STUDIES ON THE SULPHUR CHEMISTRY OF A TROPICAL ESTUARINE SYSTEM

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BEENAMMA JACOB

CHEMICAL OCEANOGRAPHY DIVISION - SCHOOL OF MARINE SCIENCES
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 016

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COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

Dr. N.CHANDRAMOHANA KUMAR
SENIOR LECTURER,
CHEMICAL OCEANOGRAPHY DIVISION

SCHOOL OF MARINE SCIENCES
FINE ARTS AVENUE
COCHIN-682 016, INDIA

CERTIFICATE

This is to certify that this thesis is a bonafide record of research carried out by Mrs.Beenamma Jacob, under my guidance, in partial fulfillment of the requirements for the degree of Philosophiae Doctor of the Cochin University of Science and technology

Cochin-682 016,
June 1993

Dr.N.Chandramohanakumar
Supervising Teacher

PREFACE

Stress on the environment is caused not only by pollution but may also be a normal facet of oceanic conditions. In the course of evolution, this some times resulted in the development of very specilaised ecosystems or living communities which are adapted to such special conditions. The presence of biologically active substances and its biochemical and geochemical transformations can derive such a special condition, the study of which is still a complicated field. The existence of such substances were suspected long ago but only with the advent of highly sensitive and selective techniques, which could detect and estimate considerably low concentration of chemical entities, the role of these substances came into limelight.

Sulphate is always considered as a major ion with a reasonable conservative character in the aquatic system but on the same time almost all the sulphur species (including sulphate) are biologically active. The various transformation processes, that determine the concentrations of the different species of sulphur, define the quality of the aquatic environment. Living organisms contain highly variable amounts (0.01-5.00%) of sulphur and the sulphur chemistry has attracted a considerably high interest among the environmental scientists as it is involved in a number of biogeochemical processes such as sulphate reduction, pyrite formation, metal cycling, ecosystem energetics and atmospheric sulphur emissions.

The investigations reported in this thesis are a modest attempt at identifying the major sulphur fractions, and the possible processes that can modify the distribution of the various sulphur fractions in the sedimentary environments of the tropical Cochin estuary and the Kerala coast.

The work embodied in this thesis is under publication/under preparation as indicated below,

1. The distribution and seasonal variations of acid volatile sulphides in the sedimentary environments of a tropical estuary. Beenamma Jacob and Chandramohanakumar, N., *Chem. Geol.*

2. Distribution of iron sulphides in the sediments of tropical Cochin estuary. Beenamma Jacob and Chandramohanakumar, N., *Geochim. Cosmochim. Acta.*

3. Seasonal dynamics of elemental sulphur in the surficial sediments of a tropical estuary. Beenamma Jacob and Chandramohanakumar, N., *Indian J. Mar. Sci.*

(4). A steady state model for the diagenesis of sulphur in surficial sediments of a tropical estauary. Beenamma Jacob and Chandramohanakumar, N., *Geochim. Cosmochim. Acta.*

5. The distribution of inorganic and organic sulphur fractions in the Kerala coast. Beenamma Jacob and Chandramohanakumar, N., *Indian J. Mar. Sci.*

CONTENTS

CHAPTER-I

INTRODUCTION

1.1. Sulphur Occurrence

Sulphur is an essential element for all plants, animals and microorganisms. It usually accounts for less than 1% of the dry weight biomass (Anderson, 1978; Schlegel, 1981) and is commonly in the range of 0.4% to 0.8% for microorganisms (Postgate, 1968; Bauld, 1986). Much of this sulphur is present as the secondary constituent of amino acids, proteins and enzymes, while lesser amounts occur in certain molecules such as co-enzyme A, vitamins, ferredoxins, glutathione etc.(Siegel, 1975). Cellular sulphur may also be present in structural components and storage compounds (fungi) in the form of sulphate esters (Roy and Trudinger, 1970; Siegel, 1975).

Generally the amount of sulphur in the biosphere is small when compared to annual consumption by living organisms (Anderson, 1978). Localized concentrations of sulphur species may occur in the geosphere, eg. elemental sulphur (S^0), metal sulphides mainly pyrite, gypsum, barite, epsom salts, petroleum and coal. Traces of sulphur occur as H_2S in volcanic gases. In marine environment, sulphur in the form of sulphate is a major dissolved constituent, and is originated from the volatiles which have distilled from the interior of earth under the influence of radioactive heating (Riley and Chester, 1971). Considerable amounts of sulphate reach the sea from the weathering of sulphide minerals also; the geochemical balance is probably maintained by deposition of sulphide minerals and sulphur in the sediments via bacterial reduction (Berner, 1964).

1.2. Sulphur Cycle

The cycling of sulphur at the Earth's surface has been greatly increased since the start of the Industrial Revolution due to the demand for fuel, metals and fertilizers. It is noticeable that the majority of the anthropogenic effects lead to an increase in oxidation state for the sulphur, whereas the biologically mediated natural cycle of sulphur has a large component in which the oxidation state is reduced (O'Neill, 1985). The cycles of sulphur and nitrogen have a number of similarities, but one most important difference is that the major reservoir for nitrogen is the atmosphere, whereas the major available reservoir for sulphur is the crust.

Sulphur exists in large number of oxidation states. Transformations between the various oxidation states of sulphur occurring within the biosphere are dominantly microbial mediated (Bauld, 1986). Species transformations may occur during assimilatory and dissimilatory processes. The assimilatory sulphate reduction is a process by which plant and most of the microorganisms utilize sulphate as their sole source of sulphur in order to meet bio-synthetic requirements (Anderson, 1978). Dissimilatory processes may be oxidative or reductive in character. The former commonly provide a source of electrons for energy generating metabolism and/or a source of reducing power for autrotrophic CO_2 fixation. The latter employs oxidized sulphur species as terminal electron acceptors for anaerobic respiration.

Under natural conditions the biogeochemical cycle of sulphur is inextricably linked with other elemental cycles through the biosynthetic requirements of, and the dissimilatory utilization by microbial communities. The interactions between C, Fe and S cycling can be explained in a stratified ecosystem. The establishment of a stratified ecosystem is driven by the primary production of organic matter which may be of allochthonous or autochthonous derivation. Subsequent aerobic decomposition depletes oxygen, particularly at lower light intensities, and some H_2S is produced from the anaerobic decomposition of organic thiol (-SH) groups. Dissimilatory reduction of oxidized S species can now proceed and the resultant H_2S produced is removed via precipitation with Fe^{2+} released from sediments. The relative abundance of Fe in most natural habitats compared to other metals such as Zn, Pb, Ni and Cu ensures that only iron sulphide precipitate can be a major sulphur sink to sediments.

The important biogeochemical processes into which sulphur can enter involve sulphate reduction (Howarth and Teal, 1979), pyrite formation (Lord and Church, 1983), metal cycling (Boulgue *et al.*, 1982; Luther *et al.*, 1982), salt marsh ecosystem energetics (Howarth and Teal, 1979; Howarth, 1984), formation of important resources like petroleum hydrocarbons and coal (Casagrande *et al.*, 1979b), atmospheric sulphur emissions (Adams *et al.*, 1981; Steudler and Peterson, 1984), metal corrosions (Fjerdingstad, 1967), acid rain (O'Neill, 1985) and regulation of global climate (Andreae, 1990).

The sulphur cycle has received considerable attention due to the pivotal role of sulphate reduction in anaerobic respiration and the resultant production of sulphide minerals (Goldhaber and Kaplan, 1974). Also, as a part to understand the processes leading to the formation of important resources like petroleum hydrocarbons and metal sulphide ores which probably occur in anoxic basins.

Pyrite formation is another important biogeochemical process whereby sulphide toxicity is reduced and promote plant production. Pyrite can store reduced sulphur compounds and its oxidation is believed to support salt marsh food webs. Once buried, pyrite appears geologically stable and is a primary reservoir of iron and sulphur in salt marsh sediments.

The involvement of sulphur in metal cycling can be explained by the enrichment of metals in anoxic waters as metal sulphides. In salt marsh pore waters and sediments, certain organic sulphur compounds will form the precursors of sulphur in fossil fuels such as coal. The emission of certain sulphur compounds to the atmosphere which when oxidized act as remote acid rain precursors along with other sulphur compounds contributed by the burning of fossil fuels and extraction of metals from sulphide ores or from volcanoes etc..

Part of the biologically produced organic sulphur compounds like dimethyl sulphide diffuses into the atmosphere where it is oxidized mostly to aerosol sulphate. The ability of these aerosol particles to nucleate cloud droplets and thereby influence the reflectivity and stability of clouds form the basis of the proposed theory of partial regulation of global climate through sulphur cycle. Microbial corrosion has become a major problem in which also sulphur plays a critical role.

1.3. Estuarine Processes and Sulphur Chemistry

Estuaries are regions of fundamental importance with respect to biogeochemical processes occurring on a global scale, for they represent the major route whereby weathered lithosphere material is transported to the oceanic sedimentary domain. Since the estuary represents the interface of three quite separate and contrasting environments namely seawater, fresh water and land, processes occurring within the estuary are dependent on the fluctuations in the magnitude of the marine, limnetic and terrestrial influences. Variability is an inherent and essential property of estuarine systems. The distribution of properties and the occurrence of *in situ* processes undergo short term, seasonal and large term fluctuations, although many of the fluctuations have a cyclic nature.

Both major and minor elements take part in estuarine chemical interactions involving dissolved and particulate phases. The processes of primary production, respiration and mineralization, because they can cause significant change to the oxygen and carbon dioxide concentrations of aquatic environments, are able to alter the Eh and pH of the system and thus alter the speciation of many chemical constituents. The magnitude of the primary production of estuarine plants is an important factor in the organic processes occurring in estuaries.

Estuarine organic matter consists of an autoclithonous contribution resulting from primary production within the estuary and alloclithonous contribution from adjacent ecosystem. The latter include domestic and industrial sewage discharges. In estuaries, the amount of organic matter is usually greater than that in the open sea. Under conditions of poor water exchange, the levels of organic matter in estuaries can build upto concentrations such that, oxygen is reduced to very low concentrations or completely removed from the water.

Large deposition of organic matter converts the sedimentary profiles to a strongly reducing environment in the estuary, particularly in its upper part. Oxygen deficiency can enter already at the sediment-water interface in the upper part of an estuary, while further seawards, the redox discontinuity occurs a few millimeters or centimeters below the sediment surface. This stratification provides the basis of transformations of sulphur compounds through a cyclic series of redox processes.

Jorgensen (1977) calculated for the Limfjorden, Denmark, that 53% of the mineralization of organic matter is taking place due to sulphate reduction. Similarly, Jorgensen and Fenchel (1974) found in a laboratory model of a marine sediment, that more than 50% of the organic matter was mineralized by bacterial sulphate reduction. Thus sulphate reduction plays a major role in the mineralization processes in estuarine areas.

1.4. The Cochin Estuarine System

India has a coastline with numerous rivers and estuaries. Estuaries with their associated river systems form an integral part of coastal features.

Estuarine ecosystems are extremely fertile and are excellent nursery for a variety of commercially important fishes and crustaceans. Over 80% of the biological activity and associated fisheries take place in nearshore waters.

The Cochin estuarine system, the largest along the west coast in the Kerala state extends between $9^{o}\ 40'$ N and $10^{o}\ 12'$ N , $76^{o}\ 10'$E and $76^{o}\ 30'$E. It has a length of about 70 km and width varies between a few hundred meters to about 6 kms. The Cochin estuarine system covers approximately an area of 300 square kilometers. As a shallow semi-enclosed body of water, it falls under the category of a tropical positive estuary (Pritchard, 1967).

The south-central part of the state of Kerala is characterized by the presence of the two large basins of Periyar river and Muvattupuzha river, north and south respectively, extending the entire breadth of the land sloping westward. These rivers empty into the Cochin backwaters which is having a tidal area of approximately 500 square meters. A channel of about 450 meters wide forming the entrance to the Cochin harbour and another opening located towards the north at Azhikode have linked the backwater permanently with the Arabian Sea.

The increase in population around this estuary and the rapid industrialization, have resulted in the discharge of a heavy load of inorganic and organic wastes. The enormous expansion in industrial activity during the last century, production and use of power, diversity of manufactured material, transportation, fishing intensity and human population have all caused increasing pressures of diverse nature on these waters.

Since the year 1976, the hydrographic condition of this estuarine system had undergone extensive changes by way of:

1. interbasin transfer of water from Periyar to Muvattupuzha river to facilitate a hydroelectric project,

2. construction of a saltwater barrier (The Thanneermukkam bund) on the southern part of the estuary and

3. extensive dredging and harbor operations.

Apart from these, the waterway receives considerable amount of pollutants from:

1. industrial units like the Fertilizers and Chemicals Travancore Ltd., Travancore Cochin Chemicals, Indian Rare Earths, Hindustan Insecticides Ltd., Cochin Refineries, Hindustan Newsprint Factory, Hindustan Organic Chemicals etc..

2. domestic sewage and storm water channels

3. port area handling large quantities of crude and refined petroleum products and industrial chemicals

4. coconut husk retting yards and

5. fish processing industries.

The knowledge on the various aspects of the physicochemical parameters of this estuary turns out to be essential, for assessing the water quality and various biogeochemical processes and also in providing future guidelines on the estuarine management. The status of earlier scientific works conducted in this system can be summarised as follows.

The hydrography of the estuary was investigated by several investigators including George and Kartha (1963); Cherian (1967); Qasim and Gopinathan (1969); Josanto (1971); Haridas *et al.*, (1973); Pillai *et al.*, (1973); Jayapalan *et al.*, (1976); Balakrishanan and Shynamma (1976); Anto *et al.*, (1977); Ramaraju *et al.*, (1979); Saraladevi *et al.*, (1979); Varma *et al.*, (1981 and 1987); Lakshmanan *et al.*, (1982); Anirudhan *et al.*, (1987); Pillai (1989); and Pylee *et al.*, (1990). The information available include spatial and seasonal distribution of temperature, salinity, dissolved oxygen, pH, alkalinity and suspended solids of surface and bottom waters of the region as a whole or a part.

The biological characteristics of the estuary have been investigated by Kurian *et al.*, (1975); Unnithan *et al.*, (1977); Sankaranarayanan and Rosamma (1978); Pillai (1979); Saraladevi *et al.*, (1979); Remani *et al.*, (1983); Anwar (1985); Gopalan *et al.*, (1987); Joseph *et al.*, (1988); Joseph (1989); Saraladevi and Venugopal (1989) and Joy *et al.*, (1990).

Studies on nutrients include those of Sankaranarayanan and Qasim (1969); Manikoth and Salih (1974); Sankaranarayanan and Panampunnayil (1979); Lakshmanan *et al.*, (1982); Sankaranarayanan *et al.*, (1984); Anirudhan (1988); Saraladevi *et al.*, (1991).

The greater awareness on the potential health hazards due to industrial and domestic effluents added to this estuary prompted several research works to take up toxicological studies (Lakshmanan, 1982; Sivadasan, 1987; Baby, 1987; Latha, 1987; Krishnakumar, 1987 and Prabhudeva, 1988). Considerable data is now available on the toxic effects of several of the pollutants especially of trace metals on several of the fauna of the Cochin estuary and adjoining marine environments (Lakshmanan and Nambisan, (1977, 1979, 1980, 1983, 1985a, 1985b and 1989); Nambisan *et al.*, 1977; Baby and Menon, 1986; Menon, 1986; Sivadasan *et al.*, 1986; Prabhudeva and Menon, 1987; Suresh and Mohandas, 1987; Sathyanathan *et al.*, 1988; Sivadasan and Nambisan, 1988; Krishnakumar *et al.*, 1990; Geetha, 1992).

Studies on trace metals have been carried out by Sankaranarayanan and Rosamma (1978); Sankaranarayanan *et al.*,. (1978); Murty and Veerayya (1981); Jayalakshmi and Sankaranarayanan (1983); Paul and Pillai (1983a, 1983b); Ouseph (1987 and 1990); Shibu *et al.*, (1990) and Nair *et al.*, (1990); Nair *et al.*, (1991); Nair (1992) etc.

Studies on the sediment characteristics include those of Veerayya and Murty (1974); Murty and Veerayya (1981) and Mallik and Suchindran (1984). The other studies include those of Vijayan *et al.*, (1976) on the effect of organic pollution on some hydrographic features, Balchand and Nambisan (1986) on the effects of pulp paper effluents, Nair *et al.*, (1989) on hydroxylated aromatic hydrocarbons, Balchand *et al.*, (1990) on the survey of protein content and Sujatha (1992) on distribution of pesticides in the estuary etc.

1.5. The South-West Coast of India

India with a coastline of about 5600 Kms. and an operational advantage over a very wide marine sector, is in a commanding position as regards the utilization of its coastal seas. The coastal zone can be characterized by its own socio-economic and political activities related to the distribution and availability of resources.

The many and diverse human activities involved in the use of coastal zone will impose an excessive and competitive stress and may affect the ecological balance of this zone. Thus the multiple use of these coastal zone calls for a greater need for its protection so that it could continue to provide, for the benefit of the mankind, a source of exploitation of different types of resources without depleting the most important and perhaps the most sensitive of all the living resources.

The study of the chemical and physical aspects of the nearshore environment provides the background information necessary for the understanding of the coastal processes. Compared to open ocean systems, where the composition are temporally invariant and chemical processes are rather in a steady state, the coastal region exhibits environmental gradients occurring spatially and temporally on micro or macro scale.

The south-west coast of India is characterized by the upwelling phenomenon (Sankaranarayanan and Qasim, 1969). The coastal shelf can be distinguished into two distinct sediment facies depending on the distribution of surficial sediments (Nair and Pylee, 1968). The inner shelf from about 3m water depth to about 65m consists of silts, clays, high organic carbon and low $CaCO_3$ (Nair and Pylee, 1968; Murty *et al.*, 1969). Within this zone of terrigenous silts and clays, mudbunks are formed seaward, from 65 m to the continental shelf edge, represents the outer shelf where the sediments are relict sand-size carbonate material in the form of oolites, shells of mollusks, foraminfers, coral and coralline algal debris (Nair, 1971). In terms of age, the inner shelf is of recent origin where as the outer shelf is of pleistocene period.

The Kerala coast under study has an area of 38,860 sq.km (8^o 15' to 12^o 45' N; 75^o 52' to 77^o 8' E) with a coastal line of 560 km. Relatively high sediment yields during the monsoon climate indicate that Kerala coast falls under the category of "trailing edge" (Inman and Nordstrom, 1971). More than 20 rivers cut the land surface of this coastal area. The features identified along the coast include beaches, beach cliffs, stacks, islands, shore platforms, spits bars, beach ridges, estuaries, lagoons, mudflats, tidal flats and deltaic plains (Nair, 1987). The wave and beach characteristics show that the direction of littoral drift is towards south in June and July months and towards north during other months (KERI, 1978).

The status of scientific work conducted along this coastal region is given below briefly.

Some wave characteristics studies have been conducted along the south-west coast of India by Bala and Harish (1985) and Baba *et al.*, (1989). Seasonal variability of the temperature has been investigated by Shetye (1984) and thermal efficiencies and OTEC potentials at some selected stations along the Indian coast has been reported by Babu *et al.*, (1983). The presence of upwelling during the south west monsoon season is well documented in several studies (Sharma, 1966; Banse, 1968; Venugopal *et al.*, 1979).

Certain beach studies include those of Trevallion *et al.*, (1970); Varma *et al.*, (1985) and Kumar and Murty (1987). Sediment movement along the shoreline has been described in the studies of Reddy and Varadachari (1973). Studies on sediment characteristics were carried out by Nair and Pylee (1968); Murty *et al.*, (1969); Stackelberg (1972); and Rao *et al.*, (1983). Preliminary studies on mud banks along the Kerala coast was carried out by Varma and Kurup (1970); and later detailed study was conducted by Nair (1990).

The biological aspects include the studies conducted by Goswami *et al.*, (1981); Qasim *et al.*, (1969); Sankaranarayanan and Qasim (1969); Devi (1969); Selvakumar (1970); Dwivedi (1973); Rao (1973); Achuthankutty (1975); Venugopal *et al.*, (1979); Kamat *et al.*, (1981); Madhupratap (1981); Sumitra *et al.*, (1982); Nair *et al.*, (1982); and Rao *et al.*, (1985) Studies on chemical characteristics include those of Anand *et al.*, (1968) and Rao *et al.*, (1987) on the variation of general hydrographic parameters, Siddiquie (1968); Reddy and Sankaranarayanan (1968); Sankaranarayanan and Reddy (1970); Rao *et al.*, (1978, 1987); Naqvi and Sen Gupta (1985); Naqvi *et al.*, (1990) on the distribution of nutrients, Rao (1978) and Shirodkar and Sen Gupta (1985) on the distribution of certain major ions in the sediments and interstitial waters respectively, Murty *et al.*, (1968, 1970, 1973 and 1980), Rao *et al.*, (1972), Singbal (1978) and Nair and Ouseph (1992) on certain metal studies, DeSouza and Kamat (1984) on the distribution of bromide, Sarkar and Sen Gupta (1987 and 1989) on chlorinated pesticide residues in sediments, Shirodkar *et al.*, (1982) on the distribution of boron, Sen Gupta *et al.*, (1978) on the survey of petroleum hydrocarbon concentration, Joshi (1987) on the equilibrium studies of certain radioactive metals. Interaction at the sediment water interface in coastal region was studied by Joshi and Ganguly (1981). Some pollutional aspects have been dealt with Qasim and Sen Gupta (1988) and Qasim *et al.*, (1988) along the coastal region.

1.6. Scope of the present study

Considerable research work expended in elucidating the physical, biological and chemical characteristics of the Cochin estuarine system has helped in assessing the water quality and various biogeochemical processes and also providing future guidelines on the estuarine management. The biogeochemistry of sulphur, though vital, still remains unattended. Indeed such an information is lacking from any of the estuaries along the Indian coast.

Studies on sulphur chemistry in aquatic environment has been concentrated mostly in salt marsh ecosystems, lakes and some marine sediments. Being a major constituent of sea water, the sulphur cycle has received considerable attention recently due to the pivotal role of sulphate in anaerobic oxidation of organic matter and the various biogeochemical processes sulphur undergoes.

The present study is an attempt to generate adequate information on the role of sulphur in estuarine processes and sediment chemistry. From earlier studies it was found that dissolved sulphur forms are not reliable indicators of sulphate reduction but solid phase reduced sulphur forms are especially informative, as these are never detrital. So in this study, both the dissolved and solid phase reduced sulphur forms have been examined.

The understanding of sulphur fluxes and transformations has been restricted due to the lack of information available on organic sulphur compounds. The works dealing with organic sulphur compounds have been very limited, but recently improved.

This report characterizes the regional distribution and temporal variability of sulphur in dissolved forms and sedimentary fractions, transformations and the interactions between the sulphur species and the mechanisms of formations. An attempt has been made for a comparative study with the coastal environment also. The sulphur species examined were sulphate and sulphide in water and acid volatile sulphide sulphur, greigite sulphur, pyritic sulphur, elemental sulphur, sulphate sulphur, organic sulphur and total sulphur in sediments. In addition to this general hydrographic parameters and sedimentary characteristics have also been dealt with.

The data collected provide an added information on estuarine processes and sediment chemistry and the detrimental effects of pollution also. In addition, this shall form the basis for further research on this topic.

1.7. Scheme of the work

The work incorporated in this thesis deals with the systematic study of pH, salinity, dissolved oxygen and various sulphur fractions in the Cochin estuarine system and selected stations along the Kerala coast. Monthly collections were made from the estuarine system, over a period of one year while single sampling was done along the Kerala coast during the premonsoon period.

The work is presented in six chapters

Chapter 1 gives a general overview of the subject. The importance of the sulphur chemistry and the aim/scope of the present study have been mentioned.

Chapter 2 describes the location of the study area and the sampling sites. The sampling procedures for water and sediment and the analytical methods adopted for the determination of various parameters are discussed in detail. The general hydrography and the sedimentary characteristics are also discussed in this chapter.

Chapter 3 deals with the distribution profiles of dissolved and the sedimentary sulphur species in the Cochin estuarine system. An attempt has been made to correlate between the sulphur species and the hydrographic parameters.

The fourth chapter capsulates the distribution of sulphur species along the Kerala coast. Efforts were made to correlate the data with the results of the estuarine system.

Chapter 5 is an effort to explain the results obtained in chapters 3 and 4 by generating a mathematical model.

The salient features of the work expended in the thesis is concluded in chapter 6 followed by the list of references.

CHAPTER-II

MATERIALS AND METHODS

2.1 Description of the Study area

The areas of the study and the stations sampled of the Cochin estuarine system and the Kerala coast are shown in Fig. 2.1 and Fig. 2.2. The estuarine stations were so fixed as to give a fairly good representation of the prevailing complex environmental conditions of the estuary and the coastal stations were selected for a comparative study giving a good coverage of the whole coastal area of Kerala.

13 stations were selected in the Cochin estuarine system covering whole range of salinity. The following is a brief description of the characteristics of the stations where the present study was carried out.

Station 1 is situated in the river Muvattupuzha which drains in to the Cochin estuarine system through the southern side, about 20 km. away from the barmouth. This station represents a fresh water riverine system. Station 2 is about 1 km. down to the station 1 and is located at the mouth of the river Muvattupuzha, where it joins the estuary. During monsoon months the station behaves as a fresh water zone.

