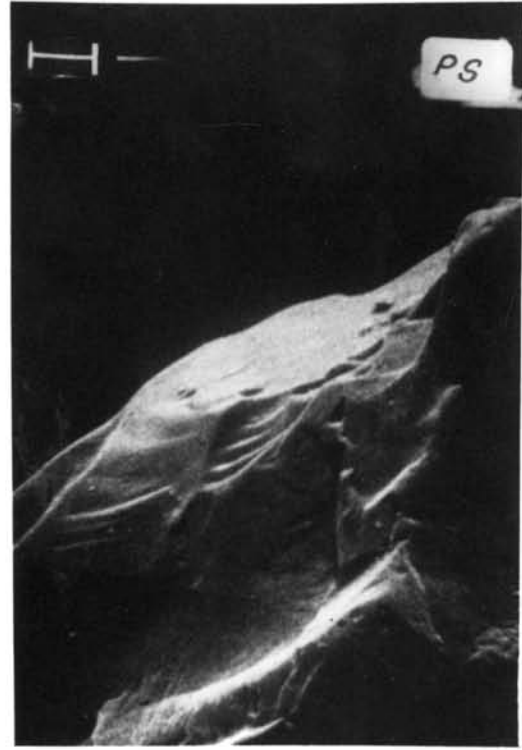


Plate 2



Plate 3

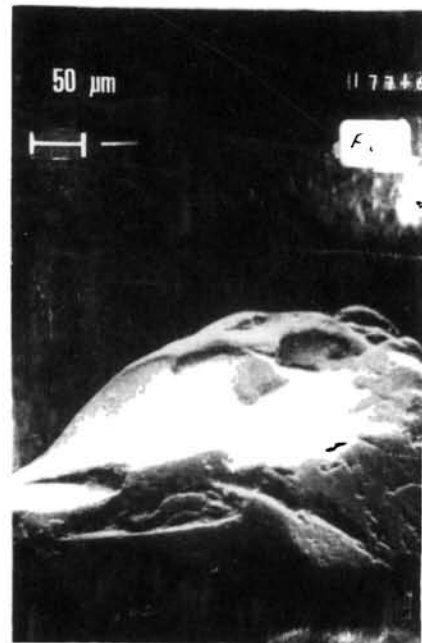


Plate 4

Plates 5 and 6

Quartz grains from a depth of 75 cm. Note the reaction structures (etch features, pitted surfaces, and other un-oriented etch pits) indicating of strong diagenesis at depth. Also note an authigenic feldspar precipitation (box in Plate 6) over quartz grain (with a composition of Si and Al. See Fig. 27c - EDX spectrum).

Plates 7 and 8

Feldspar grains from a depth of 75 cm with reaction structures.