Stations 3 and 4 are separated by a distance of about 4 kms. and station 3 is about 3 kms down the station 1. During monsoon months, these stations exhibit riverine characteristics and as the season advances to the post and premonsoon, estuarine conditions are prevalent. The sediments are

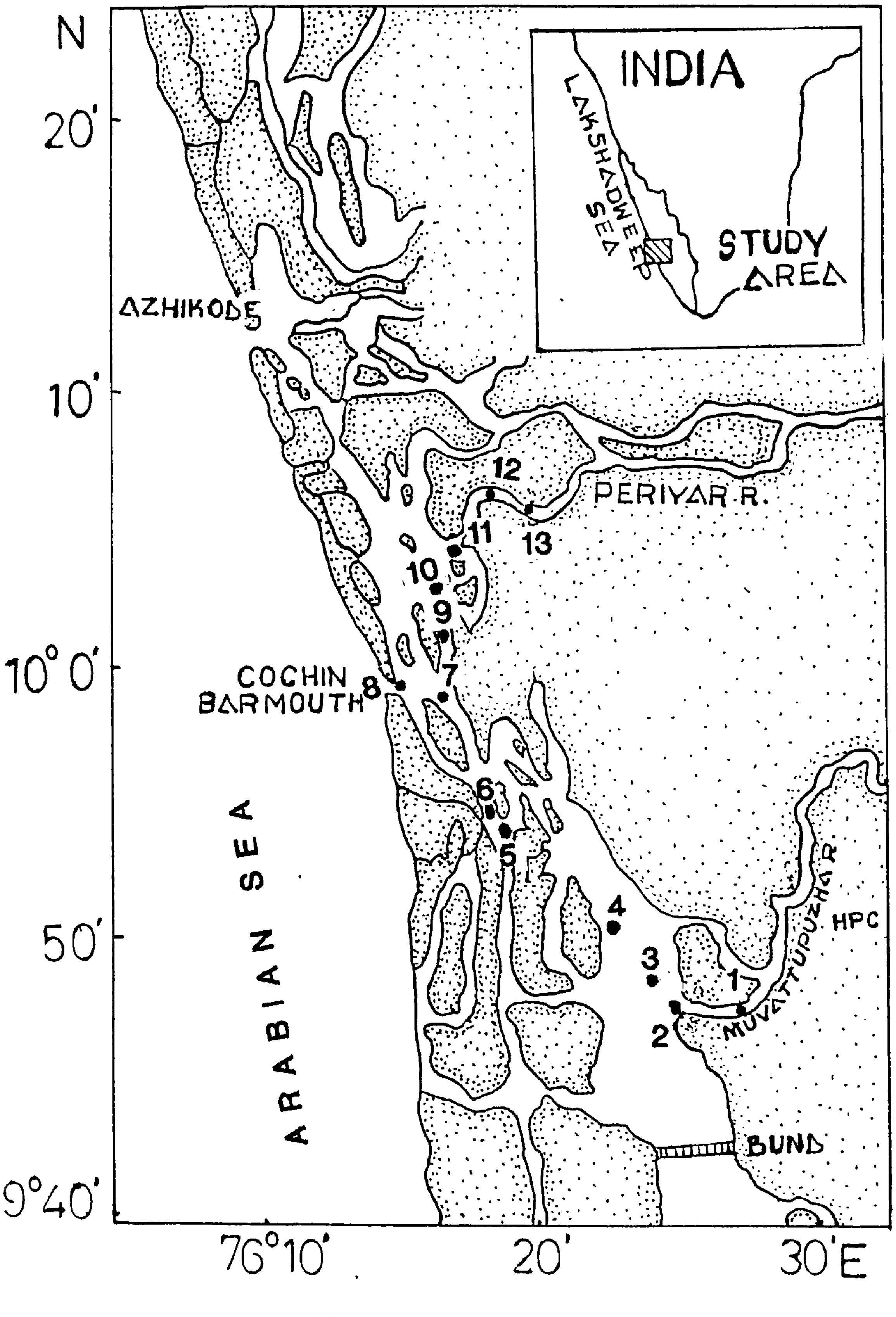


Fig. 2.1. Map of Cochin estuarine system: location of stations.

characterised by a major part by sand during monsoon with increasing silt and clay portion during the rest of the period.

About 3 kms down the station 4, station 5 is located. This is also fresh water dominated during monsoon, but estuarine during the other seasons. Significant quantities of organic matter is found embedded in the sand, silt and clay mixed sediment. Station 6 is situated at about 5 kms. from the barmouth and is estuarine in nature. This station is influenced mostly by the wastes carried by the Chithrapuzha river from the Ambalamugal industrial belt and sewage out falls.

Station 7 is also estuarine in nature and is characterised by navigational and port activities, numerous irrigation channels and discharges from various industrial and sewage out falls.

Station 8 represents the barmouth region. Station 9 is located in the northern arm of the estuary where the river Periyar empties its flux into the sea. This station is always typically estuarine. Sewage and wastes from oil mills, food industries etc. are discharged into this area.

Station 10 also represents an estuarine station in the northern arm of the estuary. The retting of coconut husks is the major activity in this area and huge amounts of plant pith get accumulated in this region. The sediments of this region contain large quantities of pith and yarns of coconut husk.

Station 11 is riverine region in the Periyar river. Salinity intrusion occurs during post and premonsoon seasons. The sediment is always sandy in nature. Station 12 is located at the effluent discharge point of the Fertilizers and Chemicals Travancore (Ltd.) and is also influenced by the effluents from industrial concerns like Hindustan Insecticides Ltd., the Travancore Cochin Chemicals Ltd., Indian Rare Earths

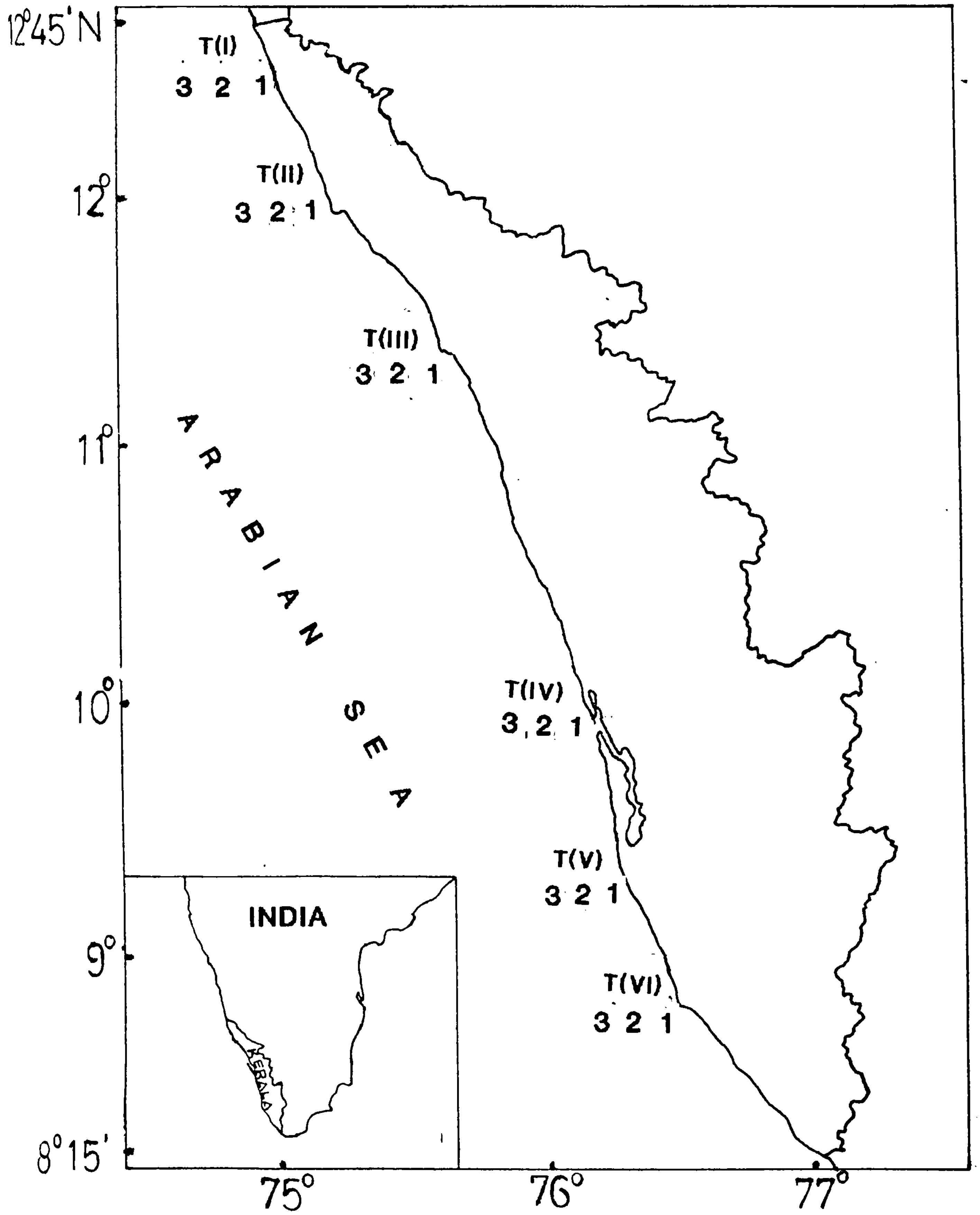


Fig. 2.2. Map of Kerala coast: location of stations.

etc.. Station 13 is about 20 kms. from the barmouth and is purely riverine in nature.

The monthly data were pooled and divided into the three seasons for getting reliable trends for analysing the features. (Random odd values observed were not included in averaging for the seasonal values). The monsoon season comprises of the months May, June, July and August. The postmonsoon season is of September, October and November and, December, January, February, March and April constitutes the premonsoon season. This classification was arrived at based on the rainfall data (Table 2.1.) in the region.

Along the coastal region six transects (T) were selected for the study, each transect comprising 3 stations (1 represents near shore station; 2 mid station and 3 offshore station) situated in seaward direction. The first transect is located at the northern end of the Kerala coast, and the sixth one is representing the Quilon region. South of Quilon was exempted from the study area because of terrigenous sandy nature of sediments, which is of poor biological activities.

2.2. Sampling Procedures

Water samples were collected from all the stations, while sediment samples were collected from 8 selected stations. Surface and bottom water samples and sediment samples were collected at monthly intervals from April 1990 to April 1991. Along the Kerala coast, the sampling was done during the premonsoon period of 1991.

Surface water sample was collected using a clean plastic bucket and bottom water was drawn using a Niskin sampler. Sub-samples were drawn out first for sulphide and oxygen in glass bottles. The sulphide was fixed by zinc acetate solution and oxygen by Winkler's reagents. Samples for other parameters were collected in polythene bottles.

Table 2.1. Rainfall data (April '90 - March '91)

Month	Rain in mm.
Apr '90	54
May '90	555
Jun '90	437
Jul '90	688
Aug '90	190
Sep '90	80
Oct '90	291
Nov '90	212
Dec '90	2
Jan '91	-
Feb '91	-
Mar '91	-

Sediment collection was done using a hand operated Van - Veen grab made of brass. The top 4 cm in the middle of the undistributed sample was collected by means of a plastic spatula in order to avoid contamination from the metallic part of the grab. The sample was then transferred to acid cleaned dry polythene bottles and kept in ice during transport and then kept at 4°C until analysis was carried out.

2.3. Analytical Methods

2.3.1. General Hydrographic Parameters

pH was measured immediately after collection using a portable pH meter (PHILIPS model PP 9046). Salinity was determined by an electrode less induction type Salinometer (DIGl - AUTO, model 3-G, Tsurumi Seiki, Japan) after bringing the samples to the lab. Dissolved oxygen was estimated by Winkler's method (Strickland and Parsons, 1972).

2.3.2. General Sedimentary Characteristics

The sediments were analysed to determine the organic carbon content by the dichromate method (Walkley and Black, 1934 as modified by El Wakeel and Riley, 1957). The texture analysis was performed as per the techniques described by Krumbein and Pettijohn (1938). *In situ* Eh determination was done using a Platinum electrode.

2.3.3. Dissolved Sulphur Fractions

Sulphate was determined gravimetrically after precipitating with barium chloride solution in acid medium (Am. Public Health Assoc. 1975 . The interference of alkali metals was minimised by adding picric acid and the co-precipitation of calcium and strontium was reduced by adjusting the concentration of HCl. To ensure good crystallisation, precipitation was done from hot solution.

Sulphide was determined spectrophotometrically following the method of Cline (1969). The samples, fixed with zinc acetate solution were treated with (N,N) dimethyl p-phenylene diamine dihydrochloride and ferric chloride reagents to develop a blue colour. The absorbance was recorded at 630 nm.

2.3.4. Sedimentary Sulphur Fractions

Different sulphur fractions in sediment samples were estimated by evolving the corresponding 'Sulphur' content as H_2S using suitable reagents. The liberated H_2S was trapped in 5% zinc acetate solution (Jorgensen, 1977) the value was then determined spectrophotometrically using the Cline's methylene-blue method, (1969). The apparatus used for hydrogen sulphide liberation consists of an inlet for the carrier gas and an outlet for trapping the evolved H_2S. (Fig. 2.3). The inlet is movable and can be inserted when the carrier gas is necessary. Inside the reaction tube, the carrier gas as well as the reagents added will reach only the bottom of the outer tube in which the sediment sample for analysis is taken. The bottom end of the inner tube is bulged and has got pores also, so that even supply is ensured.

Nitrogen gas of A.R. grade was used as the carrier gas. The gas carried was regulated at a rate of one bubble per second initially, with slight increase in rate. All the reagent solutions used were purged with N_2 gas to avoid any oxygen interference. Special care was taken in handling the sediment samples to minimize the oxygen contact.

Determinations of acid volatile sulphide and greigite were done using the method of Cutter and Oatts, (1987) with the above mentioned modification for H_2S trapping. Hydrogen sulphide was generated from sedimentary acid volatile sulphides (AVS) via acidification with dilute HCl, and from greigite using sodium borohydride and potassium iodide. Wet/dry weight ratio was determined on a separate aliquot.

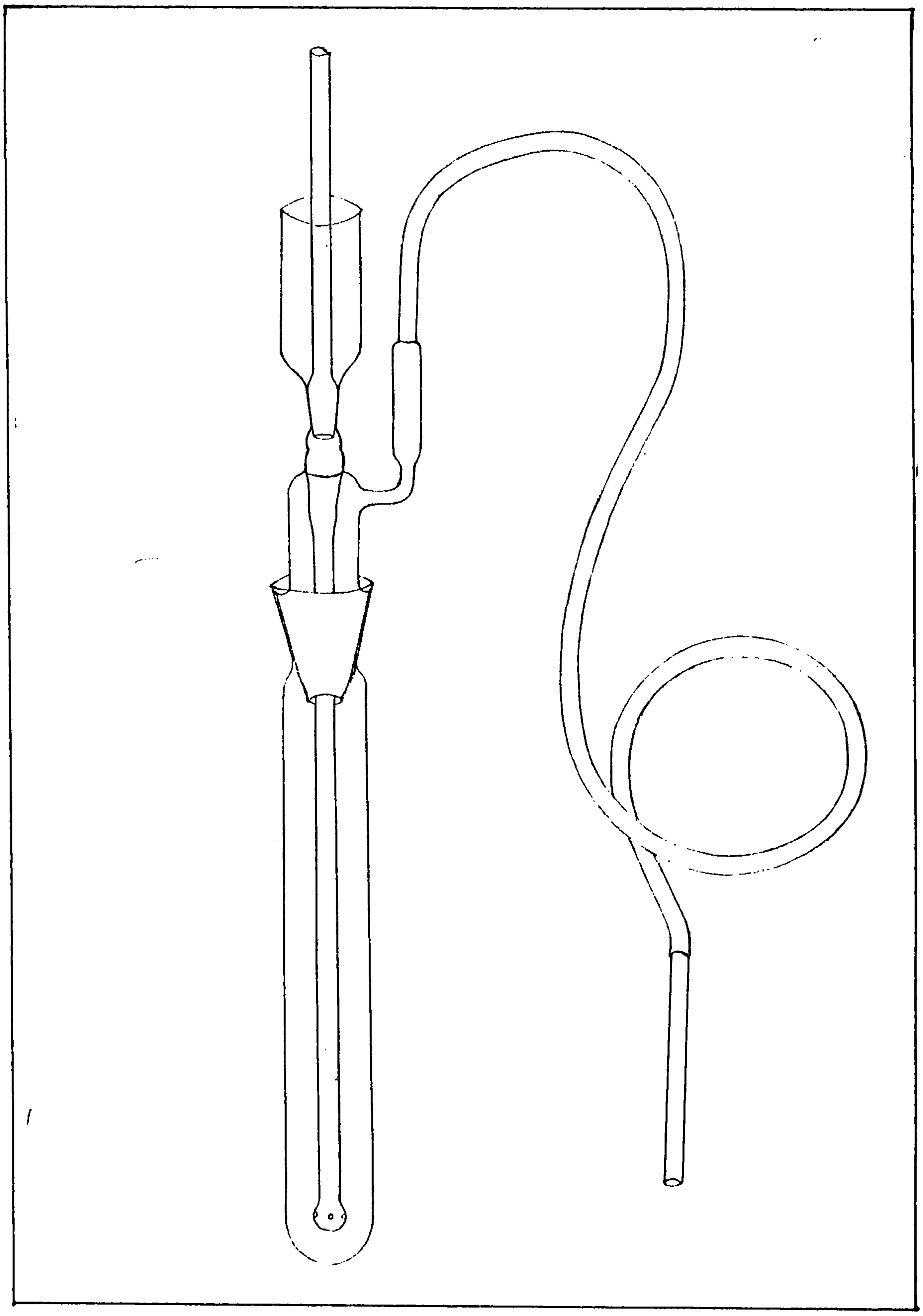
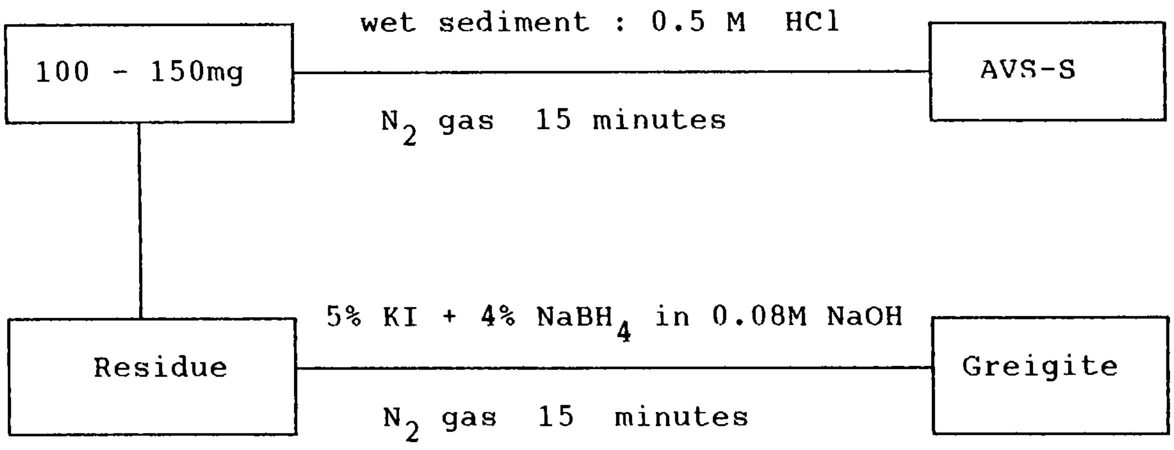


Fig. 2.3. Apparatus for H_2S liberation.



For the determination of pyrite, sediments were dried and then ground. The homogenised sediment was extracted with CCl_4 to remove elemental S and then redried (Cutter and Oatts, 1987). Approximately 100 mg of extracted, dried sediment was taken for analysis. Hydrogen sulphide was liberated with zinc and 6N HCl (Nriagu and Soon, 1985) after expelling any residual H_2S from FeS and greigite with their appropriate reagents (0.5 M HCl plus potassium iodide and sodium borohydride solution).

Elemental S was determined based on the procedure described by Berner, (1964). After fixing any dissolved sulphide with zinc acetate solution (Jorgensen, 1977), the sediment sample was dried and then ground to a fine powder. Extraction with acetone was carried out for 16 hours in a Soxhlet extractor, having copper mesh sheets (one cm square) to get coated with sulphur as sulphide. These sulphide coated copper mesh were then treated with dilute HCl to liberate hydrogen sulphide to be estimated.

Sulphate S was determined by the method of Tabatabai and Bremner, (1972). Dried sediment sample was extracted with 0.1 M LiCl, by shaking for 30 minutes and then centrifuging. The extracted sulphate was then determined gravimetrically by precipitating with barium chloride solution.

The existing methods for the determination of total S in sediments were carried out with dried sediment samples. Beaton *et al*,. (1968) have described a digestion procedure with HNO_3-$HClO_4$, in which samples are dried at 60^oC. In another method frozen dried and ground sediments are fused with 2:1 mixture of MgO and anhydrous Na_2CO_3 (Eschka fusion). According to Tatatabai and Bremner (1970), an alkaline permanganate oxidation of dried soil sample is suggested. Estimation of total S with elemental analyser also follows a drying procedure (Cutter and Velinsky, 1988).

In the present study, a modified version of the method given by Vogel (1985) was employed with wet sediment samples. The procedure involved gravimetric determination after oxidising all the sulphur forms to sulphate and extraction with dilute HCl. The oxidation was done with hydrogen peroxide and dilute nitric acid.

1 to 2 gm. of wet sediment sample is taken in a polypropylene centrifuge tube of 100 ml. capacity. A separate aliquot also is taken to determine the wet/ dry ratio. 1 ml. of H_2O_2 (30% volume) is added and heated in a water bath. The temperature is kept below 80^o C. Care is to be taken to avoid spilling of the contents with CO_2 production. After the effervesence is ceased, H_2O_2 is added in small quantities upto 5 ml. 1 ml. of 20% HNO_3 is also added. The heating is done for 5 hours. For sediment samples with high organic content, digestion is to be lengthened with additional H_2O_2. The samples become white in colour once oxidation is over. After cooling, the oxidised sediment is extracted with 0.05 M HCl, in small quantities upto 100 ml. The extracted sulphate is then estimated gravimetrically by barium chloride precipitation. The producibility and the reliability of the method was checked with the method prescribed by Beaton *et al*., (1968) and found to be in comparable limits.

Organic S was determined from the total S by subtracting the concentrations of total inorganic forms.

2.4. Genearl Hydrography of the Estuarine System

2.4.1. Salinity

The salinity values of surface and bottom waters at differnet stations are given as appendix. The seasonal and spatial variation is depicted in Fig. 2.4.

In the upper reaches, both on the southern and northern arms (stations 1 and 13), the salinity was generally low ranging from 0 to 2.70 X 10^{-3}. Seasonal variation was not much pronounced at these stations showing the greater fresh water inflow and lower salinity intrusion. Towards the downstream, the salinity values gradually increased with seawater intrusion and thus at station 8, highest values were recorded. The values recorded at station 8 varied between 1.26 and 13.07 X 10^{-3} at surface and 15.92 and 35.01 X 10^{-3} at bottom during monsoon. This high vertical salinity gradient indicates the development of a distinct stratification during this period. As the season advanced to postmonsoon and premonsoon, higher values ranging from 22.70 to 30.82×10^{-3} at surface and 32.20 to 35.50×10^{-3} at bottom were observed.

The data on salinity clearly establishes the influence of the influx of freshwater from rivers and intrusion of seawater into the estuary through the barmouth, on salinity distribution. The stratification developed near the barmouth has been reported already by Lakshmanan *et al.*, (1982); Anirudhan (1988) and several others.

2.4.2. Dissolved Oxygen

The dissolved oxygen values of surface and bottom waters at different stations are given as appendix. The seasonal and

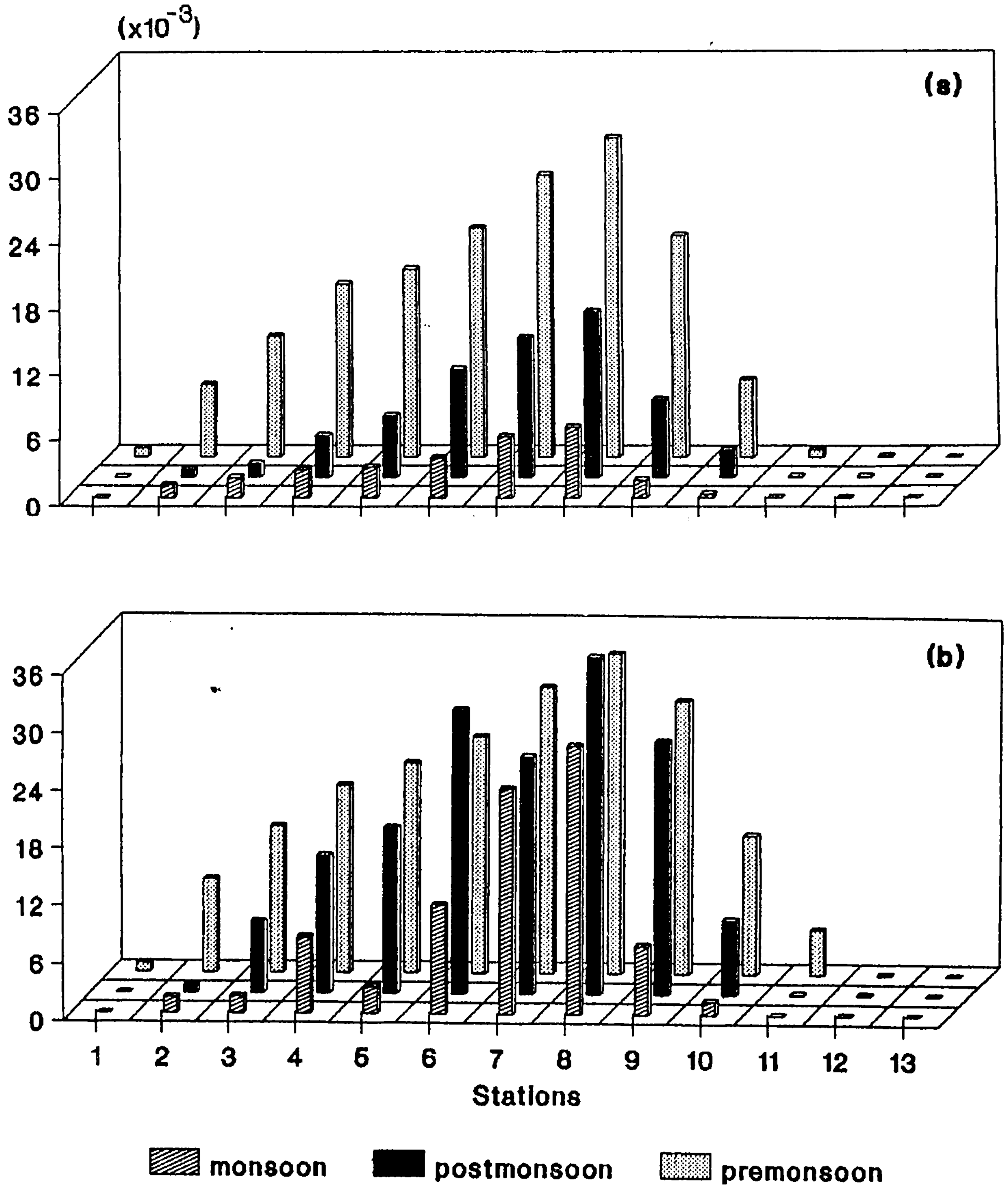


Fig. 2.4. Seasonal distribution of salinity.