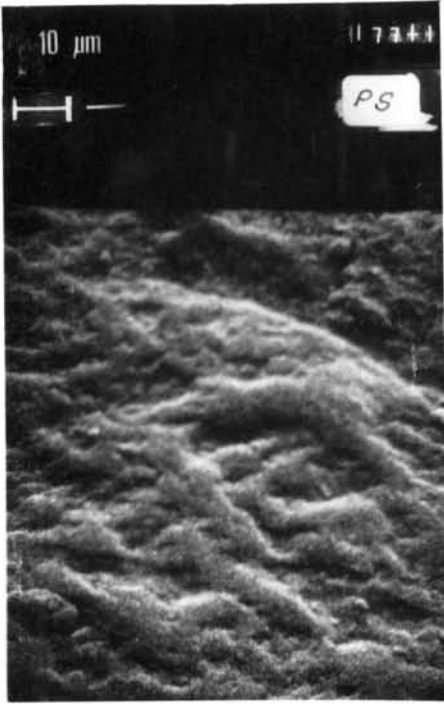


Plate 5



Plate 6

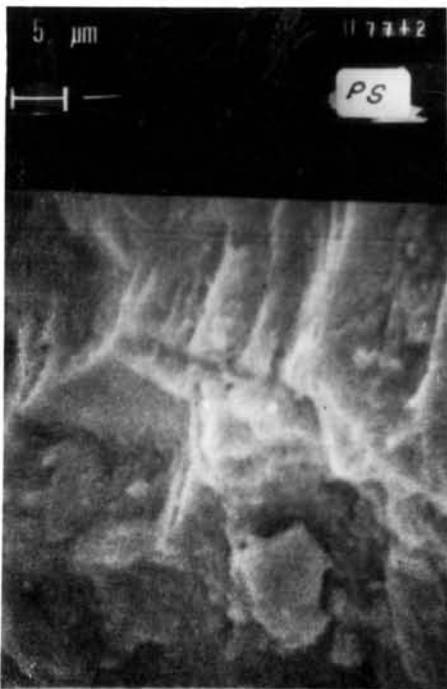


Plate 7

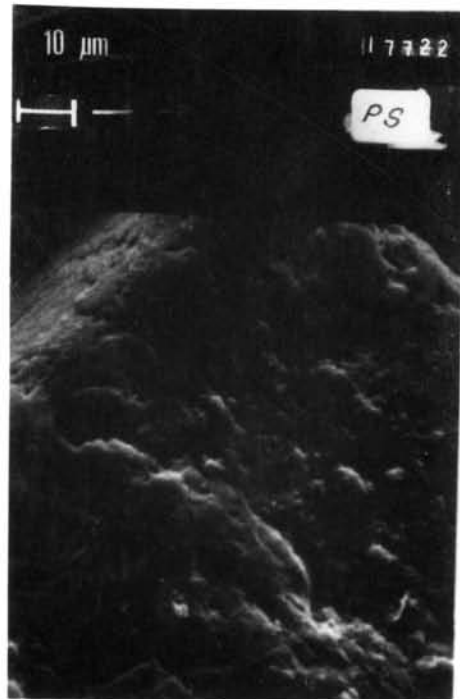


Plate 8

Plate 9

Authigenic crystals from the surficial sediments with calcium and sulphur as composition (Calcium sulphate).

Plate 10

Authigenic crystals at a depth of 45 cm. Composition same as plate 9. See Fig. 27c - EDX spectrum)



Plate 9

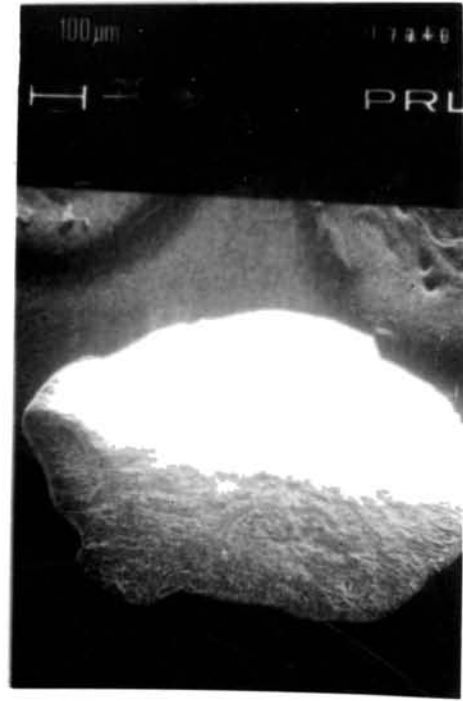


Plate 10

Chapter 6

Summary and Conclusion

The Geochemistry of interstitial water-sediment from three environments namely river, estuary and marine has been studied with the help of 18 core sediments in order to understand the variations of chemical processes between environments as well as with in the sediment column. Simultaneous investigations on various parameters and their role in the diagenesis of sediments is rather limited. The study also throws light to a limited extent on the chemical processes taking place at the sediment-water interface.

The colour of sediments vary between brown and olive green. Only the top 2 cm of the sediments are moderate brown in colour. The sub bottom sediments of riverine sediments are grayish brown in colour because of moderate reducing condition. On the other hand the estuarine and marine sub-bottom sediments exhibit olive gray colour due to intensive reducing condition. The sediments composition reveals that silt and clay dominate in estuarine and marine sediments. In estuarine area sandy clay predominates while in marine area clayey sediments are abundant. Sand content in riverine sediments are appreciable and therefore, sandy clay and sandy mud are abundant.

The salinity of riverine interstitial waters is negligible. The marine interstitial waters show similar salinity values as that of the overlying waters. However, in the estuarine region, because of dilution effect by fresh waters, low salinity values are recorded at the top 20-25 cm level. As expected the pH of the fresh water riverine sediments maintain a low value. The relatively high values in the other two environments are due to high anoxic condition. The existence of reducing condition just below 2 to 15 cm of the sediment column is shown by very low negative Eh values. The river sediments show moderate reducing condition. However, high negative Eh are observed in estuarine sediments.

The reducing condition is due to the microbial degradation of organic matter. The abundant organic matter is derived from several sources such as hinterland drainage basin, coconut husk retting, urban sewage pollution, abundant salvinia population, high planktonic production due to high availability of nutrients coupled with upwelling processes in estuarine and marine areas. The microbial degradation of organic matter leads to a series of reactions/ processes in the sediment column both at nutrient and metal chemistry level as well as other related parameters. A general decrease of Eh, pH, NO_2^- , NO_3^- and SO_4^{2-} and an increase in alkalinity, NH_4^+ , PO_4^{3-} and SiO_2 are primarily microbially controlled processes. Hence, a reduction in sediment organic carbon, N and P content with depth of sediment.