(s). surface (b). bottom

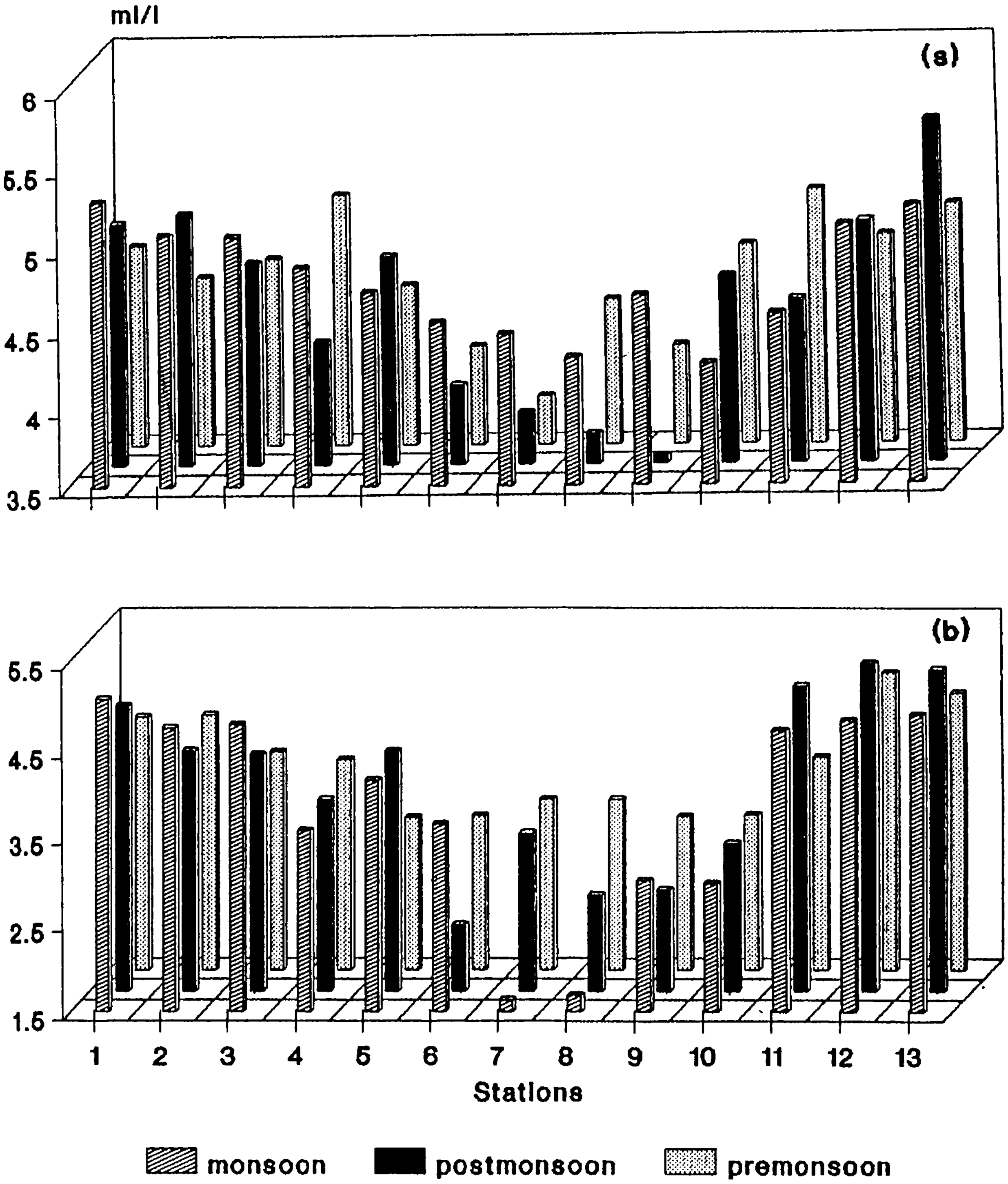


Fig. 2.5. Seasonal distribution of dissoved oxygen.

(s). surface (b). bottom

spatial variation is depicted in Fig. 2.5.

In the riverine reaches of the estuary the dissolved oxygen content was comparatively higher especially during the monsoon season. The values ranged from 3.26 to 5.65 ml/litre at surface and 2.97 to 5.40 ml/litre at bottom. The premonsoonal values varied between 3.16 and 6.21 ml/litre at surface and 2.34 and 5.43 ml/litre at bottom. In general, the values showed a decreasing trend as the season advanced from monsoon to postmonsoon and premonsoon. The lowest values (<1 ml/litre) were recorded at bottom waters of station 8. Lower values were observed at bottom waters of other stations also towards the downstream, especially during non-monsoonal months.

High dissolved oxygen recorded during monsoon is due to the greater solubility of oxygen in freshwater and high turbulance. The increase in values observed towards the upstream also bears the same reason. Low solubility of oxygen in saline waters and high input of organic wastes reaching the downstream are responsible for the low values observed there. Premonsoonal low values are partially governed by the effect of temperature on solubility.

The values observed are in conformity with the observations recorded by earlier studies (Vijayan *et al.*, (1976); Saraladevi *et al.*, (1979); Anirudhan, (1988); Nair, (1992). The depletion in oxygen observed during the non-monsoonal months, especially during postmonsoon has been reported to be due to the rapid decomposition of organic matter (Nair, 1992).

2.4.3 pH

The pH values of surface and bottom waters at different stations are given as appendix. The seasonal and spatial variation is shown in Fig. 2.6.

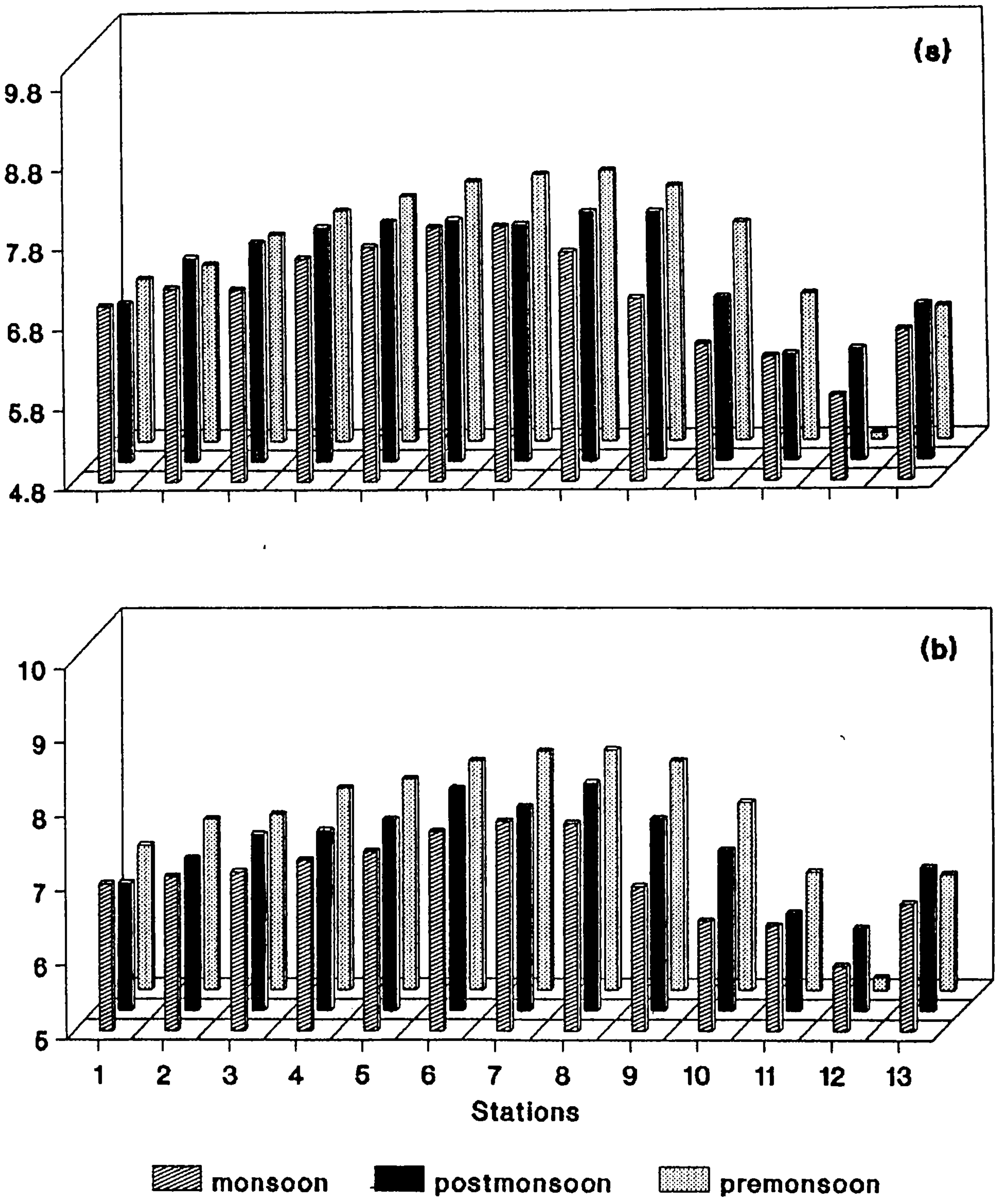


Fig. 2.6. Seasonal distribution of pH.

(s). surface (b). bottom

The pH in the entire study area remained more or less close to 7 without any significant variation being observed. The season wise distribution pattern showed a slight increase in pH during premonsoon except at station 12. The increased value may be attributed to excessive photosynthetic activity of algae and the near marine condition. High photosynthetic activity during post and premonsoon seasons in the Cochin backwaters was reported by earlier studies also (Silas and Pillai, 1975; Nair *et al.*, 1975; Anirudhan, 1988). The comparatively low values observed at station 12 is due to the acidic discharge from the fertilizer plant. This acidic effluent discharge along with decrease in flow lead to a successive decrease in pH from monsoon to premonsoon, to some extent. The difference in pH between surface and bottom water of the estuarine system during post and premonsoon is not well defined.

2.5. General sedimentary characteristics

2.5.1. Texture

The textural classification was done according to Shepard, (1954). Sand represents particles of size greater than 63μ, silt indicates sizes between 63μ and 4μ and clay includes particles less than 4μ. The seasonal means of the texture of the sediments are given in Table 2.2. Grain size analysis indicated that the estuarine region was composed of fine grained sediments where as those of riverine region was made of a major portion by sand. Thus the composition of the sediment showed a spatial variation.

In the Cochin estuarine system the bulk of the sedimentary material is being supplied by the two rivers, the Periyar on north and the Muvatupuzha on south, mainly during rainy season. The sediments are transported as bedload as well as suspended load (Veerayya and Murty, 1974). The decreasing trend in grain size observed towards the lower reaches was in conformity with

Table 2.2. Size composition of Sediments (*)

Station	Sand % (>63µ)	Silt % (4-63µ)	Clay % (<4µ)	Nature of Sediment
3	83.88	9.62	6.50	Sand
4	85.60	7.08	7.32	Sand
5	26.08	32.92	41.00	Sand, Silt, Clay
6	42.62	27.03	30.55	Sand, Silt, Clay
7	1.61	58.17	40.23	Clayey Silt
8	67.59	15.74	16.88	Sand, Silt, Clay
9	12.80	40.77	46.43	Silty Clay
10	34.91	39.04	26.05	Sand, Silt, Clay

(*). Padmalal, (1992).

the general trend of progressive decrease in size in a current in the direction of the transport as reported by Pettijohn, (1975). The settling of finer fractions of the sediments took place preferentially during the non-monsoonal months. The increase noted in the case of finer fractions during the non-monsoonal period could be attributed to the low fluvial discharge and a better mixing of saline and fresh water that facilitated flocculation and settling of suspended particles.

2.5.2. Organic Carbon.

The values of organic carbon content are given as appendix. The distribution pattern of organic carbon content exhibited distinct spatial and seasonal trends. Relatively higher values were recorded for the sediments of downstream stations. The sediments of the upstream stations were associated with the minimum content of organic carbon. Seasonal minimum was recorded mostly during the non-monsoonal periods and maximum during the monsoonal periods. The organic carbon distribution was found to follow the sediment distribution pattern, in that, finer the sediment, higher was the organic carbon content.

The present study was confined to the 0 to 5 cm layer of surface sediments, which was usually influenced by the varying inputs into the estuary. According to Qasim and Sankaranarayanan (1972), the sediment of this estuary was chemically similar to the detritus which is settled to the bottom. The seasonal variation observed in fine particle composition and organic carbon content, during the present study also indicated that surficial sediments were quite sensitive to the periodic additions of detritus, mainly composed of inorganic matter (fine silt and sand) to which organic matter adhered and formed aggregates.

2.5.3. Eh

The observed values of Eh in the sedimentary environment are given as appendix. The sediments of all the stations were observed to be at a negative potential at all the seasons. The Eh values being in the range of -75 to -330 mv indicating a reducing condition. Though the dissolved oxygen values indicated a significant oxidative environment at the bottom layer, the high sedimentary organic carbon may be imparting an oxygen deficient condition in the sediment thereby stimulating a reducing environment. The wide as well as small range of variation in the Eh values is indicative of a highly dynamic sedimentary environment.

2.6. General hydrography of the coastal region.

The observed values of salinity, dissolved oxygen and pH at the selected stations along the coastal region are shown in Table 2.3. The salinity distribution showed higher values on the southern part of the coast ($>35.00 \times 10^{-3}$) while it ranged between 33.86 and 35.46×10^{-3} at other stations. The pH values in the area of study ranged from 7.96 to 8.73 and dissolved oxygen values between 3.19 and 5.00 ml/l. The values showed a normal trend of distribution and were in conformity with the earlier studies.

2.7. General sedimentary characteristics of the coastal region

The observed values of Eh, grain size and organic carbon of the coastal sediments are given in Table 2.4. The Eh vales varied between - 74 to -330 showing a reducing condition prevailing along the coastal sedimentary environment during the period of observation. Except along the transect VI the values observed did not vary on a wide range.

The organic carbon values ranged between 1.86 and 33.30 mg/g., showing a seaward decrease in concentration. Murty *et*

Table 2.3. Coastal hydrography

Transects			pH	DO (ml/l)	S ($x10^{-3}$)	Transects			pH	DO (ml/l)	S ($x10^{-3}$)
	1	S	8.15	4.58	34.30		1	S	8.11	4.04	34.68
		B	8.20	4.36	34.32			B	8.15	3.51	34.78
I	2	S	8.16	3.92	34.45	IV	2	S	8.16	3.72	34.98
		B	8.20	4.25	34.51			B	8.19	3.19	35.02
	3	S	8.26	4.69	34.68		3	S	8.25	4.25	34.95
		M	8.28	4.36	34.63			M	8.29	3.94	35.08
		B	8.30	4.58	35.01			B	8.25	3.83	35.18
	1	S	8.19	4.25	34.56		1	S	7.96	4.25	35.18
		B	8.22	4.69	34.96			B	8.18	4.68	35.18
II	2	S	8.28	3.92	34.40	V	2	S	8.25	4.15	35.21
		M	8.27	4.58	35.43			B	8.26	3.93	35.22
		B	8.27	4.36	35.46						
	3	S	8.27	4.14	35.05		3	S	8.26	4.25	35.29
		M	8.24	3.27	35.04			M	8.27	5.00	35.25
		B	8.29	4.25	34.36			B	8.26	3.72	35.25
	1	S	8.22	4.69	34.05		1	S	8.21	3.93	35.14
		B	8.30	4.36	34.04			B	8.24	3.62	35.39
III	2	S	8.36	4.25	33.86	VI	2	S	8.28	4.36	35.45
		B	8.36	4.36	34.16			B	8.29	4.04	35.45
	3	S	8.60	3.92	34.13		3	S	8.28	4.25	35.61
		M	8.68	3.92	34.16			M	8.28	4.57	35.59
		B	8.73	4.58	34.10			B	8.25	4.36	35.58

1: Near shore station   2: Mid station   3: Off shore station
S: Surface   M: Mid depth   B: Bottom

Table 2.4. Coastal sedimentary chracteristics

Transects		Eh	Org.C %	Texture			Classification
				Sand %	Clay %	Silt %	
I	1	258	30.52	5.38	15.05	79.57	Silt
	2	285	25.98	3.27	25.78	70.95	Clayey silt
	3	330	21.10	2.01	53.25	44.74	Silty clay
II	1	281	26.96	1.32	44.10	54.58	Clayey silt
	2	295	26.22	1.79	43.25	54.96	Clayey silt
	3	330	25.14	1.94	42.05	56.01	Clayey silt
III	1	326	25.18	6.14	20.95	72.91	Clayey silt
	2	319	24.21	4.68	38.91	56.41	Clayey silt
	3	289	22.58	3.37	47.10	49.53	Clayey silt
IV	1	283	28.99	16.70	44.35	38.95	Silty clay
	2	316	29.05	3.78	58.82	37.40	Silty clay
	3	308	31.57	0.34	64.75	34.91	Silty clay
V	1	277	33.30	4.57	48.25	47.18	Silty clay
	2	289	32.42	6.24	57.39	36.37	Silty clay
	3	299	32.38	9.05	34.20	56.75	Clayey silt
VI	1	74	1.86	93.95	1.71	4.34	Sand
	2	58	2.08	89.23	1.78	8.99	Sand
	3	309	15.86	10.03	1.82	88.15	Silt

1: Near shore station 2: Mid station 3: Off shore station *al.*, (1969) has reported that high content of organic matter in coastal region is due to the factors like fine grained sediments and high organic production. An exemption to this was observed at the near shore stations of transect VI, which could be due to the conspicous difference in grain size noted there. The coastal region is subjected to upwelling with varying intensities and consequently differences are observed in the primary productivity from region to region and this will explain the differences observed in the organic carbon distribution (Rao, et *al.*, 1987).

The textural analyses showed that the coastal region upto Quilon is covered by moderate silty clays or clay silts and south of which are terrigenous sands. Similar observation has been reported earlier by Stackelberg, (1972).

CHAPTER - III

ESTUARINE SULPHUR FRACTIONS

3.1. Introduction

Under natural aquatic condition, sulphur is an important redox element (Breck, 1974) and also it can exhibit a wide range of oxidation states. Sulphur is most stable in the form of sulphate and sulphate is a major constituent of sea water (Sillen, 1961; Wilson, 1975). Contrary to the situation in sea and estuarine waters, sulphate occurs in relatively very small quantities in fresh water. Sources of sulphur to natural waters are rocks, fertilizers, atmospheric transport in precipitation and dry deposition. Atmospheric sources are augmented greatly by combustion products of industry like burning of coal along with that from volcanoes. Sulphur is an important secondary constituent of amino acids and proteins in living organisms and is an essential nutrient for plants also.

In marine and estuarine systems, sulphate is especially important due to its high concentration and its use as an electron acceptor for the oxidation of organic matter (Pfennig and Widdel, 1982). In the presence of molecular oxygen, organic decomposition is dominated by organisms using oxygen as an electron acceptor (Goldhaber and Kaplan, 1974). When molecular oxygen has been used up, organic matter decomposition continues mediated by organisms, with less efficient electron acceptors like nitrate, manganese oxides, iron oxides, sulphates and carbon dioxide respectively .

In natural environments, the reaction kinetics of sulphate reduction depend on the interplay between three factors: sulphate concentration, availability of organic matter and other nutrients and the size and density of the bacterial population (Rees, 1973). If organic matter and nutrients are abundant, the bacterial population can expand to the point where sulphate activation sites are not saturated. Under these conditions, the rate of sulphate reduction is limited by the concentration of sulphate. If the population of sulphate-reducing bacteria is limited by organic matter and nutrients, sulphate reduction will be independant of sulphate concentration. In the latter case as sulphate is utilized, the rate controlling step will become dependent on either or both nutrient and sulphate concentration.

While sulphate is reduced in a water column, a number of compounds with intermediate oxidation states are formed. These include sulphite (SO_3^{2-}), thiosulphate ($S_2O_3^{2-}$), sulphide (S^{2-}), polysulphide ($S_n^{(2-)}$) and solid sulphur in colloidal or orthorhombic form. Sulphide can exist as $H_2S(aq)$, HS^-, S^{2-} or S_n^{2-} (polysulphide) and their relative stabilities are highly dependent on physiochemical conditions (Field, 1972). At a pH of about 8 in sea water, the major sulphide species are considered to be HS^- ion, followed by H_2S and S^{2-} in minor quantities (Richards, 1965; Goldhaber and Kaplan, 1974). In the highly acidic anoxic environment H_2S shows highest stability (Garrels and Christ, 1965; Krauskopt, 1967) followed by HS^-, polysulphide and S^{2-} .

Intermediate species S^0 and oxysulphur acids form during the oxidation of sulphides or vice versa and occur mostly in the region of chemocline (Richards, 1965; Sorokin, 1972; Jannasch *et al.*, 1974; Jorgensen *et al.*, 1979). $S_2O_3^{2-}$ will be the major reduced sulphur species produced during the chemical oxidation of HS^- in sea water (Cline and Richards, 1969). If the ratio of O_2 to HS^- is small, $S_2O_3^{2-}$ and SO_3^{2-} are formed.

In the presence of O_2, oxidation proceeds to SO_4^{2-} (Richards, 1965). During oxidation, $S_2O_3^{2-}$ is a major intermediate, whereas SO_3^{2-} is minor (Tuttle and Jannasch, 1973). The latter may be due to its disproportionation into $S_2O_3^{2-}$ and SO_4^{2-} because of SO_3^{2-} instability in the presence of small amounts of dissolved oxygen (Rand and Gale, 1967). H_2S may be photosynthetically oxidized to S^0 (Richards, 1965; Jorgensen *et al*, 1979). Further Almgreen and Hagstrom (1974) have reported that S^0 formation from the spontaneous decomposition of $S_2O_3^{2-}$ also can take place. With S^{2-} ion, S^0 can react to give polysulphide ions (Breck, 1974). Considerable removal of trace metals (Jacobs and Emerson, 1982) occurs in the anoxic water by the precipitation of metals as their sulphides.

The transformations of sulphur species described above may happen simultaneously or follow each other rapidly enough not to be separable. Many of the sulphur oxyacids (eg. $S_2O_3^{2-}$) are either unstable or metastable. The sulphide is easily oxidised in the presence of dissolved oxygen. Millero *et al.*, (1987) gave half-times for the oxidation of sulphide by oxygen as 26±9 hours in sea water (pH = 8 ; 25^o C) and 50±16 hours in fresh water. Anaerobic oxidation of the bisulphide ion has been suggested by Luther *et al.*, (1988) with hydrogen peroxide produced by microorganisms or solid metal oxides such as colloidal manganese oxide phases.

The site of sulphate reduction is more frequently in the overlying sediments (Goldhaber and Kaplan, 1974) than that in the water column. In either case, the production of sulphide is closely related to the availability of organic matter. A number of metal sulphides have exceedingly low solubility products and might be expected to form during diagenesis of sulphur (Goldhaber and Kaplan, 1974). However, with the exception of iron, these metals are present only in trace amounts in normal marine sediments (Chester, 1965) and estuarine sediments.

The dominant pathway of sulphide produced as a result of sulphate reduction involves reaction with iron oxide.

$$2FeO.OH + 4HS^{-} \rightarrow 2FeS + S^{0} + 4OH^{-} + H_2S$$

In addition to elemental S, the products formed includes an acid volatile sulphide phase. Two acid volatile iron sulphide phases have been identified, mackinawite and greigite. Of these, mackinawite is represented by a formula near $FeS_{0.94}$ (Ward,1970) and is the initial iron sulphide precipitate formed (Rickard, 1969) when sulphide is reacting with iron oxide.

Greigite is implicated as an intermediate in pyrite formation by its important role in producing the 'Framboidal' texture commonly observed in sedimentary pyrite (Sweeney and Kaplan, 1973). Berner (1967) assigned a composition of Fe_3S_4 to greigite and its formation from mackinawite (Berner, 1971) is represented by the equation,

$$3FeS + S^{0} \rightarrow Fe_3S_4$$

Pyrite is thermodynamically the most stable form of iron-sulphide compounds. Goldhaber and Kaplan (1974) have proposed two pathways of pyritisation.

1. Single pyrite crystals are formed rapidly through direct precipitation of Fe(II) and polysulphides.

2. Framboidal pyrite is produced by a slower reaction with a greigite intermediate.

The proposed mechanism by Rickard (1975) for the rapid formation of pyrite entails the dissolution of iron monosulphide and elemental S to form Fe(II) and polysulphides, with the consequent precipitation of pyrite as follows:

$$Fe^{++} + S_5S^{2-} + HS^- \rightarrow FeS_2 + S_4S^{2-} + H^+$$

The mechanism proposed for slow pyritisation was by Sweeney and Kaplan (1973). In this reaction sequence mackinawite combines with elemental S in the form of polysulphides to produce greigite. Greigite in turn produces pyrite, either through dissociation or by further reaction with elemental S as polysulphides.

$$Fe_3S_4 \rightarrow 2FeS + FeS_2$$
$$Fe_3S_4 + 2S(O) \rightarrow 3FeS_2$$

In addition to aqueous sulphate, reducible organic S, is also an immediate source of pyritic S in high sulphur peats, and intermediary FeS formation plays an appreciable role (Altschuler *et al.*, 1983).

The organic fraction of sulphur in sediments is either derived from sestonic matter or is formed *in situ* by the reaction of sedimentary organic matter with the reduced sulphur species such as H_2S, polysulphides and elemental S (Nriagu and Soon, 1985). The secondary enrichments of sulphur in sedimentary organic matter is chemically controlled, but the mechanism involved is still in doubt. H_2S may be liberated during anaerobic and aerobic decomposition of organic sulphur compounds containing -SH (thiol) groups, eg. from cystine, cystene and methionine present in the proteinaceous material. The degradation products also include a variety of volatile organic sulphur species such as methyl mercaptan (CH_3SH=MeSH) dimethyl sulphide (CH_3SCH_2=DMS). The decomposition of sulphate esters releases sulphate and an alcohol and is the major source of sulphate in lacustrine sediments (King and Klug, 1980).

3.2. Results and Discussion

3.2.1. Dissolved Sulphur fractions

3.2.1.1. Sulphate

The concentrations of sulphate observed at different stations are given as appendix. The seasonal variation is depicted in Fig.3.1.

The observed concentrations varied from 0.01 to 24.37 m.mol sulphate/litre at surface and 0.02 to 28.32 m.mol sulphate/litre at bottom waters from upstream extending upto the Barmouth. The sulphate concentration observed at a maximum salinity of 35.10 x 10^{-3} was 27.98 m.mol/litre which is very close to the normal sea water sulphate concentration (28.25 m.mol/litre) reported by Burton (1976). Maintaining a constant relationship with salinity, a gradual decrease in concentration was observed towards the upstream. Even when the salinity values registered zero concentrations, sulphate value had been observed as high as 0.130 m.mol/litre. But during December, station 1, which is at the upstream of the southern part of the estuary, experienced an appreciably excess quantity of sulphate which then subsided progressively. Low monsoonal values ranging from 0.00 to 5.48 m.mol sulphate/litre at surface and 0.00 to 27.57 m.mol sulphate/litre at bottom were observed registering a vertical gradient towards the downstream just like that of salinity. These values gradually increased minimising the gradient when the season advanced to postmonsoon and premonsoon.

The average concentration of sulphate in river water is 116.6 μ.mol/litre whereas in seawater (35×10^{-3}) is 28.25 m.mol/litre (Burton and Liss, 1976). The spatial distribution pattern of sulphate showed a general decreasing trend towards the upstream. Fresh water generally has a higher

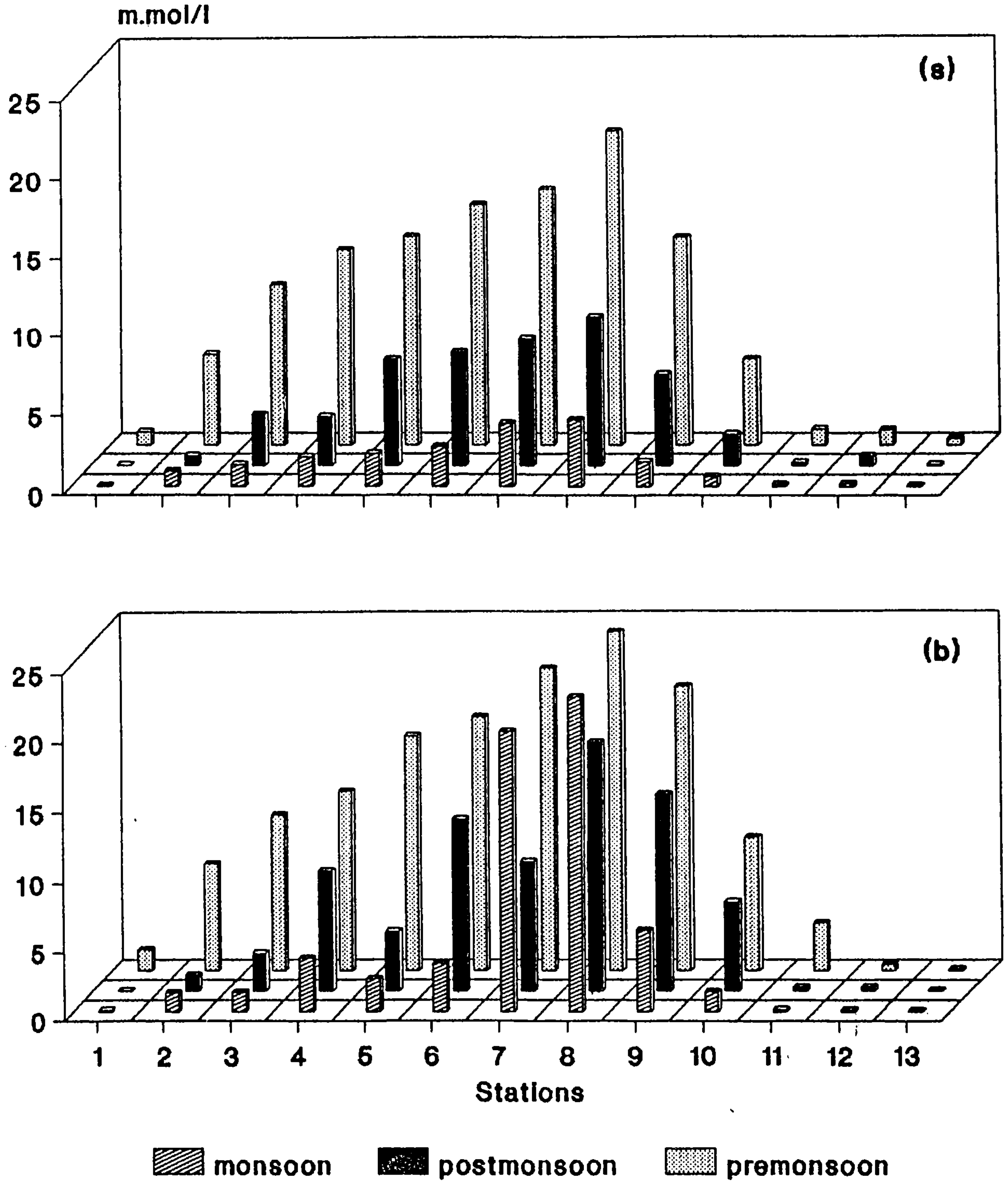


Fig. 3.1. Seasonal distribution of sulphate.

(s). surface (b). bottom

sulphate/chloride ratio but in terms of absolute concentrations, the sulphate records only a small concentration in fresh water. The decrease in sulphate concentration from the saline to fresh water thus was in tune with the expectation. The fitness of the observed data was tested by x^2 statistical evaluation procedure and the results indicated a general conservative behaviour for sulphate in the estuary. But at station 12, an appreciable concentration level of 2.52 m.mol/litre for a salinity of $1x10^{-3}$ observed might be from the effluent discharge of the nearby fertilizer plant. This was distributed to the adjacent stations also.

In open ocean, sulphate presents a conservative behaviour with a sulphate/salinity ratio of 0.808 (Dryssen and Wedborg, 1980; Stumm and Morgan, 1981). The same was reported to be valid in a number of estuaries also. In Chikugogawa estuary, Hosokawa *et al.*, (1970), and Mandovi and Zuari estuaries, Sen Gupta and Sugandhini, (1980), have reported that sulphate was found to be conservative. The geochemical character of the dissolved sulphate in the present study was constructed by the model proposed by Dryssen and Wedborg, (1980). The calculated sulphate concentrations as per the model is given as appendix.

The deviation of sulphate observed from the conservative behaviour and the subsequent depletions or enrichments sometimes occurred in the present study could be attributed to the biogeochemical activities of sulphate in the estuary. Excess sulphate has been reported to appear in mesohaline less than $10.00x10^{-3}$ waters due to run off of water with very high sulphate concentrations as in the Baltic (Kwiecinski, 1965) or due to the sulphur oxidizing activity of thiobacilli in estuarine surface sediments (Vosjan, 1974). Excess sulphate has also been reported in the upper layer of estuarine and marshy sediments and in tidal creek waters and has been attributed to a temporary excess of sulphide oxidation over sulphate reduction (Luther *et al.*, 1982; Lord and Church, 1983). The occurrence of a sulphate enrichment cycle in the estuarine waters of North Carolina has been accounted for by biochemical oxidation of pyrite in surface sediments (Matson and Brinson, 1985).

Appreciable quantities of excess sulphate had been noted at station 3 during September and January along the entire water column and also at station 5 at bottom waters during January. This could not be attributed to the additions from the run off as no corresponding increase was recorded at the upper stream stations. The enrichment factor conspicuous at the bottom waters also supported this argument. Then the excess sulphate appeared might be due to a temporary excess of sulphide oxidation over sulphate reduction or due to sulphur oxidizing activity of thiobacilli in surface sediments.

An anomalous character seldom developed was the co-occurrence of enrichment and depletion of sulphate in the same water column. Thus at stations 4 and 5 during November and at station 9 during September, a sulphate depletion phenomena was noted at the bottom waters with excess sulphate simultaneously appearing in surface waters. The excess sulphate observed could be accounted for by the mixing of sea water having high sulphate content with fresh water having low sulphate content. The excess sulphate noted at station 1 during December also could be attributed to the same reason.

The negative deviation resulting in low sulphate values was more pronounced than the positive deviation. At the estuarine and downstream stations, the deviation started in August and went through a period of six months and after that the conservative behaviour was more or less maintained. Since oxygen was not depleted to very low values in the water body, most of the time, the use of sulphate as an electron acceptor for the oxidation of organic matter in the water body is not appropriate to be suggested. Then the sulphate depletion could be the result of involvement of sulphate for the mineralization of organic matter in sediments. The high load of organic matter that the sediment receiving in the estuarine system could be a reason for bringing in conditions favourable for such a process.

In the Cochin estuarine system, previous studies have reported high concentrations of organic wastes reaching the estuaries from the fishery industries, sewage works and coconut retting grounds etc. (Anirudhan, 1988). These organic matter will be subsequently decomposed depending on the availability of the electron acceptors. During monsoon, when oxygen concentration was maximum, oxidation of organic matter might have taken place using oxygen, or the involvement of sulphate for the oxidation of organic matter might have been small to reflect in the conservative behaviour of sulphate in the water column. This will explain the observed Sulfate/salinity ratio more near to 0.808 during monsoon season. During late premonsoon also conservative behaviour was maintained.

The sulphate depletion observed at the end of monsoon and also the following seasons could be attributed to the high rate of sulphate reduction occurred in the sediments as a result of organic matter mineralisation. Transfer of sulphate from overlying water to sediments might have taken place then and hence a negative deviation from conservative behaviour Transfer of sulphate from overlying water to sediments has been reported by Berner, (1971) and Garrels and Mackenzie, (1972). The intensity of sulphate depletion though varied, kept high in bottom waters also will suggest such a possibility. In a super anoxic fjord of southern Norway, similar gradation in sulphate value towards the bottom was noted (Anderson *et al.*, 1988) where the decay of organic matter has been reported to take place mostly in the redoxcline and sediment water interface, though decay happened at all depths.

3.2.1.2. Sulphide

The observed sulphide concentrations at different stations are given as appendix. The seasonal variation is depicted in Fig. 3.2.

Most of the values observed were in the range 0-2 μ.mol/litre. The highest concentration observed was 11.5 μ.mol/litre at station 8. The riverine stations experienced lower concentrations compared to the estuarine and marine stations. The seasonal values varied between 0.47 and 1.81 μ.mol/litre, 0.54 and 2.18 μ.mol/litre and 0.76 and 4.46 μ.mol/litre during premonsoon, monsoon and postmonsoon seasons respectively.

The sulphide in the water column has two potential sources:

1. diffusive flux from the bottom sediments (Cutter *et al.*, 1987) and

2. sulphate reduction in the water column (Divan and Tuttle, 1987).

Certain biological processes (eg. in plants) also can result in the production and release of substantial amounts of H_2S in the presence of oxygen (Andreae, 1990). Once formed, and in the absence of reactive chemicals, the distribution of S^{2-} is determined by pH and the activity of complexing ligands. Dissolved sulphide transport is influenced by processes like vertical molecular diffusion, bubbling of gases from anoxic environments, scouring of muds in tidal channels, temperature or wind driven turnover etc. (Andreae, 1990; Roden and Tuttle, 1992). Sulphide is rapidly oxidized in oxygenated water. The half times for the oxidation of sulphide by oxygen has been

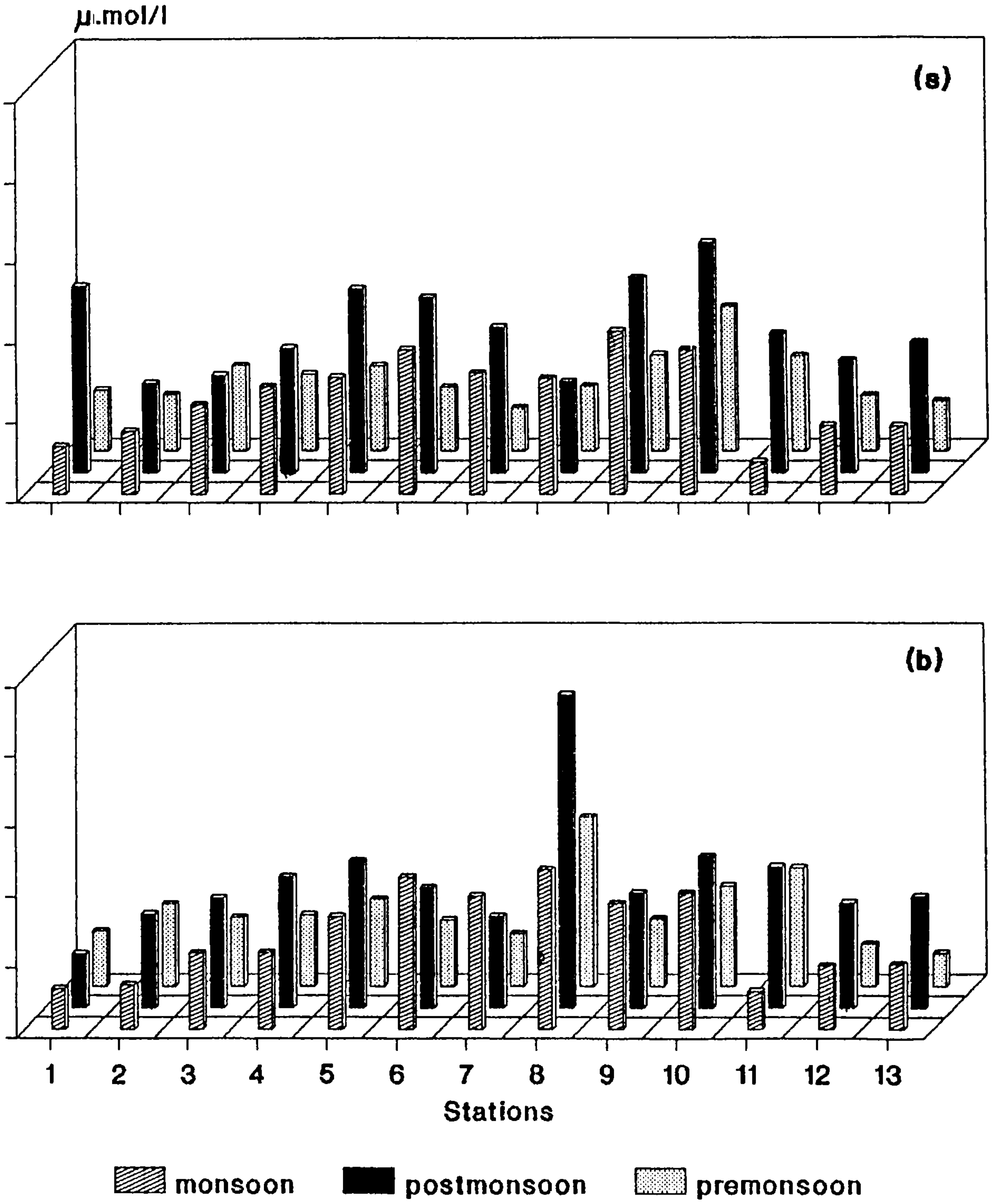


Fig. 3.2. Seasonal distribution of sulphide.

(s). surface (b). bottom

reported as 26±9 hours in sea water (pH = 8, 25^{o} C) and 50±16 hours in fresh water (Millero *et al.*, 1987).

Generally hydrogen sulphide is formed in the deep water of stagnant basins, eg. the Black Sea, the Baltic, many fjords in Norway, Greenland and Canada and the Cariaco trench of the Venezuelan coast. Many coastal lagoons are stagnant and contain hydrogen sulphide. Hydrogen sulphide was also reported in the open sea during the International Indian Ocean Expedition (Fonselius, 1983). They found hydrogen sulphide at several stations in the Arabian Sea in the oxygen minimum layer from 150m down to 1000m.

The sulphide ion like any other ion can attain a marginal stability in the water column by the formation of ion pairs with the cations present in the system and the oxidation of sulphide will be more rapid or more pronounced at lower pH levels. So one can expect trace amounts of sulphide in the water column overlying reducing sediment, even if the water is in an oxidative environment. Microbiological production of S^{2-} is not necessarily confined to anoxic environments. Cutter and Krahforst (1988) have reported concentrations of less than 0.1-1.1 nano mol/litre in surface sea water from the western Atlantic ocean.

In the present study, the sulphide concentration in the range of μ.mol/litre was observed, the highest being at the Barmouth region. As the estuarine system under investigation represents an active tropical estuary, the observed sulphide concentration is against the normal expectation, but can be due to the reasons given above. Any way no specific explanation is possible for its existence in the oxidizing environment at this juncture and an extensive study is essential to explain this anomalous behaviour.

Sulphate reduction is the principal terminal microbial process in anoxic sediments, where sulphate is abundant (Capone and Kiene, 1988). Sediments being the dominant source of dissolved sulphide, the spatial variation in the distribution pattern is related to the availability of sulphate and its reduction and the transport from the sediments. Thus the decrease in sulphide concentration observed at upstream stations could be due to the low sulphate reduction rate, which in turn depend upon the availability of sulphate and abundance of organic matter.

A high value of dissolved sulphide (5.05 μ.mol/litre) was noted at station 1 during November, which could be contributed from some local land drainage. The AVS S fraction of sediment during November also showed a correspondingly high value. The highest concentration of 11.5 μ.mol/litre observed at station 8 coincided with a low oxygen level of 1.19 ml/litre could be accounted for the high intensity of sulphate reduction. Stations like 9 and 10 experiencing high organic input from sewage and retting grounds respectively also showed high sulphide values. This could also be explained by the involvement of sulphate in the sedimentary metabolism.

Even though, sediment is the potential source of dissolved sulphide observed in the water body, a discrepancy could be noted in the vertical distribution pattern, i.e, the surface values were mostly higher than the bottom values. This might be partly due to the difference in the half-times for the oxidation of sulphide by oxygen in sea water and fresh water. In sea water, the half-time is almost half of that in fresh water. So depending on the vertical mixing of sea water with fresh water, the distribution of dissolved sulphide is influenced. Another reason attributable could be that the oxides of Fe and Mn may be partly responsible for the fast turnover of H_2S in deep waters (Millero, 1991).

The seasonal values generally showed maximum concentrations during postmonsoon and the minimum varied between monsoon and postmonsoon, station wise. The postmonsoonal maximum was related to the high intensity of sulphate reduction occurring in the sediments. This was reflected in the AVS S data of the sediments also. The minimum concentration observed might be influenced by the sulphate reduction, oxidation of sulphide as well as the transport mechanisms.

3.2.2. Sedimentary Sulphur Fractions

Sedimentary sulphur fractions identified include sulphate S, AVS S, greigite S, pyrite S, elemental S. organic S, and Total S. Generally a decrease in concentration was observed in the case of all the sulphur fractions and the organic carbon which might have resulted from the poor settling of river brought particulate/suspended materials. Also a near to sandy character of the sediments limited the holding capacity of the materials in the sediment. To add to this, the supply of sulphate, the source of which is the saline water, to the sediment from the water column, can be considerably low at these stations. Supply of sulphate to the sediment and the turn over of organic carbon have governed the concentrations of all the sulphur fractions (Nriagu, 1968; Cook, 1981) and well correlated with the present study also.

3.2.2.1. Sulphate Sulphur

Sulphate in interstitial water is originated mainly by the trapping of the overlying water within the accumulating sediment (Riley and Chester, 1971). The important sulphate mineral found in the estuarine and coastal sediments is gypsum. The sulphate S estimated include sulphate trapped in sediments and any traces of gypsum in the sediments.

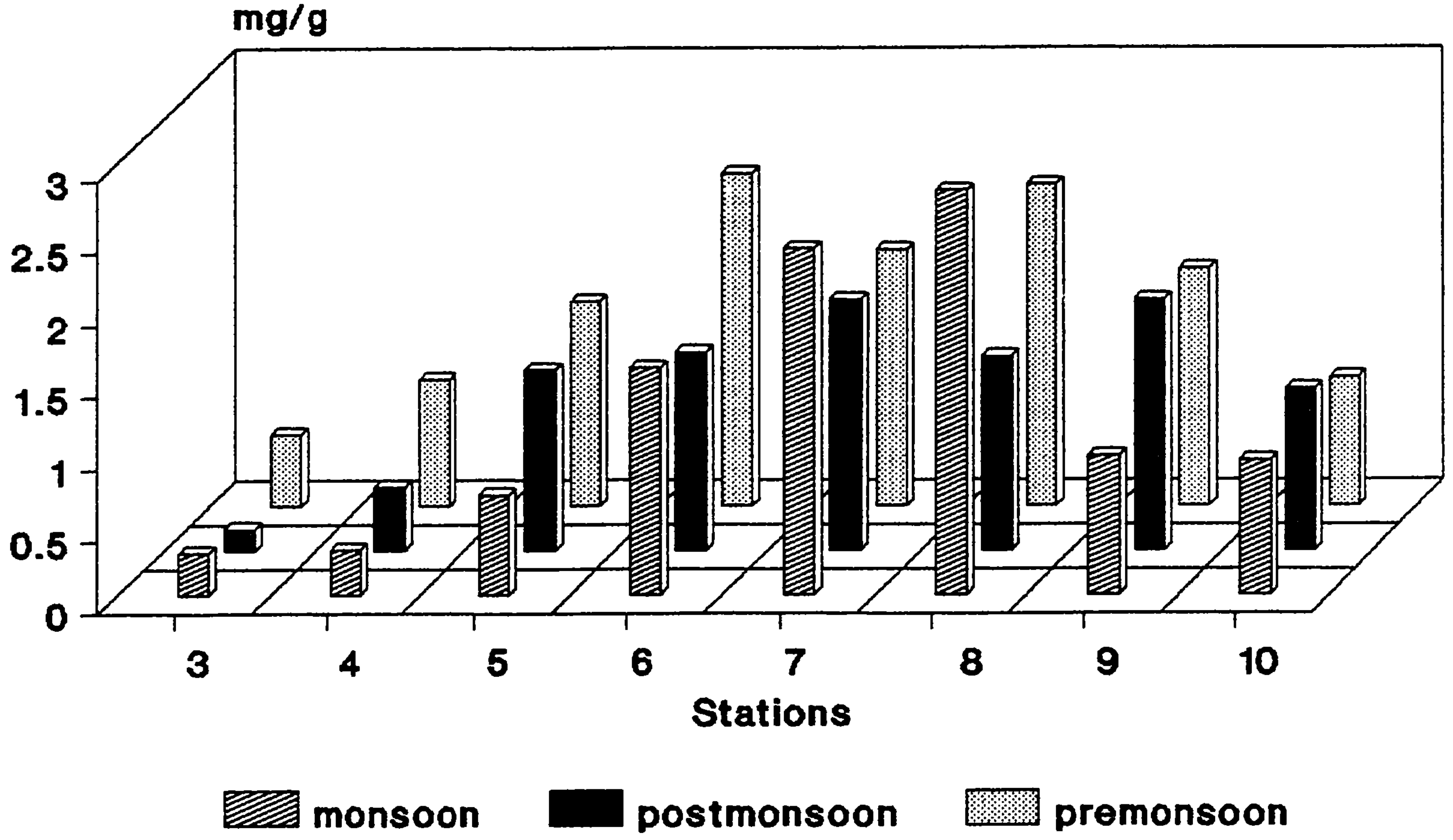


Fig. 3.3
Seasonal variation of sedimentary
Sulphate S

The observed concentrations of sulphate S at different stations are represented as appendix. The seasonal variation is given in Fig. 3.3.

The concentrations of sulphate S varied from 0.05 to 3.86 mg/g, constituting 1.09 to 20.39% of total S. The concentrations were found to decrease towards the upstream. Towards the marine region, the concentrations represented higher values. The lowest concentration was observed at station 4 and the highest at station 8.

The seasonal values varied between 0.29 and 2.80 mg/g; 0.15 and 1.74 mg/g and 0.50 and 2.31 mg/g during monsoon, postmonsoon and premonsoon respectively. Seasonal maximum was observed during premonsoon at stations 3, 4, 5 and 6; during monsoon at stations 7 and 8 and during postmonsoonat stations 9 and 10. The seasonal minimum was observed during postmonsoon season at stations 3, 6, 7 and 8; during monsoon at stations 4, 5 and 9 and during premonsoon at station 10.

The patterns of spatial distribution of sulphate S in sediments were found to be consistent with the sulphate concentration observed in this water body. With the decrease in sea water intrusion towards the upper reaches of the estuary a decrease in concentration of the SO_4^{2-} S was experienced in water and sediments. The increasing percentage of silt and clay towards the downstream might be another factor governing the spatial distribution, holding the SO_4^{2-} at the lattice sites, thereby enriching the sediments with high SO_4^{2-} content.

A general trend of premonsoonal maximum was observed at most of the stations, except at stations 7, 8, 9 and 10. The premonsoonal high values in sediments were the reflection of the same in water body having minimum dilution by freshwater discharge. But at station 10, the SO_4^{2-} from the overlying water was found insufficient to maintain a maximum value in the sediment due to high sulphate reduction rate during the premonsoon. Instead, maximum value was observed during postmonsoon. The monsoonal maximum at stations 7 and 8 might be contributed from the bottom water having considerably high salinity and sulphate than the rest of the stations. The tidal force was maximum at these stations to suit this.

The seasonal minimum observed at most of the stations during postmonsoon could be attributed to the high rate of sulphate reduction. Some other stations represented a monsoonal minimum stressing the dilution factor by fresh water more indicative.

3.2.2.2. Acid Volatile Sulphide Sulphur

Acid volatile sulphides(AVS) are so termed in order to discriminate between the soluble and insoluble iron sulphide phases in hot hydrochloric acid. On the basis of this criterion, the metastable iron sulphides plus the hexagonal pyrrhotite ($FeS_{1.1}$) are often termed "acid volatile" sulphides and are soluble in hot hydrochloric acid. The insoluble form of iron sulphide phase is pyrite. In sulphur rich environments, like marine sediments, though pyrite is assumed to be the normal end product of sulphate reduction, metastable phases also persist for considerable periods of time, because the kinetics of transformation involving various iron sulphide phases are slow. The initial product formed from reaction of ferrous iron with hydrogen sulphide (at neutral pH) is an acid soluble precipitate. Berner, (1969) found this material to be amorphous and later recognized as poorly crystallized mackinawite.

Mackinawite is pure phase in the Fe-S system and is assigned a formula $FeS_{0.94}$ (Ward, 1970). The metastable iron-sulphide phases include the mineral greigite along with amorphous iron sulphide and mackinawite. But for the present study, AVS fraction is determined using the method of Cutter and Velinsky (1987), excluding the greigite mineral.

The observed AVS S values at different stations are represented as appendix. The seasonal variation is given in Fig. 3.4.

The concentration of AVS S varied between 0.00 mg/g and 6.26 mg/g, which constituted 0.00 to 46.00% of total S. Generally, upstream stations were characterised by lower concentrations. At estuarine and marine conditions, the AVS S concentrations did not exhibit much difference. The lowest concentration was found at station 3. A significant feature noted was that a high value of 7.40 mg/g also was found at station 3 , which accounted for 76.07% of total S. Station 10 was mostly characterised by elevated levels of AVS S.