Maximum utilization of O_2 at the sediment-water interface or just below the top core is evidenced from very low positive to low negative values at the surficial sediments itself. The intensity of anoxic/ reducing condition is much severe below the sediment column. Similarly the reducing conditions is prominent in the estuarine region. The sharp decline of redox potential from the top core is caused by primarily by oxidation of organic matter first consuming O_2 and then reduction of NO_3^- , oxihydroxides of Mn and Fe and SO_4^{2-} . High alkalinity is caused by the increase of bacterial SO_4^{2-} -reduction and NH_3^+ build up. Release of PO_4^{3-} and precipitation of CaCO_3 also have an effect on alkalinity.

The sediment nitrogen shows a slight decreasing trend with depth. Nitrogen contained in the sediments as amino acids and organic forms on decomposition gives rise NH_4^+ , but in upper oxidized zone NH_4^+ is immediately converted to NO_2^- and NO_3^- . Hence invariably low values of NH_4^+ are recorded in the top interstitial waters of the cores. The intensive nitrification process is revealed by high contents of NO_2^- and NO_3^- in interstitial waters. The required O_2 for the nitrification process is supplied by bioturbation and irrigation. The

nitrification process is restricted to the top 10-15 cm level only, below which denitrification process is very prominent and therefore very high NH_4^+ but very low NO_2^- at bottom interstitial waters. The denitrification process right from the sediment-water interface is also revealed in some estuarine and marine cores. The denitrification process clearly indicates the complete utilization O_2 in the sediment column for remineralization of organic matter. Subsequent to denitrification, SO_4^{2-} reduction takes place. SO_4^{2-} concentration decreases rapidly with depth. However, just as nitrification, oxidation of S takes place in some cores just below the top layers and therefore SO_4^{2-} at this level is very high.

Sediment P is mainly derived from organic matter. The relatively high p in marine and estuarine region is partly related to increased productivity by upwelling. The sharp increasing PO_4^{3-} concentration with depth is resulted from the release of PO_4^{3-} during mineralization of organic matter and phosphorus bearing solid phases. Like PO_4^{3-} the concentration of SiO_2 also increases with depth due to dissolution of diatoms.

The major and trace metals concentrations show significant variations in accordance with the prevailing environmental conditions. Si is relatively enriched in the river sediments due to high sand content. In addition to detrital quartz other contributing factors are silicate minerals and siliceous skeleton materials. The interstitial Si is mainly originated through the dissolution of amorphous and biogenic silica. Unlike Si, sediment Al do not show any remarkable variations between environments and also with depth. Alumino-silicate and clay minerals are the controlling factors of sediment Al. Authigenic precipitation with a feldspar composition is predicted. The interstitial Al is mainly due to dissolution of detrital feldspars.

Sediment Na and K decrease with depth. The depletion is due to dissolution of feldspars and other silicates minerals in the

highly reducing condition. However, in riverine core, dissolution of Na and K are relatively less. K depletion in interstitial water is related to adsorption onto clay minerals and authigenic precipitation. Ca and Mg in sediments increases with depth. Precipitation of CaCO_3 and the calcium sulphate are the main causes for such a concentration at depth. Mg concentrations at depth in the sediments are related to clay mineral absorption.

Fe and Mn are relatively concentrated in the sediment at or just below the sediment water interface than at depth. In contrast, the interstitial concentration of Fe and Mn are more in the bottom reduced zone and this build up is caused by reduction processes of Fe and Mn. Released Fe and Mn get oxidized at the top of the cores and reprecipitated as oxyhydroxide phases. But in the reduced zones iron sulphides is the prominent mode of enrichment followed by phosphates and carbonates.

Trace metals like Cu, Co, Ni, Zn, Cd, Cr and Pb generally follow the trends followed by Fe and Mn. Maximum dissolution of metals takes place below the zone of O_2 maximum. But the enrichment in the anoxic layers are attributed to their fixation in sulphides and/or scavenging action of Fe sulphide. Contrary to the above, Sr follows the Ca distribution pattern. Scavenging of Sr by CaCO_3 and precipitation of Sr carbonate and Sr sulphide are other possible mode of enrichment at the bottom layers of sediment.

Partition analysis of a core reveals to a little extent the overall mechanism of metal enrichment in different phases. Only Mn and Zn show significant enrichment in carbonate and Fe-Mn oxide phases. However, all the metals show relatively high enrichment in sulphide phases. More than 50% of Cd enrichment and about 35% of Zn are sulphide bounded. Except these two metals other metals show a prominent lithogenic source.

The diagenetic process operating in the sediment column as well as at the sediment-water interface are discussed. A generalised diagenetic model is presented. The preservation of original surfaces of quartz and feldspar at the surficial level indicate the least diagenesis whereas the reaction structures as well as the precipitation of authigenic minerals having composition of Ca and S (Calcium sulphate) and Si and Al (Feldspar) are indications of severe diagenetic reactions at the depth.

From the above studies it is clear that anoxic conditions at the bottom layer of sediments and the moderately low oxic to sub oxic nature at or below the sediment-water interface have effected a lot in the mobilization of nutrients and sediment geochemistry of sediments.

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