The seasonal values varied between 0.17 and 1.36 mg/g; 0.26 and 1.78 mg/g and 0.20 and 2.34 mg/g during monsoon, postmonsoon and premonsoon respectively. The seasonal maximum was observed during the postmonsoon season at stations 3, 4, 5, 6 7 8 and 9 and during premonsoon season at station 10. The seasonal minimum was observed during monsoon at stations 3, 5, 7, 8, 9 and 10 and during premonsoon at stations 4 and 6.

The studies conducted in Delaware Salt marsh by Cutter and Velinsky, (1988) have reported 3% or less of AVS S fraction. In Louisiana Salt marsh soils, AVS S accounted for only less than 1% of total S (Krairapanond *et al.*, 1991). But in Kelly lake sediments, AVS fraction was found to be an important component accounting for 10 to 25 % of the total S (Nriagu and Soon, 1985). The concentration observed in the present study are more or less comparable to the earlier studies.

Most of the sediment samples were observed black in colour indicating the presence of FeS. The characteristic odour of

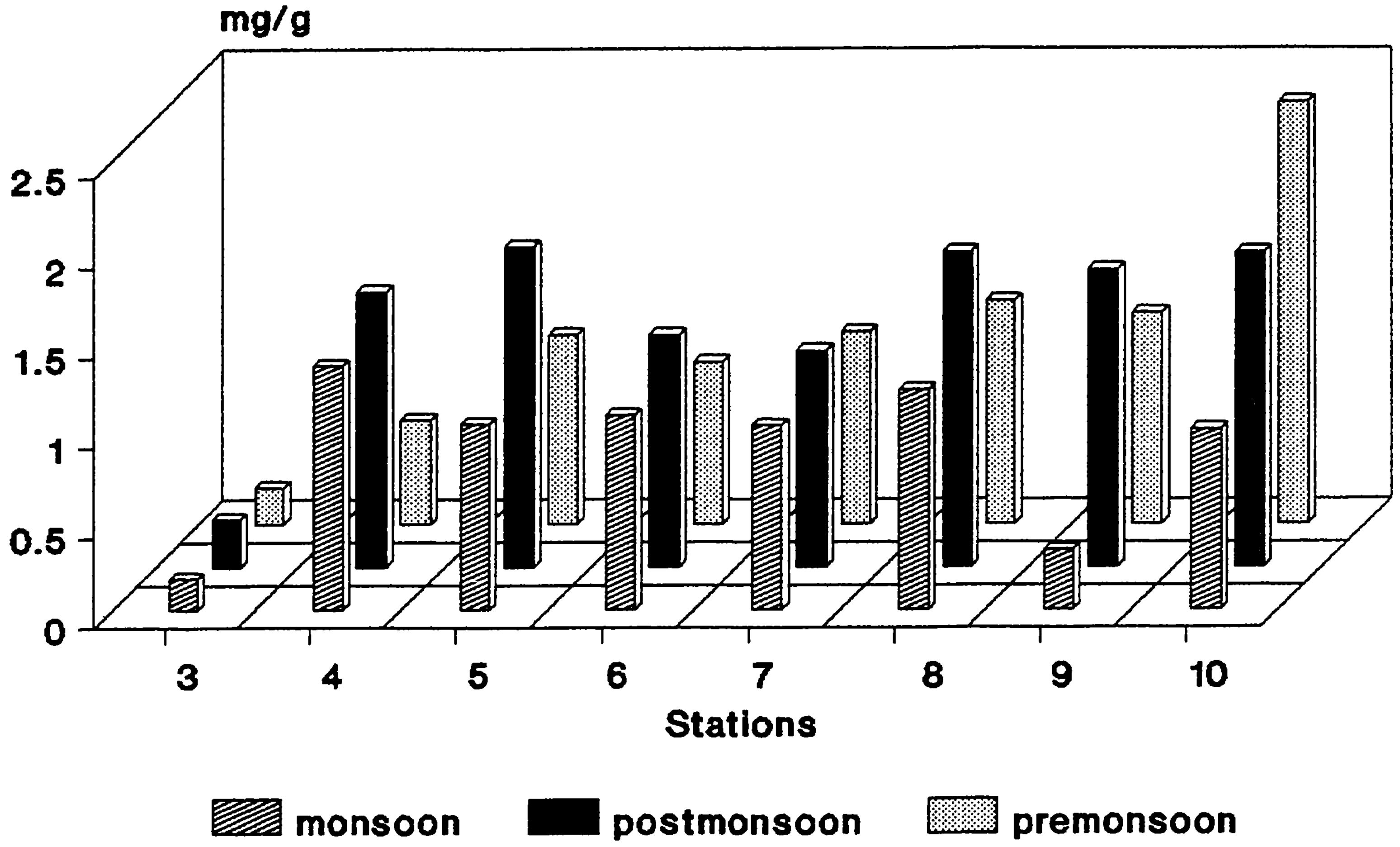


Fig. 3.4
Seasonal variation of sedimentary AVS S

H_2S also was detected sometimes. The concentration of AVS S fraction was found to decrease towards the upstream, though not in uniform. As the initial product and reliable representative of sulphate reduction (Goldhaber and Kaplan, 1974), the distribution pattern of AVS S fraction could distinguish areas with varying sulphate reduction rates. Thus high concentrations at the downstream stations could be attributed with high sulphate reduction rate.

Seasonwise distribution pattern of AVS S fraction showed a postmonsoonal maximum and a monsoonal minimum at most of the stations. This implied that intensity of sulphate reduction was high during postmonsoon and then decreased with the advancement of the succeeding seasons. A supporting evidence to this explanation was found with the sulphate data. A similar study by King *et al.*, (1985) has reported that a significant fraction of the sulphate depleted in a salt marsh reflected in the AVS data.

The highest AVS S fraction was found at station 10 during premonsoon season when the sulphate reduction rate also was high due to the highest turnover of organic carbon. The retting environment as well as the low river flow of the corresponding season were contributing factors for the sulphate reduction.

The station wise seasonal differences in the distribution of AVS fraction could be attributed to the differences in the content of organic matter. In Berner and Raiswell's (1983) review of freshwater sediments, they have come across such a finding of surface sediments with high concentration of AVS, due to high organic carbon. Similar observation was found by Davison *et al.*, (1985) in freshwater sediments.

As reported for marine sediments (Berner, 1970), the AVS fraction was found to be the major short-term end product of sulphate reduction in the present study also. Since they were not accumulating with the time, gradual disappearance into more stable forms could be expected. Goldhaber and Kaplan, (1974) have reported that in rapidly deposited sediments, AVS is present in greatest abundance relative to pyrite. Such an observation was not found in this estuarine system.

3.2.2.3. Greigite Sulphur

Greigite is a cubic iron sulphide mineral with the composition of Fe_3S_4 and a spinal structure (Skinner *et al.*, 1964). Berner, (1967) assigned a composition $Fe_3^{2+}S^0S_3^{2-}$ to greigite, but later detailed studies by Vaughn and Ridout, (1971) arrived at a conclusion that greigite is an inverse spinal structure with the composition $Fe_2^{3+}Fe^{2+}S_4^{2-}$. The reaction to form greigite from mackinawite is an oxidation process and takes place in the presence of the oxidizing agents like elemental S and iron oxides. The greigite mineral is an intermediate phase of the formation of framboidal pyrite.

The observed concentrations of greigite S at different stations are represented as appendix. The seasonal variation is given in Fig. 3.5.

The greigite S concentrations varied from 0.01 to 1.01 mg/g, constituting 0.44 to 15.62 % of the total S. A concentration of 0.84 mg/g had contributed 21.04% to the total S at station 3, which represented the highest concentration. Lower concentrations were observed towards the upstream with still higher values at stations at the intermediate salinity range. In comparison with other Sulphur fractions analysed, greigite S was found to be in smaller quantities.

The seasonwise mean values varied between 0.04 and 0.69 mg/g; 0.08 and 0.59 mg/g and 0.04 and 0.34 mg/g during monsoon, postmonsoon and premonsoon respectively. At stations 4, 5 and 6, the monsoonal contribution represented the highest value. At

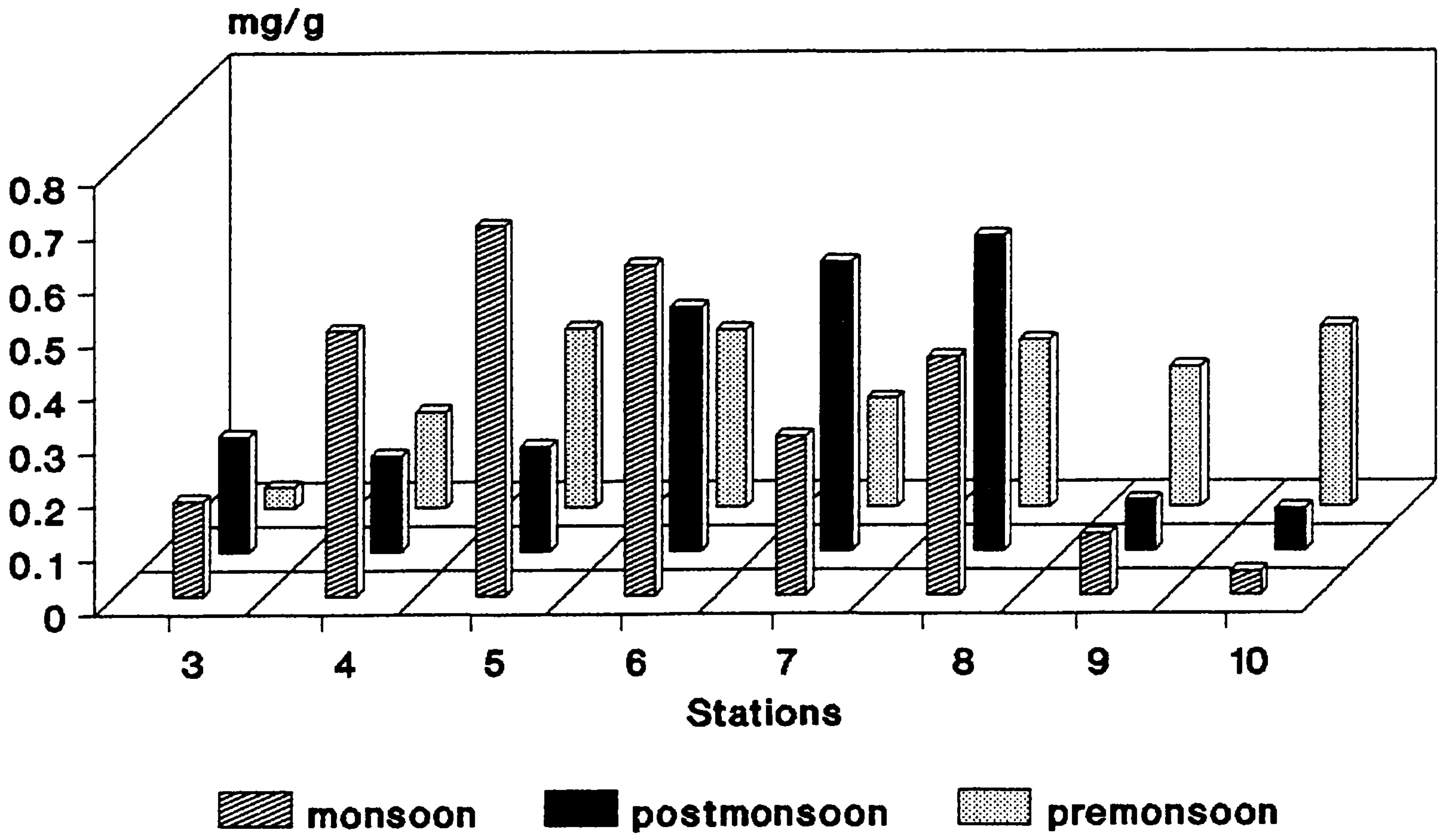


Fig. 3.5
Seasonal variation of sedimentary
Greigite S

station 4, the post and premonsoonal values remained the same. At station 5, a postmonsoonal and at station 6, a premonsoonal minimum were observed. At stations 3, 7 and 8 the highest value was observed during postmonsoon and lowest during premonsoon. The premonsoonal values constituted the highest values at stations 9 and 10, whereas their lowest concentrations differed between the seasons. At station 9, the monsoonal and postmonsoonal values did not vary much. At station 10, the monsoonal value represented the minimum seasonal concentration.

The observed concentrations are in conformity with the values reported in a salt marsh study (Cutter and Velinsky, 1988). This is the only data reported on greigite concentrations. In all other studies greigite was taken as a counterpart of AVS fraction and hence greigite concentration was inclusive in AVS concentration.

The increasing effect of salinity which suppressed iron solubility (Scholkovitz, 1976) towards the marine side was one factor which caused the increased concentration towards the downstream. Since greigite is an intermediate in the process of slow pyritisation, its presence showed that framboidal pyrite was formed in this estuarine sediments.

The temporal and spatial variation of greigite from AVS fraction showed that, in addition to the sulphate reduction process, some other factors also governed its distribution pattern. The seasonal variation exhibited maximum concentrations during monsoon season in some of the stations. Since elemental S is an important factor for the formation of greigite (Goldhaber and Kaplan, 1974), availability of the former controls the distribution of the latter. This requirement was mostly satisfied during the monsoon season since the more oxidizing condition prevailing in the sediments at that time, catalyzed the elemental S formation (Troelsen and

Jorgensen, 1981). At station 7 also the postmonsoonal maximum observed could be accounted for by the simultaneous occurrence of S^0 maximum.

At stations 3 and 8, the seasonal maximum observed during the postmonsoon and at station 10 during the premonsoon suggested that the sulphate reduction process was more influential than the elemental S contribution in controlling the greigite concentration there. Station 9, which is subjected to the highest sewage disposal, was found to encounter with hydrogen sulphide smelling wastes during premonsoon. Since this effect was not reflected in the AVS fraction, gradual conversion to the greigite form could be expected.

The premonsoonal minimum observed at most of the stations could be explained by its involvement in the pyrite formation and the concurrent occurrence of pyrite. The monsoonal and postmonsoonal concentrations did not vary much at station 9 and this represented lower concentrations than that at the succeeding season. The monsoonal value was the minimum at station 10 also. These observations could suggest the experience of pyritisation process operating there.

3.2.2.4. Pyrite Sulphur

Pyrite is a ferrous polysulphide (Morice *et al.*, 1969) and is the thermodynamically stable phase of iron-sulphide minerals. To maintain charge neutrality, the sulphur atom can be regarded as possessing a formal charge of -1 each or alternatively one atom divalent and the other zero-valent ($S^{2-}S^0$)

Two forms of pyrite have been identified ; single crystals and framboids. The pathways for the formation of each of these form are different. Sedimentary pyrite is a common authigenic mineral in recent marine and lacustrine environments as well as in sedimentary rocks, particularly dark shales (Love and Amstutz, 1966). The single crystals and framboids are present in the clay and silt-size sediment fractions or as in fillings of foram, diatoms and radiolarium tests (Golhaber and Kaplan, 1974).

The observed concentration of pyrite S at different stations are represented as appendix. The seasonal variation is given in Fig.3.6.

The concentrations ranged from 0.00 mg/gm to 4.30 mg/g which constituted 0.00 to 36.27% of total S. Generally the concentrations were found to decrease towards the riverine region. At station 3, the lowest concentrations (0.00 to 0.32 mg/g) were observed. Station 10 had comparatively higher concentrations of pyrite S throughout the period of study. The highest concentration of 4.30 mg/g was observed at station 10. An intermediate range of concentrations were observed at estuarine stations with a rise in values towards the marine region.

The seasonwise mean values of pyrite S varied from 0.04 to 2.71 mg/g; 0.01 to 1.66mg/g and 0.11 to 1.93 mg/g during monsoon, postmonsoon and premonsoon respectively. Seasonal mean value was maximum during the premonsoon season at stations 3, 4, 5, 6, and 7, whereas at stations 8 and 9 it was in postmonsoon and at station 10, it was in monsoon. At stations 3, 4, 5, 7, and 10 the postmonsoonal values represented the minimum quantities whereas at stations 6 and 9 monsoonal values and at station 8 premonsoonal value contributed the least.

The observed range of values for pyrite S are comparable with those observed in salt marsh studies (Cutter and Velinsky, 1988) and in lake sediments (Nriagu and Soon,

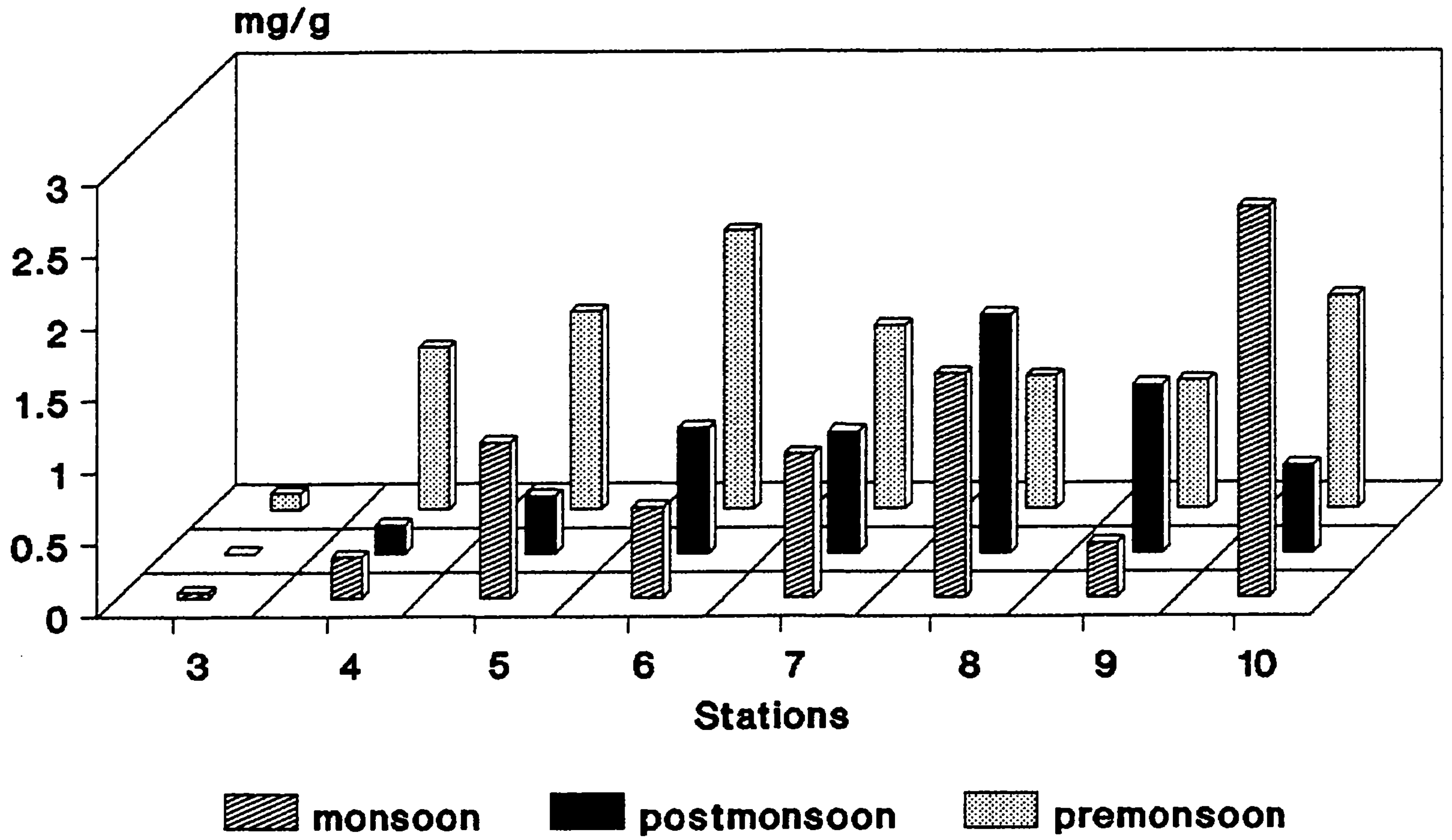


Fig. 3.6
Seasonal variation of sedimentary
Pyrite S

1985). But in salt marshes and marine sediments, the total S profiles are found very much dependent on the pyrite S concentration (Goldhaber and Kaplan, 1974 ; Rickard, 1975), unlike that in the present study. Sulphur associated with pyritic form was found to be a minor component in this estuarine sediments. In lake sediment ecosystems also, pyrite formation was reported to be a minor process of sulphur diagenesis (Nriagu and Soon, 1985).

The comparatively high concentrations observed at station 10 could be attributed to the high turnover of organic carbon taking place there because of the nearby retting yard. One of the possible origin for the pyrite formation can be diagenetic formation from slow oxidation of AVS by organic matter (Berner, 1984), because for a corresponding decrease in AVS fraction an increase was observed in the pyrite form (Nedwell and Abram, 1978). This slow pyritisation mechanism produces the framboidal form of pyrite (Sweeney and Kaplan,1973). In marine sediments pyrite is believed to form very slowly through the gradual reaction of iron-monosulphides with elemental S during sulphate reduction (Berner, 1970).

The large variations in pyritic S concentration sometimes observed, lead to the suggestion that rapid rates of formation and destruction also was taking place. The rapid pyritisation process lead to the formation of single crystalline forms (Rickard, 1975). Thus both the pyritisation mechanisms were playing in the estuarine sediments with clay and silt and contain crystalline and framboidal forms of pyrite. Single crystalline and framboidal forms of pyrite were reported to be present in the clay and silt sized sediments by Goldhaber and Kaplan, (1974).

The seasonwise distribution pattern of pyritic S showed a premonsoonal maximum at most of the stations and a monsoonal minimum at the rest of the stations. This premonsoonal maximum obtained here confirms the arguments put forth for explaining the greigite minimum. This indicated a slow pyritisation process and thereby framboidal pyrite formation during the premonsoon season. Another favourable condition for the premonsoonal maxima was the less oxidative condition prevailing in that season which favoured pyrite formation over pyrite oxidation. At stations 8 and 9 the pyritisation process was found simultaneously occurring with sulphate reduction. The monsoonal maximum observed at station 10 might have been contributed from detrital load of the catchment area (Davison *et al.*, 1985). The minimum average concentration found at the station during the premonsoon season would strengthen the above suggestion.

The seasonal difference observed for the AVS and pyritic maxima could be due to such conditions, which did not favour the formation of monosulphides, were ideally suited to the rapid formation of pyrite, according to Howarth (1979). The minimum concentration observed at most of the stations during postmonsoon would find this explanation applicable. At stations 6 and 9 the monsoonal minimum observed could be explained by the oxidative condition of the corresponding season more indicative in the oxidation of pyrite there.

3.2.2.5. Elemental Sulphur

Elemental S in sediments is of great interest, as it is postulated to play an important role in transformation among iron sulphide phases. It never builds up to high concentration due to rapid formation and removal (Kaplan *et al.*, 1963). In that case, elemental S can become the rate limiting factor in the acid-volatile sulphide to pyrite transformation (Berner, 1970). It is produced in reducing sediments by incomplete oxidation of sulphide with ferric iron.

The observed concentrations of elemental S at different stations are given as appendix. The seasonal variations is given in Fig. 3.7.

The concentrations ranged between 0.01 and 6.74 mg/g which constituted 0.10 to 20.53% of total S. Contribution of elemental S to total S sometimes overlapped this range mainly at stations 7 and 10. A decline in concentration was found towards the upstream. In estuarine stations as well as towards the marine region, the concentrations did not vary much. Highest observed concentration was found at station 7 and the lowest at station 3.

The seasonwise mean values of elemental S varied between 0.06 and 3.78 mg/g; 0.02 and 4.72 mg/g and 0.11 and 2.16 mg/g during monsoon, postmonsoon and premonsoon respectively. At stations 4, 5, 6, 8, 9 and 10 the seasonal maximum was observed during monsoon season and at station 7 during postmonsoon and at station 3 during premonsoon season. At stations 3, 8 and 10 the seasonal minimum was observed during postmonsoon and at stations 4, 5, 6, 7 and 9 during premonsoon.

The low concentrations observed are comparable to those observed in Louisiana salt marshes (Krairapanond *et al.*, 1991). But in the present study,the overall contribution of elemental S to total S was found to be higher compared to other studies.

In the spatial distribution pattern, a decline in concentration of S^0 observed towards upstream might be due to the less availability of the AVS fraction towards the upstream, which is the source of elemental S (Goldhaber and Kaplan, 1974). The relative rates of the processes leading to the formation and removal of elemental S are reported to be such that it never builds up to high concentration (Kaplan *et al.*, 1963). The absence of elevated levels of elemental S except at

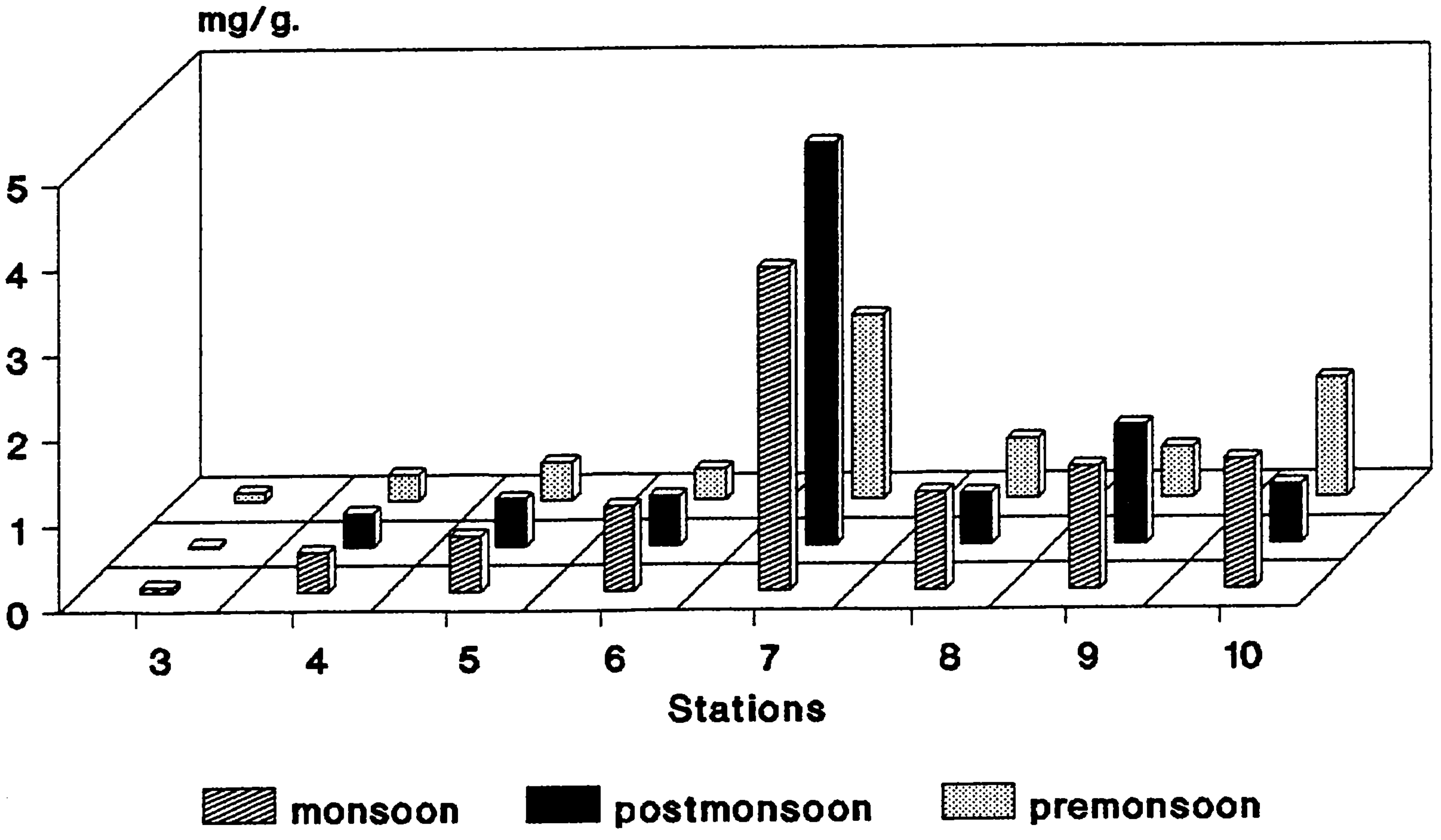


Fig. 3.7
Seasonal variation of sedimentary
Elemental S

stations 7 and 10 could be attributed to this. At station 7, where sulphur loading and unloading was carried for a fertilizer plant, observed the highest concentration of elemental S. Station 10, which was characterized by a nearby coconut retting yard was noted with high values of elemental S, sometimes might be a contribution from the retting yard.

A difference in seasonal variation of spatial distribution was noted for elemental S. This could be due to the influence of the factors affecting elemental S concentration varying spatially and seasonally. The monsoonal maximum observed at most of the stations could be due to the more oxidising condition of the corresponding season. The accumulation of S^0 in a coastal sediment due to the same reason has been reported by Troelsen and Jorgensen, (1981). At station 7, the postmonsoonal maximum might be contributed anthropogenically.

The elemental S produced can be further oxidized to sulphate (Brock and Gustafson, 1976) or can be reduced back to sulphide (Pfennig and Biebal, 1976; Postgate, 1979) bacterially. But most of the elemental S is used to form pyrite by reaction with FeS (Berner, 1970). Thus, the seasonal minimum observed during premonsoon at most of the stations could be attributed to pyrite formation. At station 8 also the observed minimum was related to a pyrite maximum. At station 10 oxidation to sulphate might have taken place. At station 3 greigite formation was found to be the governing factor in the distribution of elemental S. An active participation of elemental S in the production of organo S compounds have been reported by Nissenbaum and Kaplan (1972), Casagrande *et al.*, (1979) and Dinur *et al.*, (1980) etc. Luther *et al.*, (1986) has found that a dynamic S cycle in which sulphur is transformed from inorganic to organic and vice versa, seasonally, occur in the saltmarsh. Such a condition of dynamic S cycling could be expected in the present study also.

3.2.2.6. Organic Sulphur

The organic S constitutes the major fraction of the total S present in the estuarine and lake sediments, generally the range is found to be 50 - 60 % in the lake sediments. The compounds in this fraction have been classified into two groups according to the carbon bonding with sulphur; ester-sulphate sulphur compounds in which sulphur not directly bonded to carbon and carbon bonded sulphur compounds in which sulphur directly bonded to carbon (Johnson and Nishita, 1952). The ester-sulphate S compounds include ester sulphates (-C-O-S-), sulphamic acid (-C-N-S-) and S-sulphocysteine (-C-S-S-) and carbon bonded S compounds include peptides, proteins, coenzymes, sulphlipides, aliphatic sulphones, sulphonic acids and heterocyclics. In the present investigation, the organic S fraction comprises both the ester-sulphate S compounds and carbon-bonded S compounds.

The observed concentrations of organic S at different stations are given as appendix. The seasonal variation is represented in Fig.3.8.

The concentration of organic S varied between 0.25 and 20.87 mg/g, which constituted 5.8% to 79.13% of total S. The concentrations were found to decrease towards the upstream, contributing comparatively lesser percentage to the total S. In the present study, the organic S accounted for the major fraction of total S. Similar observation has been reported for lake sediments by Casagrande *et al* ., (1979); Altschuler *et al*., (1983); Nriagu and Soon, (1985); Weider *et al*., (1987); Haering *et al*., (1989).

The seasonal mean values varied between 0.72 and 16.89 mg/g; 1.63 and 9.74 mg/g and 1.50 and 16.77 mg/g during monsoon, postmonsoon and premonsoon respectively. The seasonal maximum was observed during premonsoon at stations 5, 6 and 8,

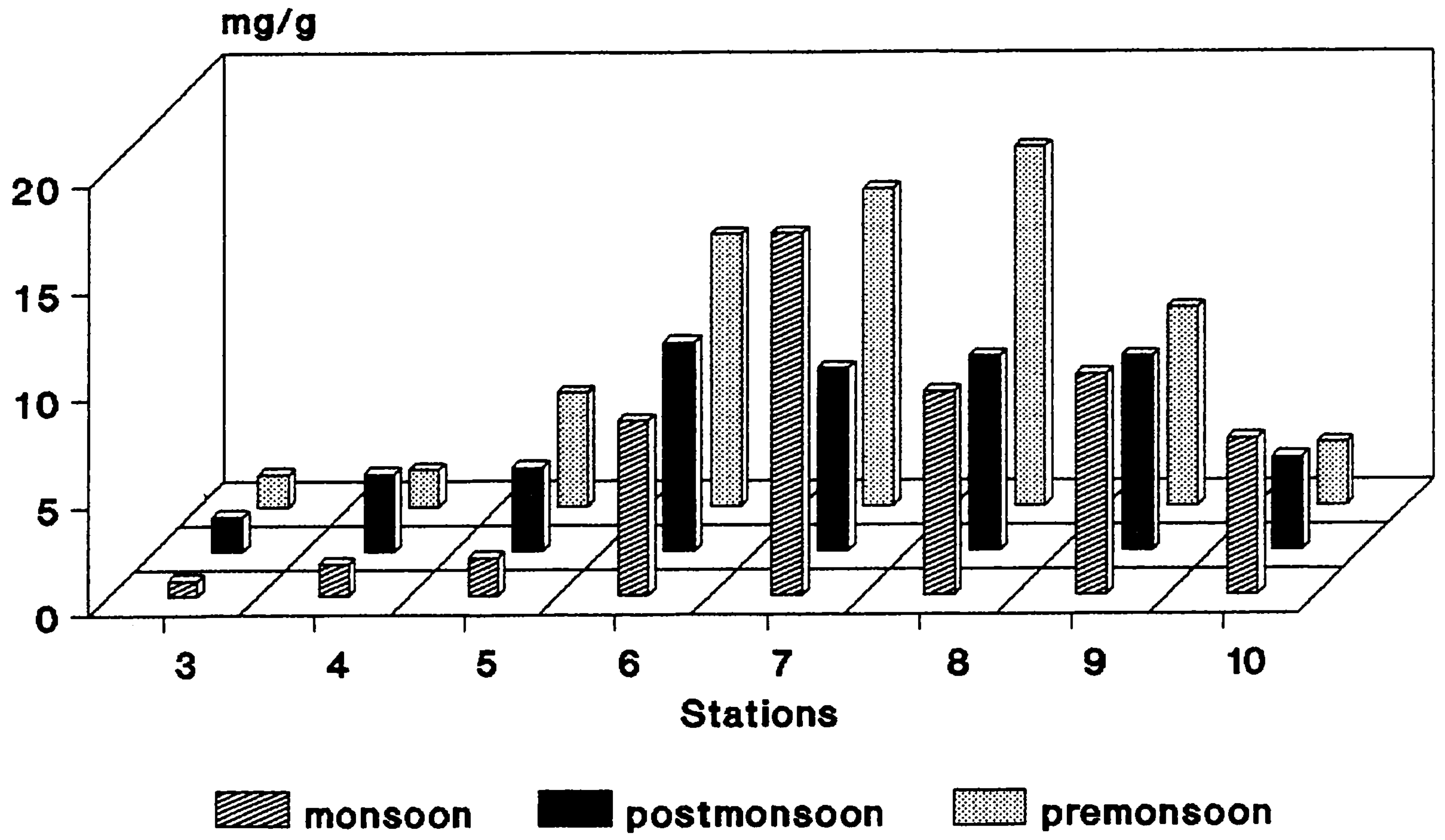


Fig. 3.8
Seasonal variation of sedimentary
Organic S

during postmonsoon at stations 3 and 4 and during monsoon at stations 7, 9 and 10. The seasonal minimum was observed during monsoon at stations 3, 4, 5 and 6, during postmonsoon at stations 7, 8 and 9 and during premonsoon at station 10.

Rudd *et al.*, (1986) have reported that sediments with higher rates of sulphate reduction have higher concentration of total S per volume and higher percentage of organic S. Thus higher rates of sulphate reduction occurred towards the high saline region might have catalyzed organic S accumulation. Again, contribution from organic matter concentrated towards the downstream also might have an added effect for organic S accumulation with the incorporation of SO_4, H_2S, S^0 ,or polysulphide (Nissenbaum and Kaplan, 1972; Nriagu and Soon, 1985).

The seasonal difference observed in the station wise organic S distribution depended on several factors. Luthur *et al.*, (1986) found that a dynamic sulphur cycle in which sulphur is transformed from inorganic to organic species during warmer, more productive seasons and from organic to inorganic forms during cooler, less productive seasons does occur in the saltmarsh. The organic S maxima observed during premonsoon at most of the stations seemed to emphasize this point and its applicability in estuarine sediments also. Since the concentration of organic S was found very high compared to inorganic sulphur species, transformation solely might not be the contributing factor. Availability of organic carbon along with incorporation of elemental S or H_2S or polysulphide would account for the difference.

The monsoonal maximum observed at stations 7, 9 and 10 could be attributed to the effect of organic S sedimentation rates (Mitchell *et al.*, 1988). At stations 9 and 10 sewage wastes comprising organic S compounds might be the source for the monsoonal maximum, because these stations are exposed to high input from sewages. At station 10, the washings containing organic S compounds from the coconut retting ground might have caused for the monsoonal maximum. In contrast to the other observations, the postmonsoonal maximum experienced at stations 3 and 4 could be due to the sulphate reduction process contributing significantly. The effluent from the newsprint factory also should have contributed to the organic S accumulation.

The minimum value observed for the organic S fluctuated spatially and seasonally. The monsoonal minimum observed could be attributed to the transformation of organic to inorganic form during this cooler, less productive season (Luther *et al.*, 1986). The dilution effect of monsoon also could operate for less sulphur accumulation in the sediments. At station 7, the premonsoonal value was still higher than that of the postmonsoon season due to the warmer, and more productive condition of premonsoon favoring the transformation of inorganic to organic S form. Thus the postmonsoonal value remained the least. At station 8, the monsoonal value did not vary much sustaining the influence of monsoonal factors in the postmonsoon also. Not much seasonal variation was observed at station 9. The premonsoonal minimum at station 10 confirmed the source at this station was land drainage.

3.2.2.7. Total Sulphur

The total S comprises both inorganic and organic S fractions.

The observed concentrations of total S at different stations are given as appendix. The seasonal variation is represented in Fig. 3.9.

The concentrations of total S observed ranged between 1.02 and 32.81 mg/g from upstream to the Barmouth. Highest

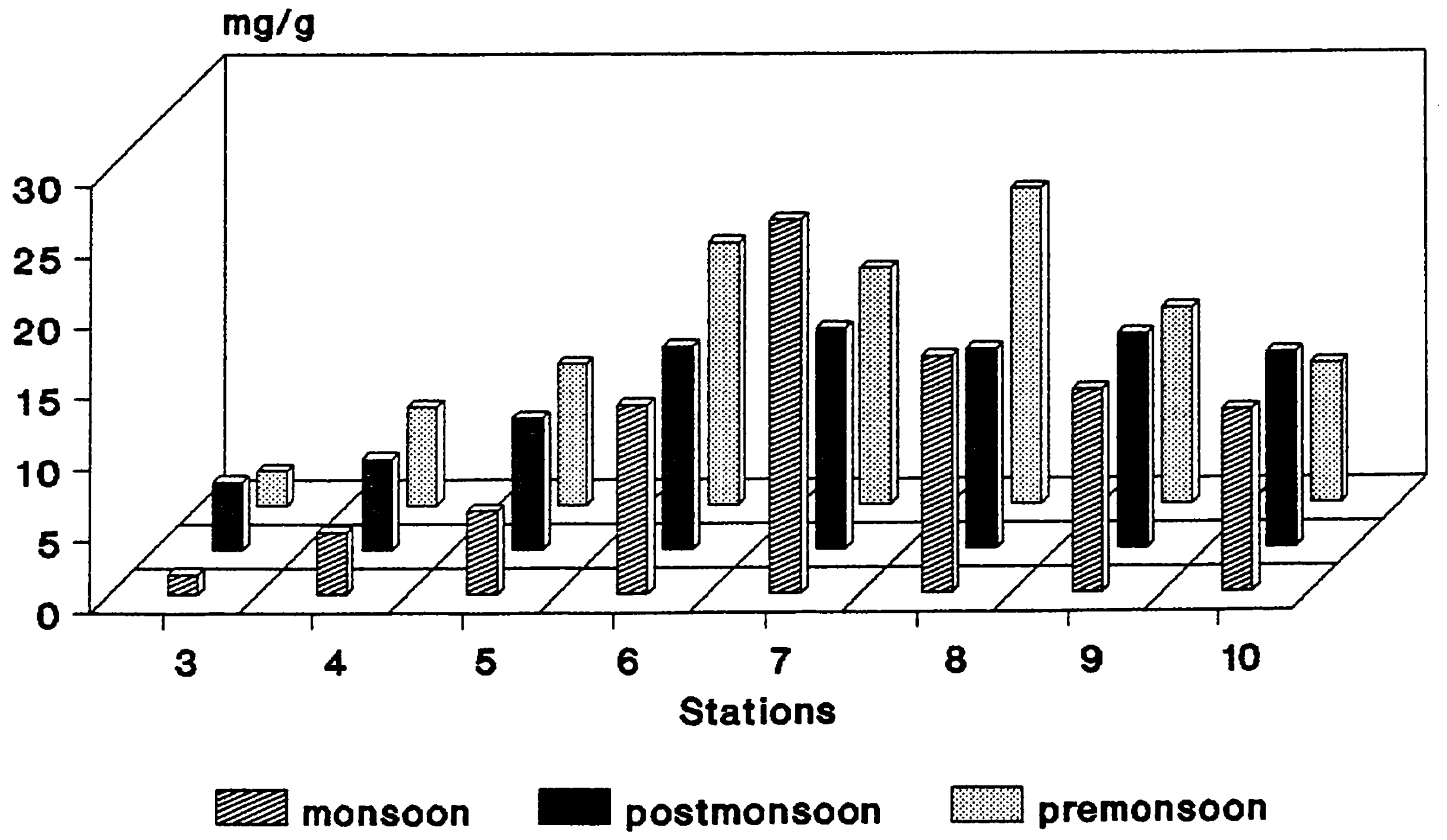


Fig. 3.9
Seasonal variation of sedimentary
Total S

concentration was found at station 7 and low concentrations were observed at upstream stations. Seasonal averages calculated stationwise ranged from 1.39 to 26.31 mg/g; 4.77 to 15.53 mg/g and 2.46 to 22.24 mg/g during monsoon, postmonsoon and premonsoon respectively. The maximum total S content was observed during premonsoon at stations 4, 5, 6 and 8 ; during postmonsoon at stations 3, 9 and 10 and during monsoon at station 7.

The temporal and spatial variability in total S contents in this study were not primarily due to variability in pyrite S but were due to a variability in organic S, similar to that shown in recent lake studies (Casagrande *et al.*, 1979 ; Altschuler *et al.*, 1983; Nriagu and Soon, 1985; Wieder *et al.*, 1987; Haering *et al.*, 1989; Krairapanond *et al* ., 1991). Quantitatively, the concentrations of total S found towards the downstream are comparable to those found in the Great Marsh of Delaware (Cutter and Velinsky, 1988) and in a Chesapeake Bay tidal marsh of Maryland (Haering *et al* ., 1989) and Louisiana saltmarsh soils (Krairapanond *et al.*, 1991) and concentrations found towards upstream are comparable to those found in lake studies (Giblin *et al.*, 1990).

Contrary to the expected high values of total S content towards the marine side, the observed maximum value at station 7 could be contributed from elemental S lost to the sediments during transport. The maximum total S content observed at stations 4, 5, 6 and 8 were consistent with the organic S content observed at these stations. During premonsoon season the estuarine water was largely constituted by sea water and proportionally high sulphate concentration was retained. Rates of sulphate reduction in sediments is increased as sulphate concentration in the overlying water increases (Cook and Schindler, 1983; Kelly and Rudd, 1984) and can induce high content of sulphur to the sediments (Nriagu and Soon, 1985; Rudd *et al.*, 1986), with long term end product of sulphate reduction as organic S (Rudd *et al.*, 1986). At stations 3 and 7 also the maximum total S content noted during postmonsoon and monsoon seasons respectively were consistent with their organic S data.

At stations 9 and 10, the total S concentration observed was high during postmonsoon season and did not vary much from the monsoonal concentrations. Inconsistent with the organic S maxima observed during monsoon season at these stations, the postmonsoonal maxima of total S content by a low margin might be contributed from short term end products of increasing rate of sulphate reduction like AVS, pyrite, S^0 etc., as the season advanced from monsoon to postmonsoon. At station 3, the maximum seasonal concentration of 4.77 mg/g during post monsoon was found to be contributed from the November value, 9.72 mg/g. This sporadic deposit was constituted mainly by AVS fraction as against other observations and might be resulted from any discharge from the upstream.

The minimum concentration observed during monsoon season at stations 3, 4, 5 and 6 could be attributed to the high freshwater inflow and the associated dilution effect. At stations 7 and 8, the minimum concentrations found during postmonsoon season were consistent with the lower organic S concentration. At station 8, the monsoonal concentration and postmonsoonal concentrations did not vary much. The freshwater flow during monsoon itself had provided lower sulphur content to the sediments, which when subjected to the higher rate of sulphate reduction during postmonsoon might have caused a loss of sulphur from the system due to regenerative process. The concentrations of organic carbon might have been high enough for adequate production of H_2S from microbiological decomposition processes and sufficiently low to avoid anomalous results due to an abundance of organic S (Davison *et al.*, 1985).

The decline in total S concentration at station 7 consistent with the organic S content during postmonsoon could be due to the increased microbial activity and the high rate of mineralization of C-bonded organic S content (Freney, 1986). But here the high rate of sulphate reduction was not sufficient to contribute higher concentrations of total S as Rudd *et al.*, (1986) reported. Thus some of the sulphur from the system could be expected lost. The postmonsoonal minimum observed at station 10 also could be attributed to the same reason since the sulphate reduction rate was high during this period without much sulphur accumulation, showing larger microbial activity leading to sulphur loss from the system.

3.3. Interrelations

Of the six sedimentary sulphur fractions studied the correlations which gave significant values are expressed in the following equations.

$[AVS] = 0.34 \times [S^0] + 0.66$ —— (1) $r = 0.30$; $n = 101$

$[AVS] = 1.18 - 0.13\ [FeS_2]$ —— (2) $r = 0.17$; $n = 101$

$[Tot\text{-}S] = 1.57\ [AVS] + 10.32$ —— (3) $r = 0.24$; $n = 101$

$[SO_4] = 0.05\ [dSO_4\text{-}s] + 0.93$ —— (4) $r = 0.36$; $n = 101$

$[SO_4] = 0.06\ [dSO_4\text{-}b] + 0.63$ —— (5) $r = 0.56$; $n = 101$

$[dS^{2-}\text{-}s] = 1.68 - 0.02\ [dSO_4\text{-}b]$ —— (6) $r = 0.22$; $n = 101$

$[dS^{2-}\text{-}s] = 1.84 - 0.05\ [dSO_4\text{-}s]$ —— (7) $r = 0.40$; $n = 101$

$[FeS_2] = 0.05\ [Tot\text{-}S] + 0.47$ —— (8) $r = 0.39$; $n = 101$

$[FeS_2] = 0.05\ [Org\text{-}S] + 0.68$ —— (9) $r = 0.30$; $n = 101$

$[S^0] = 0.07\ [\text{Org-S}] + 0.56$ —— (10) r = 0.30; n = 101

$[\text{Org-S}] = 4.23\ [SO_4] + 1.75$ —— (11) r = 0.71; n = 101

$[FeS_2] = 0.36\ [SO_4] + 0.54$ —— (12) r = 0.40; n = 101

$[Fe_3S_4] = 0.05\ [SO_4] + 0.22$ —— (13) r = 0.20; n = 101

$[S^0] = 0.38\ [SO_4] + 0.58$ —— (14) r = 0.26; n = 101

$[\text{Tot-S}] = 6.01\ [SO_4] + 4.31$ —— (15) r = 0.77; n = 101

where, the square brackets denote the concentrations of the sulphur fractions and 'd' represents the dissolved forms.

The absence of a significant relation of sulphate with AVS points to two probabilities:

1. the AVS was not formed by the reduction of sulphate though a high organic content of the sediment could facilitate the production of AVS from sulphate and

2. the highly significant exchange processes operating between the sediment and water transported part of the AVS produced in the sediment to the overlying water column.

The two probable paths of production of AVS are:

1. the reduction of sulphate which is formed either from the oxidation of organic S compounds or the inorganic sulphate reaching the sediment through exchange with overlying saline waters and

2. the direct conversion of the organic S compounds by the action of microorganisms in an oxygen deficient condition.

In the present study, no correlation of AVS was observed with sulphate or organic S compounds. The absence of these correlations and the observed correlation with dissolved sulphide supports the exchange of sulphate and AVS with the overlying water.

The AVS to FeS_2 relation was negative indicating a reduction in the FeS_2 formation is a condition which favoured the production of AVS. Such a behaviour has been reported by Howarth(1979). The negative correlation of the AVS with FeS_2 and the positive correlation between FeS_2 and organic S indicated a path which is different from the formation through AVS is a probability for the production of FeS_2.

The absence of a significant relation for the AVS with the organic S also indicated the absence of an oxidative path for the formation of pyrite. Moreover, the significantly high concentration of the organic matter in the sediment would assist only the reduction of the organic S . A similar behaviour has been observed by Altschuler *et al*, (1983).

The significant correlation given by S^0 with AVS and organic S and the absence of correlation between organic S and AVS would indicate a formation path for the S^0 from organic S other than through sulphide.

The concentration of sulphate was found to be profoundly influenced by the dissolved sulphate concentration as it gave a significant correlation with the surface and bottom sulphate concentrations. The dissolved sulphide gave a negative correlation with the dissolved sulphate.

CHAPTER IV

COASTAL SULPHUR FRACTIONS

4.1. Introduction

The major ion chemistry of the ocean is controlled over long time-intervals by reaction occurring between the aqueous phase and various solid phases of the lithogenous and biogenous origin (Sillen, 1961; Pytkowicz, 1967; Siever, 1968; Broecker, 1971; Garrels and Mackenzie, 1971; Goldhaber and Kaplan, 1974). Thermodynamic calculation indicate that the sulphate ion SO_4^{2-} should be reduced to sulphide by organic matter in the absence of oxygen (Bostrom, 1967). Two of the well documented environments with prevailing anoxic condition are the Cariaco Trench (Richards and Vaccaro, 1956) and the Black Sea (Caspers, 1957), although numerous other localized estuaries, lagoons and fjords undergo stagnation (Richards, 1965).

Water column sulphate reduction, while only locally important under present geochemical conditions, could have been of more widespread significance in the geologic past. Beneath the water column, however, anoxic conditions are frequently established at, or just beneath the water-sediment interface, again as a consequence of the accumulation of organic matter and restriction imposed on the rate of addition of oxygen. Due to the activity of heterotrophic organisms, reducing conditions are maintained in most coastal sediments below a thin oxidized surface layer (Jorgensen, 1977). This stratification provides the basis for the transformation of inorganic sulphur compounds through a cyclic series of redox processes.

In the anoxic sediment, sulphate is reduced to sulphide by the respiratory metabolism of sulphate reducing bacteria. Much of this sulphide is trapped in the sediment by precipitation with metal ions, but some may remain dissolved in the pure water and reach the oxic and photic surface layers of the sediment. Here it is oxidized back to sulphate via intermediate oxidation steps, partly by catalysis by chemoautotrophic or photoautotrophic bacteria. These processes have a strong influence on the chemical environment in the sediment. They mediate a significant part of the energy flow in detritus food chains connected to anaerobic decomposition (Jorgensen, 1977) and the balance between oxygen and sulphide is an important factor for the distribution of benthic organisms (Fenchel, 1969).

4.2. Results and Discussion

4.2.1. Dissolved Sulphur Fractions

The observed values of sulphate and sulphide along the coastal region are given in Table 4.1. and Table 4.2. respectively.

The sulphate values ranged between 26.21 and 28.19 m.mol/litre without notable deviation from the calculated values. The values agree remarkably well with the SO_4^{2-}/Cl ratio reported by several other workers (Morris and Riley, 1966; Sugandhini *et al.*, 1982). As the salinity values increased or decreased with depth there was corresponding increase or decrease in the SO_4^{2-} concentration. The variation of sulphate keeping the constancy with salinity, indicates its conservative nature and abstinence from biogeochemical involvement in the coastal region unlike that in the estuarine region.

Micromolar levels of (0.37 - 1.50 μ.mol/litre) sulphide have been detected along the coastal region but generally lower

Table 4.1 Concentration of sulphate (m.mol/l) in coastal waters.

Depth	Transect I			Transect II			Transect III			Transect IV			Transect V			Transect VI		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
S	26.83	27.29	27.18	27.56	27.67	27.74	27.18	27.52	27.64	26.21	26.58	26.64	27.02	27.22	27.34	26.58	26.75	27.38
M			27.34		27.67	27.81			27.72			27.70			27.28			27.35
B	27.45	27.53	27.59	27.93	27.95	27.94	27.06	28.19	27.85	27.56	27.72	27.11	27.10	27.30	26.58	27.30	27.41	27.42

Table 4.2 Concentration of sulphide (u.mol/l) in coastal waters

Depth	Transect I			Transect II			Transect III			Transect IV			Transect V			Transect VI		
	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
S	0.80	0.89	1.22	0.54	0.65	1.05	0.85	0.86	1.50	0.75	0.68	1.12	0.58	0.63	0.93	0.70	0.64	0.58
M			1.08		0.70	1.02			0.64			1.11			0.64			0.60
B	0.69	0.75	1.14	0.48	0.71	0.98	0.74	0.79	0.60	0.83	0.60	0.94	0.61	0.59	0.70	0.77	0.60	0.54

1 Near shore station 2 Mid station 3 Off shore station

S Surface M Mid depth B Bottom

Table 4.3.
Concentrations of the sulphur fractions (mg/g) in the coastal sediments.

Transects		AVS	Fe_3S_4	FeS_2	S^o	SO_4	ORG.S	TOTAL.S
I	1	1.50	0.53	4.82	1.58	1.17	17.31	26.90
	2	1.43	0.43	1.19	1.71	1.44	15.17	21.37
	3	1.77	0.30	0.81	1.61	1.77	12.01	16.50
II	1	1.72	0.53	1.68	3.21	1.51	7.38	16.02
	2	1.35	0.40	1.64	3.22	1.68	3.93	12.22
	3	1.58	0.41	0.67	3.81	1.57	6.25	14.30
III	1	2.71	0.46	0.95	0.71	2.27	6.65	13.76
	2	0.72	0.26	0.97	1.21	1.62	5.41	10.19
	3	0.87	0.41	0.84	3.48	2.05	2.40	10.05
IV	1	1.39	0.68	0.15	1.11	2.57	8.88	14.78
	2	1.82	0.75	0.99	0.99	2.87	5.79	13.21
	3	0.01	0.38	3.53	0.21	1.88	14.31	20.32
V	1	1.07	0.53	0.40	3.07	1.08	19.08	25.23
	2	1.53	0.26	0.14	2.56	1.34	17.99	23.83
	3	1.20	0.37	0.48	2.63	1.64	14.75	21.06
VI	1	0.01	0.03	0.04	0.00	0.86	1.19	2.13
	2	0.00	0.03	0.03	0.01	0.78	1.49	2.34
	3	0.37	0.14	1.14	0.13	1.07	4.18	7.03

1: Near shore station 2: Mid station 3: Off shore station nearshore station of transect VI. The greigite S values found in the coastal region were quite comparable with those found in estuarine sediments.

The concentrations of pyritic S varied between 0.03 and 4.82 mg/g. Except for a few high values, the concentrations observed were of the same range of AVS S concentrations. Highest concentration was observed at the nearshore station of transect I and the lowest concentration was observed at the mid-station of transect VI. Towards the northern coastal area, a seaward decrease in the concentration of pyritic S along the transects were observed. An opposite trend was observed in the southern part. An abrupt increase towards shore and sea was noted along the transects I and IV respectively.

The concentrations of elemental S varied between 0.00 and 3.81 mg/g. The values observed at a few stations were slightly greater than the normal values observed in the estuarine region. Thus along the transect II, sulphur was found in comparatively high concentration. The lowest concentration was noted at the nearshore station of transect VI. Along the transects II, III and VI, an increasing trend in the concentration was observed towards the sea while along the transects IV and V, a decrease in concentration was observed. Apart from these, transect I was characterised by its mid-station having higher concentration than the other two stations.

The concentrations of organic S varied between 1.19 and 19.08 mg/g constituting the major fraction of total S. These values are in conformity with the values recorded in estuarine region. Highest concentration was observed at the nearshore station of transect V and the lowest concentration was observed at the nearshore station of transect VI. Most of the transects were characterized by a seaward decrease in concentration with the rest showing an opposite trend.

The concentration of total S varied between 2.13 and 26.90 mg/g. The highest concentration was observed at the nearshore station of transect I and the lowest concentration was observed at the nearshore station of transect VI. Corresponding with the profiles of organic S, an increase or decrease was observed in total S along the transects. The observed range of values is comparable with the values observed in estuarine region.

In coastal sediments, reduction of sulphate by the respiratory metabolism of sulphate reducing bacteria is reported to be a common phenomenon (Jorgensen, 1977). A principal controlling factor of sulphate reduction is the abundance and type of organic matter present (Berner, 1970; 1972). So the differences observed in the distribution of sulphate could be due to the differences in abundance and type of organic matter. Spatial heterogeneity may also be responsible for the sulphate distribution pattern as suggested by Howarth and Merkel (1984).

The AVS S fraction observed along the coastal area signifies the reducing condition prevailing there and the subsequent participation of sulphate as an electron accepter for the oxidation of organic matter. The colour of the sediments was observed black. This might be due to the presence of the significant amount of AVS fraction as it could act as a pigmenting agent (Van Stracten, 1954; Love, 1967; Doyle, 1968; Berner, 1970; Goldhaber and Kaplan, 1974).

The fluctuations observed in the AVS S concentrations along the transects as well as along the coast, reflects the variations in the sulphate reduction rate, depending on the availability of organic matter (King *et al.*, 1985). Goldhaber and Kaplan (1974) have suggested that the distribution pattern of AVS S may be directly correlated with sedimentation rates, which decrease with distance from the land. Thus stations closer to the shore with higher sedimentation rates and having exposed to more organic input will exhibit high values of AVS fraction. This was found true at the nearshore stations of transects II and III. At other stations closer to the shore, transformation of AVS to other forms might have taken place. Thus at the nearshore station of transect I, pyritization process and at the nearshore stations of transect IV and V, elemental S formation favored over AVS accumulation. The appreciably low concentration observed at the offshore station of transect IV also signifies pyritization process.

Since greigite is an intermediate product in the slow pyritization process leading to the formation of framboidal forms (Sweeney and Kaplan, 1973), its presence gives the evidence of a slow pyritisation mechanism operating in these sediments similar to that in estuarine sediments. The distribution pattern of greigite S showed a more clearly increasing trend along the transects towards the shore than that of the AVS fraction. This can be due to the availability of iron in the form of iron oxides, since it is acting as an oxidizing agent in the formation of greigite (Goldhaber and Kaplan, 1974). Thus the decrease in the availability of iron towards the sea can result in decrease in greigite fraction.

A major source of iron in many sediments is clay fraction (Hirst, 1962; Moore, 1963). This will explain the low concentration of greigite S found in coarse sediments of stations along transect VI. A still higher values of greigite S than the AVS S fraction at these stations were indicative of a significantly high pyritisation.

The elemental S which is present in recent sediments seem to be formed only by the oxidation of sulphide since the known reduction processes do not yield free S^0. The oxidation of sulphide is carried out by the colorless sulphur bacteria such as Beggiatoa Spp. They can accumulate S^0 by carrying it within their cells in the form of minute droplets in invaginations of cell membrane and may actively transport the sulphur up or down in the sediment (Jorgensen, 1977).

Since S^0 can function as a dynamic intermediate in the different sulphur transformations, the variations in the S^0 can be due to the interplay of a number of factors. The bioturbation bringing oxidizing conditions in the upper sediment layers also can lead to an irregular S^0 distribution (Troelsen and Jorgensen, 1981). The elemental S pools of considerably big sizes could be attributed to the high microbiological population prevailing at these stations. Most of the S^0 produced is usually taken for pyrite formation by reaction with FeS (Berner, 1970). The overweighing of competitive microbiological S^0 over the pyritisation also can result in a greater S^0 concentration.

Pyrite formation in nearshore sediments with abundant organic matter was suggested as a major phenomenon associated with the sediment layers at or immediately below the sediment-water interface. Even though pyrite is the thermodynamically most stable form of iron-sulphur compounds, its distribution pattern suggests a relatively slow pyritization process in coastal sediments. The formation of single crystals of pyrite might also has happened either by direct precipitation or by reaction of mackinawite with elemental S. Crystalline and framboidal forms of pyrite have been reported in clay and silt-size sediments (Goldhaber and Kaplan, 1974).

The factors influencing the distribution pattern of other sulphur fraction are found to be operative in the case of pyritic S also at the first two stations near to the shore, where a decline in values was observed.

Earlier studies in marine sediments have suggested that only less than 10% of total S is represented by the organic S fraction (Berner, 1964; Goldhaber and Kaplan, 1974). Pyrite was reported as the major fraction of total S in several studies (Goldhaber and Kaplan, 1974). Contrary to these earlier studies, organic S was found as the major form of sulphur species in the present study of coastal region, showing similarity to the estuarine observation.

The higher percentage of organic S is indicative of high rates of sulphate reduction occurring in coastal area (Rudd *et al.*, 1986). The diminishing trend of organic S along the transects towards the sea suggests that sulphate reduction rate is higher at nearshore stations. The organic carbon data also supports this suggestion.The influence of land drainage also is a contributing factor. An exceptional case observed along the transect IV may be due to some degradative process happened there.

The spatial variation of total S is primarily due to variability in organic S content. Similar observation has been reported by Casagrande *et al.*, (1979), Altschuler *et al.*, (1983) and Krairapanond *et al.*, (1991). Along the transects, a decreasing trend towards the sea was observed similar to the organic S distribution.

The observed decline in values of all the sulphur fractions at stations situated along the transect VI could be due to the special sedimentary characteristics. At these stations the sediments are mostly sandy in nature compared to the clayey and silty sediments of other stations.

Even though, the sulphate from the overlying water is the chief source of sulphur to the sediments, a significant accumulation tendency is observed in these sediments. This suggests that coastal sediments can act as traps for sulphur, mainly retaining sulphur in the form of organic S. This is an ad hoc evidence for addition of sulphate S to sediments during or after burial in amounts larger than that trapped in the interstitial fluids.

CHAPTER V

SEDIMENTARY SULPHUR PARTITIONING - A CONCEPTUAL MODEL

5.1. INTRODUCTION

The presence and the ambient concentrations of various elements in the marine environment are the result of a dynamic balance of various biogeochemical processes operating in the system. The individual total concentrations of an element and the concentrations of various species of compounds or ions that constitute the total concentration are thus, will be regulated by the extend of the biogeochemical processes, the time interval required to attain the steady state and the chemical and physical environmental conditions. The major ions like sulphate have a very long time interval and tend to be conservative in their relations with other ions by reactions occurring between the aqueous phase and solid phase of lithogenous and biogenous origin (Sillen, 1961; Pytkowicz, 1967; Garrels and Mackenzie, 1971). In defining the various biogeochemical processes, the microorganisms play a key role and the transformations which cannot be envisaged by the thermodynamic concepts are general features in biologically mediated processes. The transformations of sulphur compounds which are brought in by the microorganisms for the purpose of energy utilisation are the best example for the above.

Elevated amounts of dissolved sulphate through the saline waters, are in contact with the sediments of coastal and estuarine environments and the activity of the heterotrophic organisms under the influence of high organic carbon maintain most of these sediments in a reducing condition. This stratification provides the basis for the transformations of inorganic sulphur compounds through a cyclic series of redox processes. Sulphate is reduced in both the epilimnetic and hypolimnetic sediments (Cook and Schindler, 1983; Kelly and Rudd, 1984) and the rates of sulphate reduction in sediments can increase as sulphate concentrations in the overlying water increase (Cook and Schindler, 1983; Kelly and Rudd, 1984). The acid volatile sulphide which later converts to pyrite was considered as the sole product of sulphate reduction till recently (Berner, 1984), but recent studies based on isotopic traces are well conclusive that the predominant end product on a long term basis, is the organic sulphur compounds (Nriagu and Soon, 1985 and Rudd *et al.*, 1986). These observations set apart the earlier controversy over the source of organic sulphur compounds in sediments stemmed from the apparently incompatible facts that organic sulphur sedimentation rates are significantly low as compared to sulphate reduction rates (King and Klug, 1982; Cook and Schindler, 1983), yet most of the sulphur in sediment is organic.

A number of models have been proposed to explain the behaviour of sulphur in the sedimentary environments of which most of them defined the formation of sulphide by the reduction of sulphate, and the formation of iron sulphide and organic S from the formed sulphide as the major pathway (Jorgensen, 1977; Luher *et al.*, 1986). The argument proposed in the study has but leniency to the suggestions of Rudd *et al.*, (1986). In this context, the organic matter plays the dominant role in the formation of both the iron sulphides and organic S. The transformation pathways of sulphate, diffusing through the sedimentary surface, are as follows:

1. formation of iron sulphides

$$9CH_2O + 4FeOOH + 4SO_4^{2-} + 8H^+ \dashrightarrow 9CO_2 + 4FeS + 15H_2O$$

$$8CH_2O + 4SO_4^{2-} + 8H^+ \dashrightarrow 8CO_2 + 4H_2S + 8H_2O$$

$$Fe_2O_3 + 4H_2S \dashrightarrow 2FeS_2 + 3H_2O + H_2$$

2. formation of organic S

Two types of organic S compounds are identified to be forming from the interaction of inorganic sulphur and the sulphate esters. The production of carbon bonded sulphur starts with H_2S and there are many possible reactions of H_2S with organic compounds *eg.*, reaction with hydroxyl groups:

$$H_2S + R\text{-}C\text{-}OH \dashrightarrow R\text{-}C\text{-}SH + H_2O$$

The formation of sulphate esters does not contain sulphate reduction *eg.*,

$$R\text{-}OH + 2\,H^+ + SO_4^{2-} \dashrightarrow ROSO_3^- + H^+ + H_2O$$

Though it is not clear which is the predominant pathway of organic S fractions, it seems reasonable that carbon bonded S would be more likely to remain in the sediments in the long term since sulphate esters are quite labile (King and Klug, 1980).

In the present study, the organic S was found to constitute the major fraction of the total S, more than 50%, in almost all the stations at all the seasons (Fig. 5.1 to Fig. 5.4).

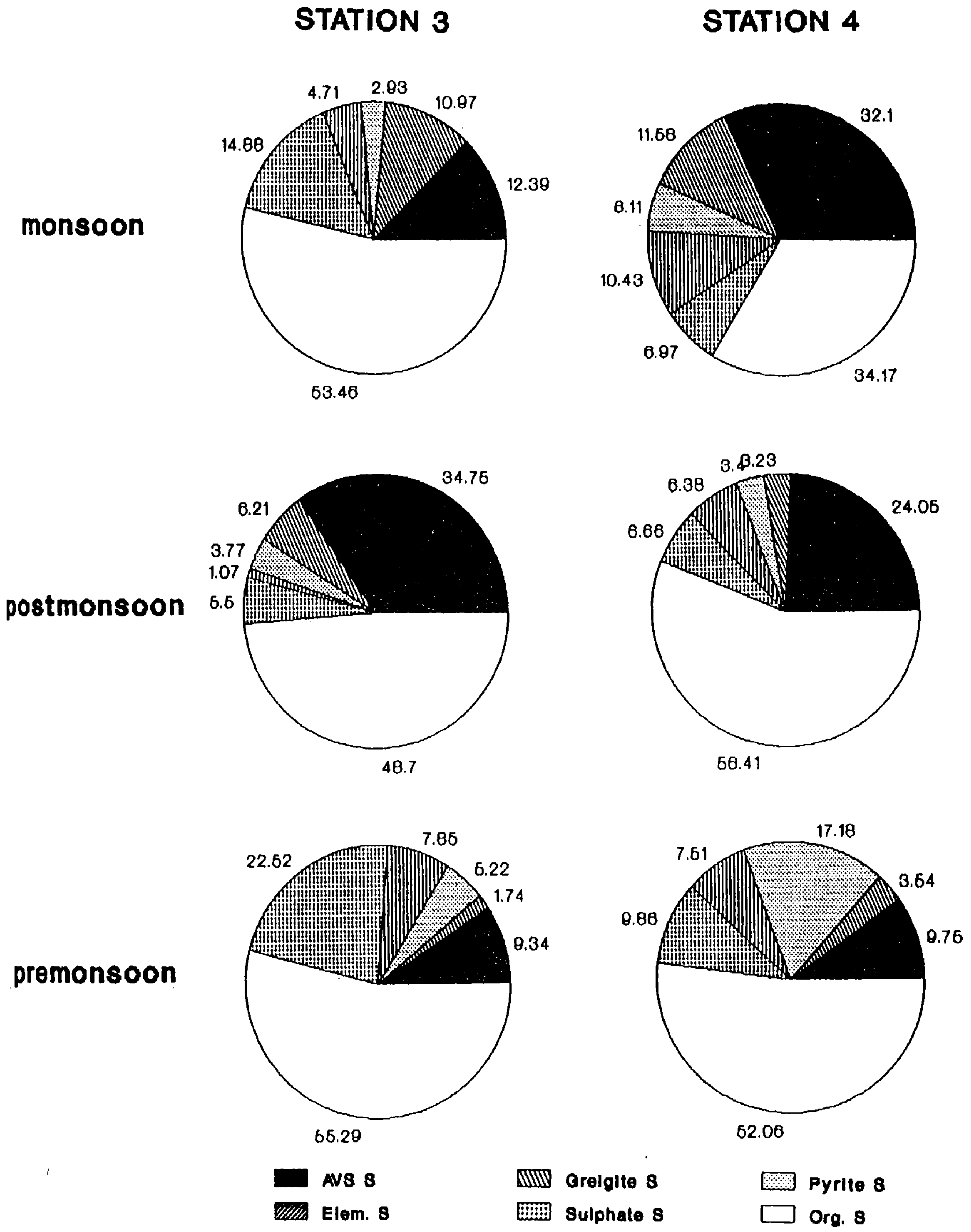


Fig. 5.1. Seasonal contribution of different sulphur fractions to total sulphur.

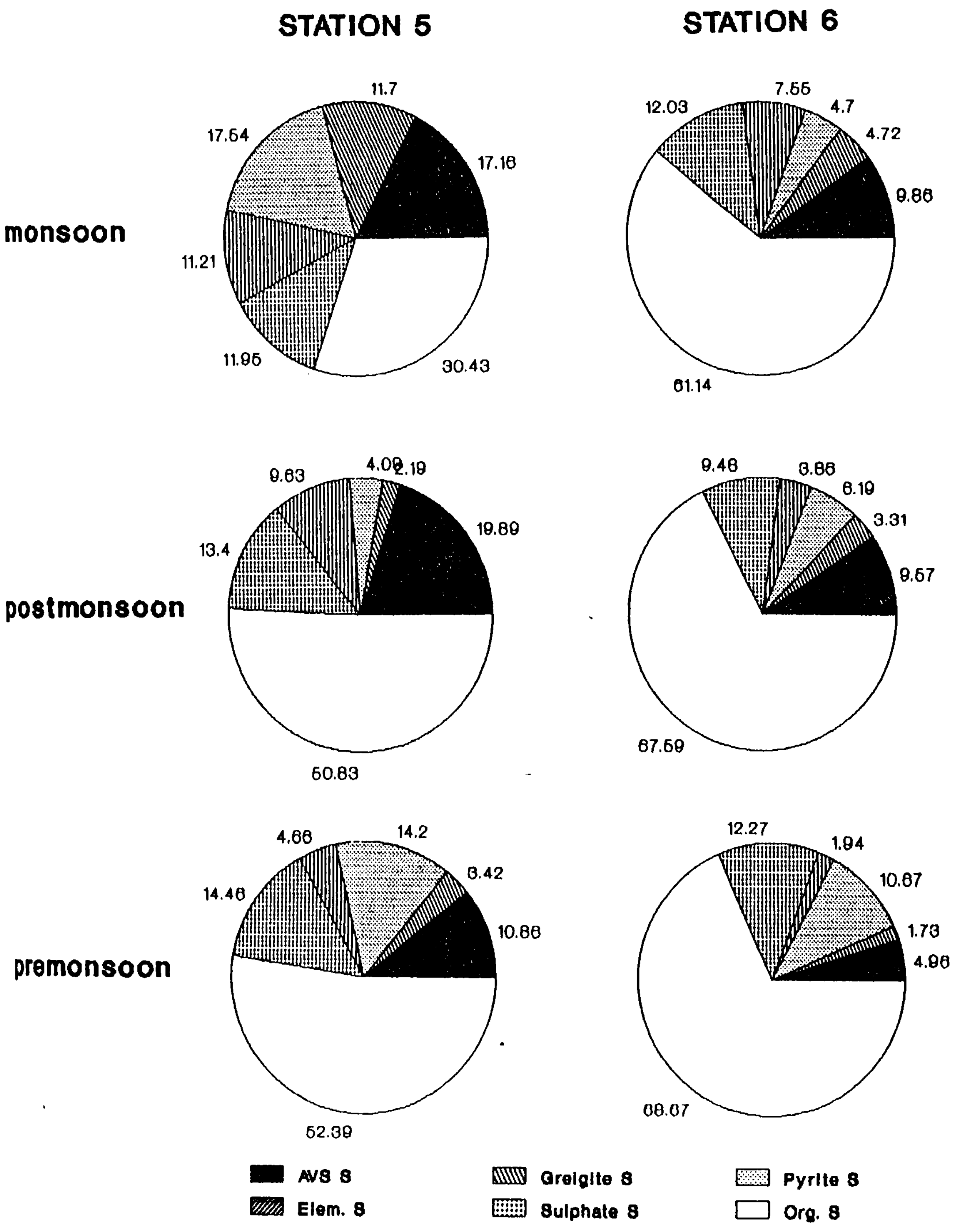


Fig. 5.2. Seasonal contribution of different sulphur fractions to total sulphur.

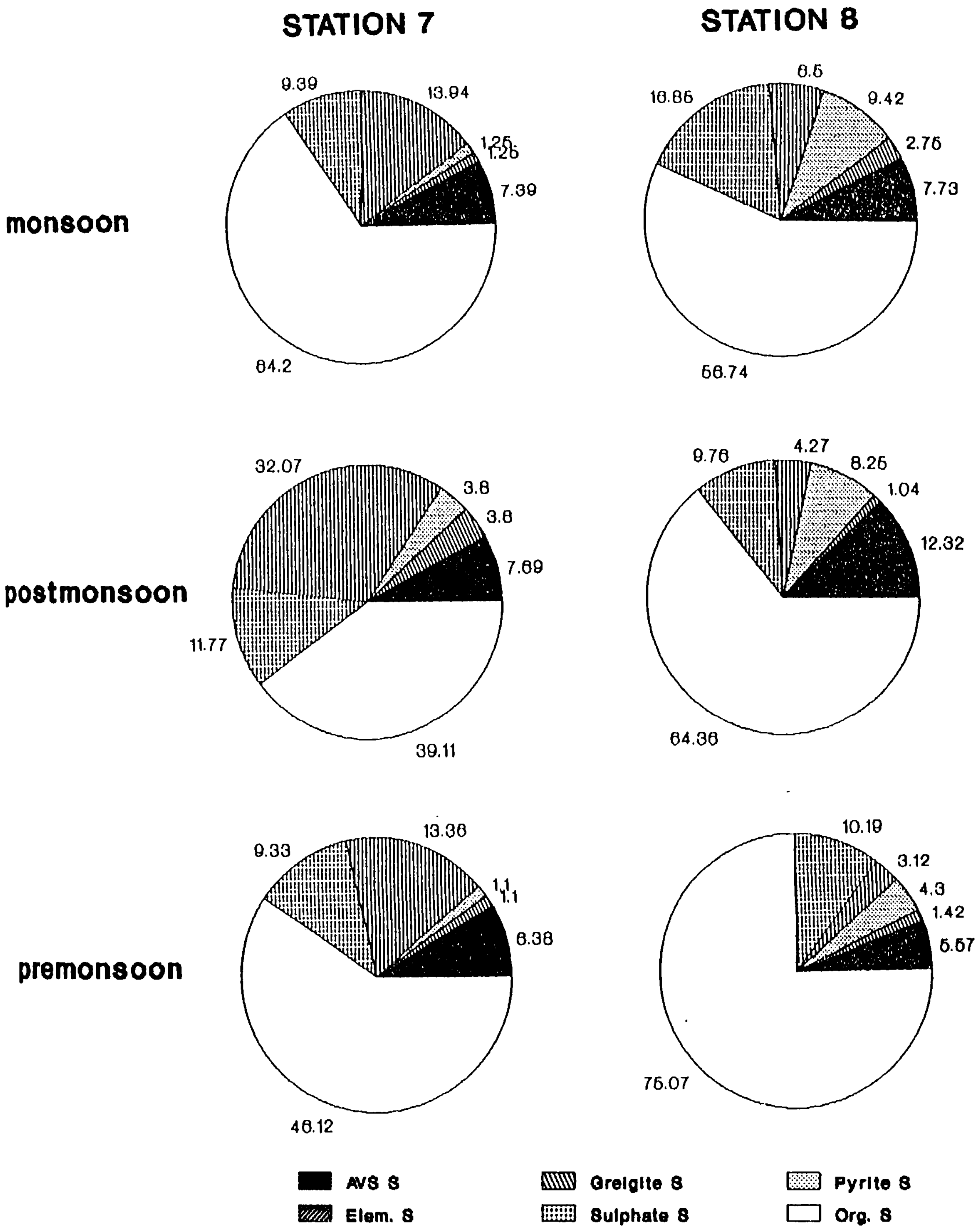


Fig. 5.3. Seasonal contribution of different sulphur fractions to total sulphur.

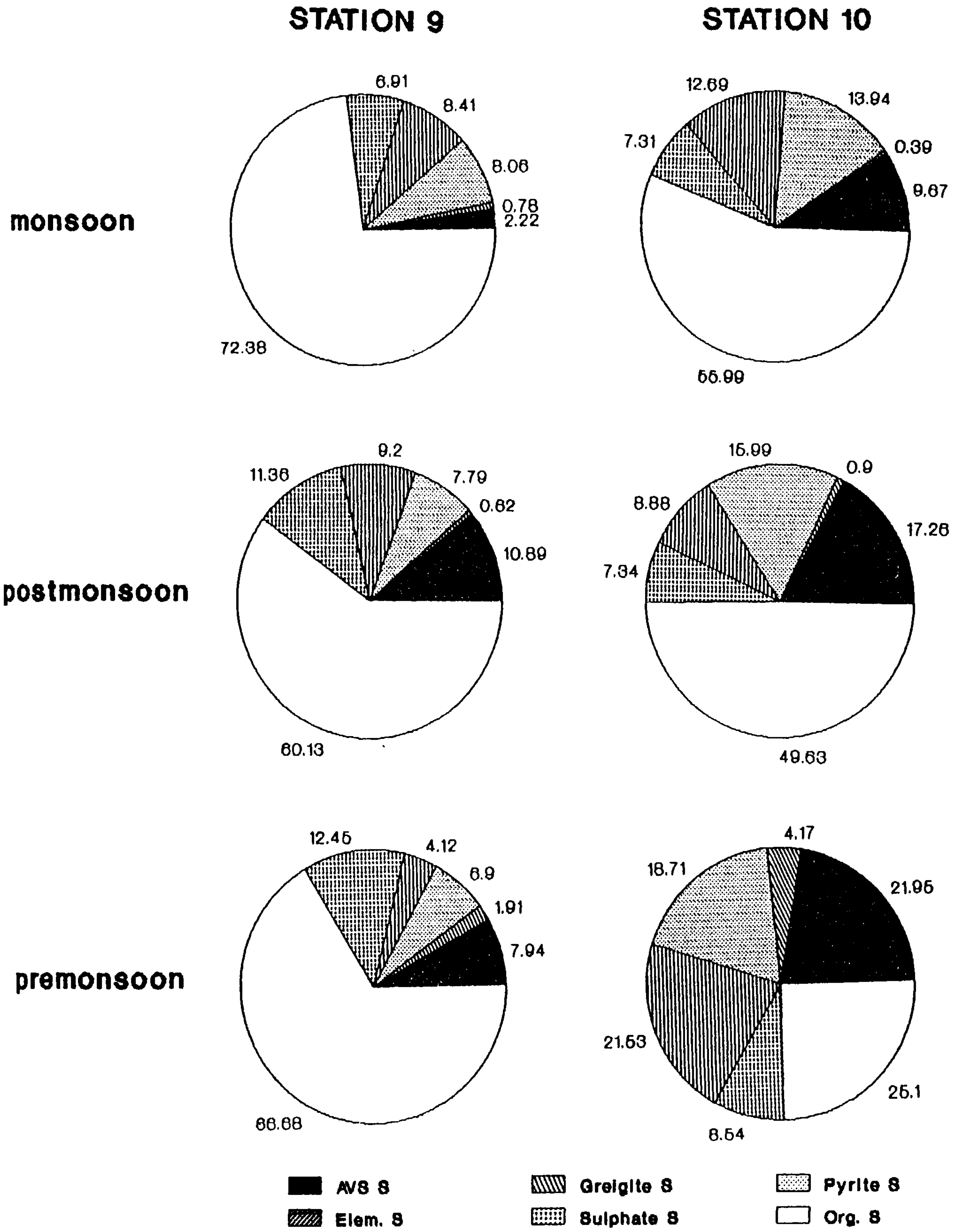


Fig. 5.4. Seasonal contribution of different sulphur fractions to total sulphur.

The model proposed here is developed on the major assumption that the formation of inorganic reduced sulphur(IRS) and the organic S is simultaneous.

5.2. The Model

The model comprises of two phase four compartment system in which the overlying water and the sediment constitute the phases, and dissolved sulphate, sedimentary sulphate, organic S and IRS constitute the compartments. The derivations of the model are based on the various reports on the behavior of sulphur and biogeochemical processes involved in the Sulphur Cycle.

5.2.1. Basic Assumptions

1. In a positive tropical estuary like the Cochin estuary where the average depth of the water column is in the range of 3-20 meters, the water will, due to significant mixing processes, have sufficient dissolved oxygen to keep even the bottom layers in an oxidative environment.

2. The sediment, due to the high input of organic matter would be at a negative potential which favours sulphate reduction.

3. The major contributor of the sulphate in the sediment is the dissolved sulphate, generally from the ambient salinity.

4. The sulphate reduction is considered to be the major source of inorganic reduced forms of sulphur and the organic S compounds.

5. The rates of sulphate reduction increase with the concentration of dissolved sulphate (Cook and Schindler, 1983; Rudd *et al.*, 1986) in water and the contribution of the

organic S towards the IRS is significantly low at the prevailing temperatures (25-30^{0}C) of the sediment (Nedwell and Floodgate, 1972).

6. The organic S is formed mainly from the interaction of sulphate with organic carbon, and is supplemented by the reaction of organic carbon with reduced sulphur (Rudd *et al.*, 1986). The sedimentation rate of organic S is slow compared to sulphate reduction rates (King and Klug, 1982 ; Cook and Schindler, 1983; Nriagu and Soon, 1985).

7. The pyrite and the organic S are considered to be the short term end products of the sulphate reduction.

5.2.2. Evolution of the model.

Based on the radiochemical studies on the Sulphur cycle in the sedimentary system two models have been suggested, one by Jorgensen (1977) and the other by Rudd *et al.*, (1986).

The Jorgensen model, based on the rate of sulphate reduction and the effect of sulphate reduction on the mineralisation of organic matter, was mainly intended to illustrate the dynamic nature of sediment and to indicate the danger of drawing conclusion from pool sizes to process rates. Though the model takes into consideration of the amount of sulphur that recycles between the sediment and water through reduction of sulphate and oxidation of sulphide, no attempt is made to differentiate the total S into the various species of sulphur that are involved in the cycle. The major observations of Jorgensen are (1) the average rate of sulphate reduction in the upper 10 cm of the sediment contributes to 65% of the total sulphate reduction in the whole sediment column (2) the contribution of the organic S from detritus for the reduction processes is significantly low (3%) and (3) out of the total sulphide production only about 7% of the sulphur was precipitated as iron sulphide in the upper 10 cm of the sediment, and below 10 cm, somewhat less is precipitated. This indicates that the sulphide leaves a sediment almost quantitatively after reoxidation at the surface. In general, the coastal sediments can be considered as a very open system with respect to sulphur cycle, even in the deeper layers.

In the model suggested by Rudd *et al.*, (1986) also, the major contributor of the sulphur in the sediment was considered to be the sulphate reduction process. The major observations of their work are, (1) a large proportion of the sulphate reduced was rapidly converted to organic S which was found to be more persistent than the iron sulphides in the sediments , suggesting that with time the distribution of sulphur among the end products will be dominated increasingly by organic S (2) different rates of sulphate reduction should be reflected in different rates of sulphur storage within the sediments. (3) the diffusion of sulphate in a few cm into the pore water, where it would beinitially converted to both organic and inorganic end products, lead to an increased concentration in the total and organic S, and on a long term basis the preferential loss of iron sulphide would result in an accumulation of primarily organic S.

Though there is close similarity in the conceptual development of the two models, the model proposed by Rudd *et al* is considered as more suitable for adaptations in the present study due to the following reasons. (1) The Jorgensen model does not prescribe any definite partition of the products of the sulphate reduction whereas Rudd *et al.*, (1986) present a clear partitioning of the reduced sulphur into organic and inorganic sulphur. (2) The Jorgensen model considers the release of sulphate by the oxidation of sulphide as complete (100%), while a retention of about 34% within the sediment is proposed by Rudd *et al.*, (1986). Probably, the variation in the dynamic character of the system is the reason for this discrepancy.

The results of the present study indicate the following features.

1. The C/S ratio was observed to be very low, which could be attributed to the absence of a significant contribution of the sulphur by the sedimentation of sulphur containing detritus (Table 5.1). A similar condition has been reported in earlier works also (Nriagu and Soon, 1985; Baker *et al.*, 1992).

2. An almost definite pattern of distribution of the three groups of sulphur compounds namely, IRS, sulphate S and organic S was observed in all the stations on an annual basis, which is indicative of a completely inter-dependent dynamic system. The inter-relationships of these fractions between themselves and to the total S are given below:

1. [Tot.S] = 2x[IRS] + 5.05   r = 0.6 $p > 0.001$ n = 101
2. [Org.S] = 0.85x[IRS] + 4.25   r = 0.32 $p > 0.001$ n = 101
3. $[SO_4]$ = 0.15x[IRS] + 0.79   r = 0.32 $p > 0.001$ n = 101
4. [Org.S] = 4.23x[IRS] + 1.75   r = 0.71 $p > 0.001$ n = 101

3. The sediments presented a significantly high organic carbon content which could offer a substantial increase in the sulphate reduction supplemented by the remineralisation of the organic matter. These findings hold a close similarity to the observations and the model suggested by Rudd *et al.*, (1986).

This model identifies the entire processes in the cycle into two, (1) a set of biogeochemical processes and (2) the physical transport processes. In the biogeochemical processes

Table 5.1. C/S Ratio

MONTH	STATIONS 3	4	5	6	7	8	9	10
APR '90	3.65	1.71	2.83	0.93		0.98	1.51	1.29
MAY' 90	1.63	1.44	4.05	2.04	0.93	1.01	1.57	1.25
JUN '90	2.08	1.93	3.30	1.33	0.98	1.27	2.28	1.40
JUL '90	1.19	2.21	5.01	1.42	0.67	1.27	1.86	1.88
AUG '90	1.91	2.23	2.46	1.44	0.90	1.47	1.81	5.03
SEP '90	1.39	1.66	2.40	1.55	2.08	1.56	1.32	4.58
OCT '90	0.84	1.83	3.34	1.02	3.07	1.77	1.76	1.86
NOV '90	1.19	2.53	3.01	1.59	1.22	1.74	2.24	1.68
DEC '90	5.87	1.82	2.48	1.94	1.27	1.24	1.26	2.23
JAN '91	14.56	1.92	2.90	0.92	2.85	1.07	1.24	2.44
FEB '91	0.79	1.03	2.15	1.15	1.15	1.16	1.63	1.76
MAR '91	0.53	1.93	2.21	1.06	1.37	1.06	2.96	3.50
APR '91	1.29	1.37	2.01	1.12	1.37	1.07	1.75	3.71

the reduction of sulphate and conversion into the organic S and the IRS species and the oxidation of the organic as well as the IRS to sulphate are included. The physical transport processes are limited to the transfer of the sulphate from the sediment into the overlying water. The redox condition of the sediment, the organic carbon content and the population of the interacting biological species, all control the rate of biogeochemical processes whereas the availability of the sulphate for reduction determines the effective concentrations of the sulphur species, except sulphate. The concentration of the sulphate at any time is governed by the extent of transfer of sulphate from the sediment to the water, and so is controlled by the dynamics of the aquatic system.

The relative percentages of the sulphur species remaining in each compartment of the model prescribed by Rudd *et al.*, (1986) with respect to the initial amount of sulphur transported into the sediment by sulphate reduction and with respect to the total S remaining in the sediment during the complete cycle are given in Table 5.2. The percentages of sulphate S,IRS and organic S with respect to the total S are given in Table 5.3.

The comparison of the results of this study with the data derived from the model suggested by Rudd *et al.*, (1986), indicates that though the general features observed by Rudd *et al.*, (1986) is valid in this estuarine system, there is significant variation in the effective percentages of the sulphur species. This variation can be due to the changes in the magnitudes of the reaction rates resulted from the highly dynamic character of the estuarine system as well as the high organic carbon content in the sedimentary system (Rudd *et al.*, 1986). The most pronounced variation is the very low percentage of sulphate S, less than half of the value expected from the Rudd *et al.*, (1986) model, which can be attributed to

Table 5.2. Percentage of sulphur fractions estimated from the model proposed by Rudd et al., (1986). (*)

S Fractions	% Retention w.r.t. SO reduction	% w.r.t. Total S remaining in sed.
Organic S	30.21	41.82
IRS	17.39	34.10
Sulphate S	24.63	24.08

(*)

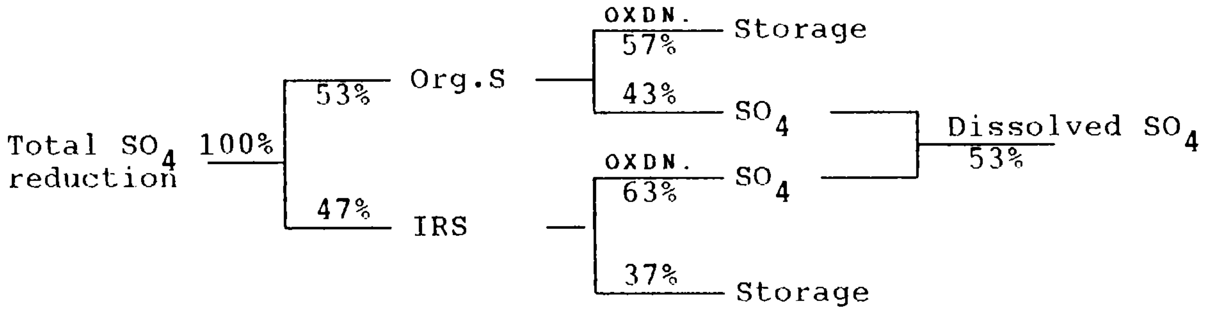
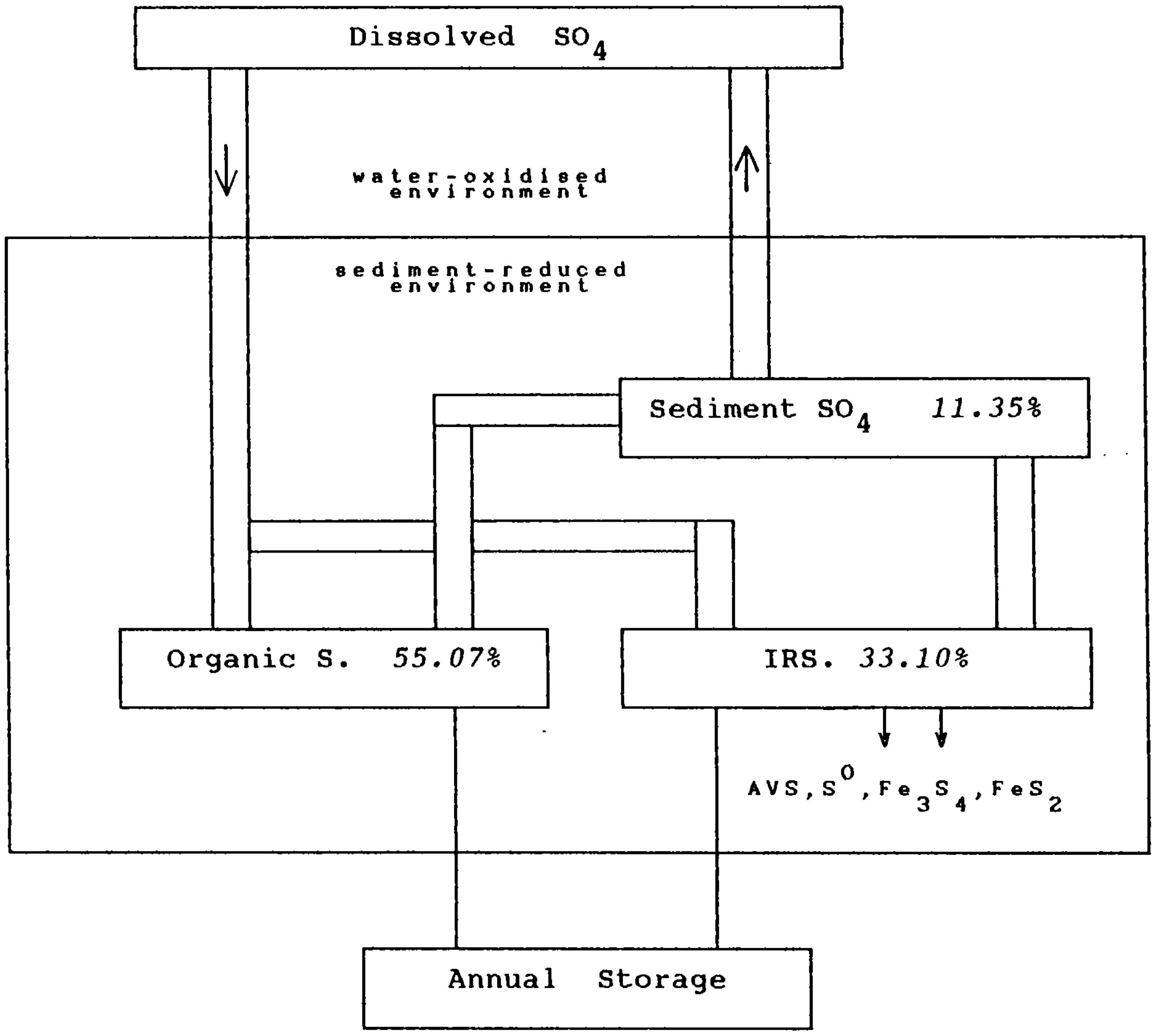


Table 5.3. Seasonal contribution of different sulphur fractions to total S

SEASONS		STATIONS							
		3	4	5	6	7	8	9	10
MONSOON	IRS	31.00	60.22	57.62	26.83	23.84	26.41	19.46	36.70
	SO_4	14.88	6.97	11.95	12.03	9.39	16.85	6.92	7.31
	Org. S	53.46	34.17	30.43	61.15	64.20	56.75	72.38	55.99
POSTMONSOON	IRS	45.81	37.05	35.77	22.93	47.36	25.88	28.51	43.03
	SO_4	5.49	6.66	13.41	9.48	11.77	9.76	11.36	7.34
	Org. S	48.70	56.41	50.83	67.59	39.11	64.36	60.13	49.63
PREMONSOON	IRS	16.30	30.47	28.49	17.36	8.57	11.29	16.74	44.83
	SO_4	22.52	9.86	14.46	12.27	9.33	10.19	12.45	8.54
	Org. S	55.29	52.06	52.39	68.67	46.12	75.07	66.68	25.10

the high leaching of the sediment by the highly dynamic overlying water. This transfer of the sulphate S from the sediment would modify the total S value, thereby increasing the relative percentages in organic S and inorganic reduced sulphur. The data obtained for organic S and the IRS suggest either a preferential retention of the organic S during the oxidation by the sediment or a preferential formation of the organic S during the reduction of sulphate which can be assisted by the presence of the high organic carbon or a combination of the effects of both the processes. Stations 4 and 5 exhibited increased concentrations of IRS during the monsoon period and, the station 10 during the premonsoon period. No concrete explanation is offered here. Similarly, low percentage of IRS was observed at stations 6, 8 and 9 during the entire period. Stations 6, 7, 8 and 9 are highly estuarine in character and the dynamics associated with the seawater intrusion might have resulted in the preferential oxidation of IRS as it is more labile for oxidation than the carbon bonded organic S. The sedimentary characteristics would also have contributed to these results. Except these odd observations, generally the percentages of the three sulphur species were found to be more or less comparable, making the model acceptable for this estuarine system with slight modifications. The model evolved is given below.

The proposed model is identical to the model proposed by Rudd *et al.*, (1986). The whole system is partitioned into two, the oxidising environment, mainly the overlying water and the reducing environment or the sedimentary system. The sedimentary sulphur system is further compartmentalised into three, the organic S, IRS and the sulphate S.



The major processes are consolidated into

(1) the reduction of the sulphate whose sole contribution can be considered as the dissolved sulphate which diffuses through the sediment boundary

(2) the oxidation of the organic and inorganic reduced sulphur to sulphate

(3) the transfer of the organic and inorganic sulphur towards annual storage and

Table 5.4. Contribution of different sulphur fractions to total S

	IRS	SO_4	Org. S
Transect I	26.93	7.26	69.38
Transect II	47.97	11.39	40.65
Transect III	40.60	17.63	41.77
Transect IV	25.75	16.14	58.11
Transect V	20.39	5.90	73.71
Transect VI	10.58	29.73	59.70

(4) the transport of the sedimentary sulphate to the overlying water.

Of these processes, (1) and (2) determine the effective concentrations that would be present in the sedimentary system and the nature of the sediment, especially the organic carbon content plays a significant role in these two processes.

The values given in the sedimentary sulphur compartments are the mean values of the relative percentages of sulphur in the respective compartments to the total S remaining in the sediment.

The percentages of sulphur species given in the above model were found to be almost same to the values obtained in the coastal region (Table 5.4), thus indicating acceptability of the model even for coastal system. The model as now can only be considered as incomplete, in the sense that it does not include the kinetic part of the processes, but can be applied successfully to coastal and estuarine systems to get an insight into the various biogeochemical processes in the sulphur cycle in these systems. Works are on vogue for the kinetic part.

CHAPTER VI

SUMMARY

In the marine environment, though the sulphate is a major ion and exhibits a conservative behaviour, the redox possibilities with the sulphur is well known for its role in modulating the biological and chemical rhythm of the system. The role of sulphur to modify the environment as an essential nutrient to plants, as an electron acceptor to sustain the biological life in the system from the organic load by decomposition and as a strong redox element to define the redox condition of the system, has received a high attention from environmental scientists even in a global scale.

The present thesis embodies the results of a comprehensive attempt to define the general characteristics of the sulphur species in the tropical Cochin estuarine system and in the coastal belt of Kerala with special emphasis to the distribution of the various sulphur species.

More than 70% of the industrial activities in the state of Kerala are centered around Cochin and the effluents of these concerns are discharged into the rivers that drain into the Cochin estuary. In addition, the estuary receives a large variety of allochthonous and autochthonous inputs and urban and domestic wastes.

A large number of small and medium rivers drain its contents to the coastal line of Kerala, modifying the physico chemical characters of the coast. A comparably high nutrient content, productivity and regular formation of mud banks are the few specialities of this coastal line.

The investigations contained in this thesis pertains to the studies conducted on the water and sedimentary environments of the Cochin estuarine system between April 1990 and April 1991 and along the coastal belt of Kerala during premonsoon season of 1991. Besides characterising the various sulphur fractions in the water and sediments, analysis of the hydrographical parameters like dissolvedoxygen, salinity, and pH, and the general sedimentary parameters like sedimentary organic carbon, Eh and texture, have been carried out.

The distribution of dissolved sulphate in the estuary exhibited more or less conservative nature throughout the period of study. The observed concentrations are compared with the concentrations calculated from the salinity using the geochemical model proposed by Dryssen and Wedborg, (1980). Within the general conservative nature, a few stations exhibited either depletion or enrichment of sulphate. The enrichment may be due to a temporary excess of sulphide or sulphur oxidation over sulphate reduction at the sedimentary surface and or to the mixing of seawater of high sulphate content with fresh water of low sulphate concentration. The depletion cannot be attributed solely to the sulphate reduction due to the significant dissolved oxygen level prevailing in the water column and so could only be assigned to the involvement of sulphate in the mineralisation of organic matter in the sediment.

The observed dissolved sulphide concentration was against the normal expectations based on the redox conditions of the water column. No specific explanations can be offered here except the following general observations:

1. Though the sulphide gets rapidly oxidised in an oxidative environment, a marginal stability can contribute towards the significant presence of sulphide in the water column overlying a reducing sediment,

2. The half life of sulphide oxidation by oxygen in seawater is almost half of that in fresh water and so the vertical mixing of the fresh water with sea water can affect the distribution of sulphide in the water column.

Apart from the total S, the sedimentary sulphur fractions identified for this study are sulphate S, AVS S, greigite S, pyrite S, elemntal S and organic S. Generally all the sulphur fractions and the organic carbon presented a decrease in concentration towards the upstream. The poor settling of the brought particulate/suspended materials, the low holding capacity of the sandy sediment and the low salinity observed at these upstream stations may have contributions towards this decrease in sulphur fractions in the upstream stations.

A premonsoonal maximum was observed with sulphate for most of the stations and a post monsoonal minimum. The maximum is a reflection of the same in a water body having minimum dilution by poor fresh water discharge. The minimum can be attributed to the high rate of sulphate reduction.

AVS S fraction showed a postmonsoonal maximum and a monsoonal minimum at most of the stations. The postmonsoonal maximum can be attributed to the higher sulphate reduction which supports the postmonsoonal minimum of the sulphate and the high organic can contribute to such a high sulphate reduction.

Greigite is generally considered as an intermediate in the slow pyritisation process and the presence of it is an indicative of the formation of framboidal pyrite in this estuarine system. A definite pattern of spatial or temporal distribution was not observed with greigite. This observation may be due to the prevailing varying conditions in modifying the formation of greigite from AVS and S^o and the transformation of greigite to pyrite.

Pyrite is one of the end products of sulphate reduction and in this estuary, for most of the stations, a pyrite maxima was observed at premonsoon and a minimum at post monsoon. Depending on the formation pathway, two types of pyrites are identified, the single crystalline and framboidal of which the slow pyritisation from greigite gives the framboidal form and the rapid pyritisation yields the single crystalline form. The premonsoonal maximum is attributed to the formation of framboidal pyrite and the less oxidative condition prevailing in this season.

Though the concentration of elemental S observed was low during the entire period of investigation, the overall contribution of S^o to the total S was found to be higher compared to other studies. Most of the stations showed a monsoonal maximum and a premonsoonal minimum. The oxidising condition was found to be favorable for the formation and stabilisation of the elemental S resulting in a maximum and the pyrite formation leads to a minimum. This observation was in line with the variation in pyrite concentration.

Organic S constituted the major fraction of the total S. The seasonal averages were found to be showing spatially varying maximum and minimum. This can only be attributed to the interplay of several factors. The dynamic transformations of inorganic S to organic S in the presence of organic carbon is considered to be the major formation path of organic S. In a number of stations the occational maximum can be due to sedimentation of organic S compounds from the industrial or sewage sources. The fresh water discharge and dilution of seawater, productivity of the overlying water column and the water temperature can lead to a variation in the organic S^o compounds.

In the coastal waters the dissolved sulphate showed the conservative nature . The coastal data on the sedimentary sulphur fractions are indicative of the prime role played by the sulphate reduction in partitioning the sulphur into various fractions. The sediments indicated a reducing condition along the coastal sedimentary environment which promotes the participation of sulphate as an electron accepter for the oxidation of organic matter. The high organic S content in the sediments is indicative of sulphur accumulation tendency with the sediment, storing part of the sulphate from overlying water column in the form of organic S.

The data of the sedimentary sulphur fractions are grouped into organic S, inorganic reduced sulphur and sulphate S and was applied to a conceptual model suggested by Rudd *et al* ., (1986) modified to suit to the general condition of the estuarine and coastal systems. It was observed that while the sulphur fraction retained the general character of the formation of the three fractions, the effective concentration of the sulphate in the sediment is dependent on the dynamics of the overlying water system which controls the transport of sulphate from the sediment to the water column. The relative percentages of inorganic reduced sulphur and organic S indicate either a preferential retention of the organic S during the oxidation to sulphate, as the inorganic reduced sulphur compared to the organic S is more labile, or a preferential formation of organic S during the reduction of sulphate assisted by the high organic carbon content or a combination of both the processess.

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